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NMAM

PART 1 of 3

NIOSH

NIOSH Manual of Analytical Methods

4th Edition

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health

CDC
CENTERS FOR DISEASE CONTROL AND PREVENTION

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NIOSH MANUAL OF ANALYTICAL METHODS

4th EDITION

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
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National Institute for Occupational Safety and Health
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A trademark application is pending for the designation "NMAM" for this manual.

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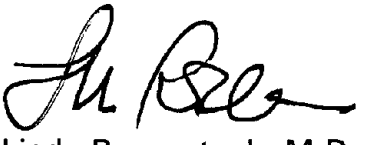
FOREWORD

Adherence to exposure control limits has been an important strategy in the prevention of occupational disease for almost 60 years. Methods of monitoring exposure in the occupational environment are vital to this prevention strategy. They produce the information needed to modify and improve control systems so as to protect the worker from occupational health hazards. These methods are also a necessary part of all standards that set limits for environmental exposures to toxic substances.

The methods presented in this improved Fourth Edition are intended to be accurate, clear, and concise. They incorporate the results of recent research by NIOSH. Applicable methods are also incorporated into Criteria Documents produced by NIOSH for recommending standards to the Occupational Safety and Health Administration.

It is a pleasure to present this Manual for your use and welcome your comments about it.



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and Prevention

ABSTRACT

One of the functions of the National Institute for Occupational Safety and Health (NIOSH) is the development of sampling and analytical methods for monitoring occupational exposures to toxic substances in air and biological samples. These methods are published in the NIOSH Manual of Analytical Methods (NMAM), now in its fourth edition. The monitoring methods cover the collection of aerosols, gases, and vapors in air with active samplers (filters, sorbent tubes, impingers) followed by laboratory analysis, as well as with diffusive samplers and direct-reading field instruments. Additions to the fourth edition are: method classification, estimate of accuracy, RTECS numbers, and a method finder.

The purpose of method classification is to quickly identify the usefulness of the method; therefore, methods in the NMAM, 4th ed., are classified into three evaluation categories: Full, Partial, and Unrated.

An accuracy estimate, which indicates how closely the method compares to the NIOSH ±25% criterion for a valid method, has been added to the summary page of the method.

The methods are arranged in alphabetical order by method name. The Method Finder provides a simple means of locating a method for a specific chemical. The Method Finder is a table in which the names of common chemicals are listed alphabetically with the corresponding method name and number, type of sampler, sampling rates and volumes, and analytical technique.

Indices of chemical names and synonyms (alphabetical), Third and Fourth Edition method numbers, and Second Edition method numbers are provided for cross reference.

The NMAM also includes chapters that discuss several topics of special interest. Notable among these are quality assurance, strategies for sampling airborne substances, method development and evaluation, and discussions of some portable direct-reading instrumentation.

The NIOSH Manual of Analytical Methods, 4th ed., is available in electronic format through private software vendors.

ACKNOWLEDGMENTS

More than fifty people contributed to the publication of the 4th edition of NMAM. The authors of individual methods and introductory chapters are indicated. These include NIOSH scientists in the Division of Physical Sciences and Engineering; Division of Biomedical and Behavioral Sciences; Division of Respiratory Disease Studies; Division of Surveillance, Hazard Evaluation, and Field Studies; and Division of Training and Manpower Development; and personnel at DataChem Laboratories, Salt Lake City, Utah.

The revision was accomplished under the direction of Laurence J. Doemeny, Ph.D., Acting Director, Division of Physical Sciences and Engineering, NIOSH.

Special thanks for manuscript preparation are due to Grace A. Fannin and Deanna L. Elfers.

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Dimethylarsenic acid
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- Manganese
- Molybdenum
- Nickel
- Platinum
- Silver
- Strontium
- Tin
- Titanium
- Zinc

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- Aluminum
- Arsenic
- Beryllium
- Calcium
- Cadmium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Molybdenum
- Nickel
- Phosphorus
- Platinum
- Selenium
- Sodium
- Silver
- Tellurium
- Tin
- Titanium
- Thallium
- Tungsten
- Vanadium
- Yttrium
- Zinc
- Zirconium

ENDRIN 5519
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EPN 5012
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- n-Amyl acetate
- sec-Amyl acetate
- n-Butyl acetate
- sec-Butyl acetate
- t-Butyl acetate
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- Ethyl acrylate
- Isoamyl acetate
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Cyclohexane	n-Hexane	n-Pentane
Cyclohexene	Methylcyclohexane	Toluene

HYDROCARBONS, AROMATIC 1501

Benzene	a-Methylstyrene	Vinyltoluene
p-tert-Butyltoluene	Naphthalene	Xylene
Cumene	Styrene	
Ethylbenzene	Toluene	

HYDROCARBONS, HALOGENATED 1003

Benzyl chloride	1,1-Dichloroethane
Bromoform	1,2-Dichloroethylene
Carbon tetrachloride	Ethylene dichloride
Chlorobenzene	Hexachloroethane
Chlorobromomethane	Methylchloroform
Chloroform	Tetrachloroethylene
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Coal tar naphtha | Petroleum ether | Stoddard solvent
Kerosene | Petroleum naphtha
Mineral spirits | Rubber solvent
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NICKEL CARBONYL 6007
NICOTINE 2544
NITRIC OXIDE and NITROGEN DIOXIDE 6014
p-NITROANILINE 5033
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4-Chloronitrobenzene | Nitrobenzene | Nitrotoluene
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Acenaphthylene | Benzo[a]pyrene | Indeno[1,2,3-cd]pyrene
Anthracene | Benzo[e]pyrene | Naphthalene
Benz[a]anthracene | Chrysene | Phenanthrene
Benzo[b]fluoranthene | Dibenz[a,h]anthracene | Pyrene
Benzo[k]fluoranthene | Fluoranthene

POLYNUCLEAR AROMATIC HYDROCARBONS (GC) 5515

Acenaphthene	Benzo[ghi]perylene	Fluorene
Acenaphthylene	Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene
Anthracene	Benzo[e]pyrene	Naphthalene
Benz[a]anthracene	Chrysene	Phenanthrene
Benzo[b]fluoranthene	Dibenz[a,h]anthracene	Pyrene
Benzo[k]fluoranthene	Fluoranthene	

PROPYLENE DICHLORIDE 1013
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o-TERPHENYL 5021
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1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and
1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE 1016
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VANADIUM OXIDES 7504
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VINYL CHLORIDE 1007
VINYLIDENE CHLORIDE 1015

WARFARIN 5002

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METHOD FINDER (Key on page MF-14)

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Acenaphthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Acenaphthylene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Acetaldehyde	2538	ACETALDEHYDE	0.01-0.05	1	12	GC-FID	XAD-2/HMP
Acetaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD2/HMP
Acetaldehyde	3507	ACETALDEHYDE	0.1-0.5	6	60	HPLC-UV	BuB
Acetic acid	1603	ACETIC ACID	0.01-0.1	20	300	GC-FID	CCT
Acetic anhydride	3506	ACETIC ANHYDRIDE	0.2-1.0	25	100	VIS	BuB
Acetone	1300	KETONES I	0.01-0.2	0.5	3	GC-FID	CCT
Acetone cyanohydrin	2506	ACETONE CYANOHYDRIN	0.2	0.3	12	GC-NPD	Por OS
Acetonitrile	1606	ACETONITRILE	0.01-0.2	3	25	GC-FID	CCT
Acetylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2	5	GC-FID	CCT
Acetylene tetrabromide	2003	1,1,2,2-TETRABROMOETHANE	0.2-1.0	50	100	GC-FID	SG
Acetylene tetrachloride	1019	1,1,2,2-TETRACHLOROETHANE	0.01-0.2	3.0	30	GC-FID	PCT
Acids, inorganic	7903	ACIDS, INORGANIC	0.2-0.5	3.0	100	IC	SG (washed)
Acrolein	2501	ACROLEIN	0.01-0.1	1.5	48	GC-NPD	XAD-2/HMP
Acrolein	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Acrylonitrile	1604	ACRYLONITRILE	0.01-0.2	3.5	20	GC-FID	CCT
Aldehydes, screening	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2
Aldrin	5502	ALDRIN & LINDANE	0.2-1.0	18	240	GC-ECN	GFF & BuB
Alkaline dusts	7401	ALKALINE DUSTS	1 - 4	70	1000	Titration	PTFE
Allyl alcohol	1402	ALCOHOLS III	0.01-0.2	1	10	GC-FID	CCT
Allyl chloride	1000	ALLYL CHLORIDE	0.01-1.0	16	100	GC-FID	CCT
Allyl glycidyl ether	2545	ALLYL GLYCIDYL ETHER	0.01-0.2	1.5	8	GC-FID	Tenax
Allyl trichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	2	60	GC-FID	CCT
Alumina	0500	PARTICULATES N.O.R.	1 - 2	7	133	Grav	PVC, tared
Aluminum	7300	ELEMENTS by ICP	1 - 4	5	100	ICP-AES	MCEF
Aluminum	7013	ALUMINUM & CPDS, as Al	1 - 3	10	400	FAAS	MCEF
Amines, aliphatic	2010	AMINES, ALIPHATIC	0.01-1.0	3	30	GC-FID	SG
Amines, aromatic	2002	AMINES, AROMATIC	0.2-1.0	30	150	GC-FID	SG
Aminobenzene	2002	AMINES, AROMATIC	0.2-1.0	30	150	GC-FID	SG
2-Aminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4	24	GC-FID	SG
2-Aminoethanol	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5	300	IC	IMP
p-Aminophenylarsonic acid	5022	ARSENIC, ORGANO-	1 - 3	50	1000	IC-HYAAS	PTFE
2-Aminotoluene	2002	AMINES, AROMATIC	0.02-1.0	10	150	GC-FID	SG
Ammonia	6015	AMMONIA by VIS	0.1-0.2	0.1	90	VIS-Auto	SG + H_2SO_4
n- and sec-Amyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Aniline	2002	AMINES, AROMATIC	0.02-0.2	5	30	GC-FID	SG
Anisidine	2514	ANISIDINE	0.5-1.0	24	320	HPLC-UV	XAD-2
Anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
p-Arsanilic acid	5022	ARSENIC, organo-	1 - 3	50	1000	IC-HYAAS	PTFE

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Arsenic	7900	ARSENIC & compounds, as As	1 - 3	30	1000	FAAS	MCEF
Arsenic	7300	ELEMENTS by ICP	1 - 4	5	2000	ICP-AES	MCEF
Arsenic trioxide	7901	ARSENIC TRIOXIDE, as As	1 - 3	30	1000	GFAAS	MCEF
Arsine	6001	ARSINE	0.01-0.2	0.1	10	GFAAS	CCT
Asbestos	7400	ASBESTOS FIBERS by PCM	0.5-16	400	varies	PCM	MCEF
Asbestos	7402	ASBESTOS FIBERS by TEM	0.5-16	400	varies	TEM	MCEF
Asbestos	9000	ASBESTOS, CHRYSOTILE by XRD	NA	NA	NA	XRD	bulk
Asbestos	9002	ASBESTOS (bulk) by PLM	NA	NA	NA	PLM	bulk
Aspartame	5031	ASPARTAME	1 - 3	70	1200	HPLC-UV	PTFE
Azelaic acid	5019	AZELAIC ACID	1 - 3	200	1000	GC-FID	PVC
Azinphos methyl	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12	240	GC-FPD	OVS-2
B[a]P	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Barium	7056	BARIUM, SOLUBLE COMPOUNDS	1 - 4	50	2000	FAAS	MCEF
Benz(a)anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzene	3700	BENZENE by portable GC	> 0.02	NA	80% capac	GC	air bag
Benzene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	5	30	GC-FID	CCT
Benzene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2	30	GC-FID	CCT
Benzidine Dyes	5013	DYES	1 - 3	150	500	HPLC-UV	PTFE
Benzidine	5509	BENZIDINE and 3,3'-DICHLORO-BENZIDINE	0.2	20	100	HPLC-UV	GFF
Benzo(a)pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzo(b)fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzo(e)pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzo(k)fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzo(ghi)perylene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzoyl peroxide	5009	BENZOYL PEROXIDE	1 - 3	40	400	HPLC-UV	MCEF
Benzyl chloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	6	50	GC-FID	CCT
Beryllium	7300	ELEMENTS by ICP	1 - 4	1250	2000	ICP-AES	MCEF
Beryllium & compounds	7102	BERYLLIUM and cpds, as Be	1 - 4	25	1000	HGAAS	MCEF
Biphenyl	2530	DIPHENYL	0.01-0.5	15	30	GC-FID	Tenax GC
Boron carbide	7506	BORON CARBIDE	1.7 or 2.2	100	1000	XRD	CYC & PVC
Boron oxide	0500	PARTICULATES N.O.R.	1.5-2.0	25	133	Grav	PVC
Bromine	6011	CHLORINE and BROMINE	0.3-1.0	8	360	IC	Ag F
Bromoform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	4	70	GC-FID	CCT
Bromotrifluoromethane	1017	TRIFLUOROBROMOMETHANE	0.01-0.05	0.3	1.0	GC-FID	2 CCT
Bromoxynil	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	2	400	HPLC-UV	PTFE
Bromoxynil octanoate	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	90	400	HPLC-UV	PTFE
',3-Butadiene	1024	1,3-BUTADIENE	0.01-0.5	5	25	GC-FID	CCT
2-Butanone	2500	METHYL ETHYL KETONE	0.01-0.2	1	12	GC-FID	Amb XE-347

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
2-Butoxyethanol	1403	ALCOHOLS IV	0.01-0.05	2	10	GC-FID	CCT
n-, sec-, & t-Butyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
tert-Butyl alcohol	1400	ALCOHOLS I	0.01-0.2	1	10	GC-FID	CCT
n- & sec-Butyl alcohol	1401	ALCOHOLS II	0.01-0.2	2	10	GC-FID	CCT
n-Butylamine	2012	n-BUTYLAMINE	0.01-1.0	2	100	GC-FID	SG + H_2SO_4
Butyl cellosolve	1403	ALCOHOLS IV	0.01-0.05	1	10	GC-FID	CCT
Butyl glycidyl ether	1616	BUTYL GLYCIDYL ETHER	0.01-0.2	15	30	GC-FID	CCT
n-Butyl mercaptan	2542	MERCAPTANS	0.1-0.2	10	150	GC-FPD	GFF/HgAc
p-tert-Butyltoluene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	29	GC-FID	CCT
Butyraldehyde	2539	ALDEHYDES, SCREENING	0.05	5	5	GC-FID/MS	XAD-2/HMP
Cadmium	7300	ELEMENTS by ICP	1 - 4	13	2000	ICP-AES	MCEF
Cadmium & compounds	7048	CADMIUM and cpds, as Cd	1 - 3	25	1500	FAAS	MCEF
Calcium	7300	ELEMENTS by ICP	1 - 4	5	200	ICP-AES	MCEF
Calcium & compounds	7020	CALCIUM and cpds as Ca	1 - 3	20	400	FAAS	MCEF
Camphor	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Carbaryl (Sevin)	5006	CARBARYL	1 - 3	20	400	VIS	GFF
Carbon black	5000	CARBON BLACK	1 - 2	30	570	Grav	PVC
Carbon dioxide	6603	CARBON DIOXIDE	0.02-0.1	NA	80% capac	GC-TCD	air bag
Carbon disulfide	1600	CARBON DISULFIDE	0.01-0.2	2	25	GC-FPD	CCT & drying tube
Carbon tetrachloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	3	150	GC-FID	CCT
Chlordane	5510	CHLORDANE	0.5-1.0	10	200	GC-ECD	MCEF & Chrom 102
Chlorinated camphene	2547	CHLORINATED CAMPHENE	0.2-1	2	30	GC-ECD	MCEF
Chlorinated diphenyl oxide	5025	CHLORINATED DIPHENYL OXIDE	0.5-1.5	8	200	GC-ECN	MCEF
Chlorinated terphenyl	5014	CHLORINATED TERPHENYL	1 - 3	100	1500	GC-ECD	GFF
Chlorine	6011	CHLORINE and BROMINE	0.3-1.0	2	90	IC	Ag F
Chloroacetaldehyde	2015	CHLOROACETALDEHYDE	0.05-0.2	3	16	GC-ECD	SG
Chloroacetic acid	2008	CHLOROACETIC ACID	0.05-0.2	1	100	IC	SG
Chlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1.5	40	GC-FID	CCT
Chlorobromomethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5	8	GC-FID	CCT
Chlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE	0.01-0.05	1	4	GC-FID	2CCT (lg+sm)
Chlorodiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05-0.2	1	50	GC-ECD	GFF & Florisil
2-Chloroethanol	2513	ETHYLENE CHLOROHYDRIN	0.01-0.2	2	35	GC-FID	PCT
Chloroform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1	50	GC-FID	CCT
4-Chloronitrobenzene	2005	NITROBENZENES	0.01-1.0	1	150	GC-FID	SG
p-Chlorophenol	2014	p-CHLOROPHENOL	0.05-0.2	1.5	40	HPLC-UV	SG
Chloroprene	1002	β-CHLOROPRENE	0.01-0.1	1.5	8	GC-FID	CCT
Chlorpyrifos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12	240	GC-FPD	OVS-2
Chromic acid	7600	CHROMIUM, HEXAVALENT	1 - 4	8	400	VIS	PVC
Chromic acid	7604	CHROMIUM, HEXAVALENT	1 - 4	100	1000	IC	PVC
Chromium	7024	CHROMIUM and cpds, as Cr	1 - 3	10	1000	FAAS	MCEF

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Chromium	7300	ELEMENTS by ICP	1 - 4	5	1000	ICP-AES	MCEF
Chromium, hexavalent	7600	CHROMIUM, HEXAVALENT	1 - 4	8	400	VIS	PVC
Chromium, hexavalent	7604	CHROMIUM, HEXAVALENT	1 - 4	100	1000	IC	PVC
Chrysene	5506; 5515	POLYNUCLEAR AROMATIC H/C	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Coal tar naphtha	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Coal tar pitch volatiles	OSHA 58	COAL TAR PITCH VOLATILES	1.5-2.0	480	960	Grav & HPLC-UV	GFF
Cobalt	7300	ELEMENTS by ICP	1 - 4	25	2000	ICP-AES	MCEF
Cobalt & compounds	7027	COBALT and cpds, as Co	1 - 3	30	1500	FAAS	MCEF
Copper	7300	ELEMENTS by ICP	1 - 4	5	1000	ICP-AES	MCEF
Copper (dust & fume)	7029	COPPER (dust & fumes)	1 - 3	50	1500	FAAS	MCEF
Cresol, all isomers	2546	CRESOLS and PHENOL	0.01-0.1	1	24	GC-FID	XAD-7
Crotonaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Crotonaldehyde	3516	CROTONALDEHYDE	0.1-0.2	1	49	DPP	BuB
Cryofluorane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE, & CHLORODIFLUOROMETHANE	0.01-0.05	1	4	GC-FID	2 CCT
Cumene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	30	GC-FID	CCT
Cyanides	7904	CYANIDES, aerosol and gas	0.5-1.0	10	180	ISE	MCEF & BuB
Cyanides	6010	HYDROGEN CYANIDE	0.05-0.2	0.6	90	VIS	soda lime
Cyanuric acid	5030	CYANURIC ACID	1 - 3	10	1000	HPLC-UV	PVC
Cyclohexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2.5	5	GC-FID	CCT
Cyclohexanol	1402	ALCOHOLS III	0.01-0.2	1	10	CG-FID	CCT
Cyclohexanone	1300	KETONES I	0.01-0.2	1	10	CG-FID	CCT
Cyclohexene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	5	7	CG-FID	CCT
1,3-Cyclopentadiene	2523	1,3-CYCLOPENTADIENE	0.01-0.05	1	5	GC-FID	Chrom 104/ maleic anh.
2,4-D	5001	2,4-D and 2,4,5-T	1 - 3	15	200	HPLC-UV	GFF
Demeton	5514	DEMETON	0.2-1.0	30	500	GC-FPD	MCEF & XAD-2
Diacetone alcohol	1402	ALCOHOLS III	0.01-0.2	1	10	GC-FID	CCT
o-Dianisidine	5013	DYES	1 - 3	150	500	HPLC-UV	PTFE
Diatomaceous earth	7501	SILICA, AMORPHOUS	1 - 3	50	400	XRD	PVC/CYC
Diazinon	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Diazomethane	2515	DIAZOMETHANE	0.2	6	30	GC-FID	XAD-2 (coated)
Dibenz(a,h) anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Diborane	6006	DIBORANE	0.5-1.0	60	260	PES	PTFE & CCT w/oxidizer
Dibromodifluoromethane	1012	DIFLUORODIBROMOMETHANE	0.01-0.2	2.5	10	GC-FID	2 CCT
2-Dibutylaminoethanol	2007	AMINOETHANOL COMPOUNDS	0.01-0.2	4	24	GC-FID	SG
Dibutyl phosphate	5017	DIBUTYL PHOSPHATE	1-3	50	250	GC-FPD	PTFE
Dibutyl phthalate	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	1-3	6	200	GC-FID	MCEF

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Dibutyltin bis(isooctyl mercaptoacetate)	5504	ORGANOTIN COMPOUNDS	1-1.5	50	500	HPLC/GFAAS	GFF + XAD-2
o-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1	60	GC-FID	CCT
p-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1	10	GC-FID	CCT
3,3'-Dichlorobenzidine	5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE	0.2	20	100	HPLC-UV	GFF
Dichlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1	4	GC-FID	2 CCT (lg + sm)
1,1-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5	15	GC-FID	CCT
1,2-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5	50	GC-FID	CCT
Dichloroethyl ether	1004	DICHLOROETHYL ETHER	0.01-1.0	2	15	GC-FID	CCT
1,2-Dichloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2	5	GC-FID	CCT
Dichlorofluoromethane	2516	DICHLOROFLUOROMETHANE	0.01-0.05	0.25	3	GC-FID	2 CCT (lg)
1,1-Dichloro-1-nitroethane	1601	1,1-DICHLORO-1-NITROETHANE	0.01-1.0	1.5	15	GC-FID	PCT
1,2-Dichloropropane	1013	PROPYLENE DICHLORIDE	0.01-0.2	0.1	3.5	GC-ECN	PCT
1,2-Dichlorotetra-fluoroethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1	4	GC-FID	2 CCT (lg + sm)
Dicrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Diethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5	300	IC	IMP
Diethylamine	2010	AMINES, ALIPHATIC	0.01-1.0	3	30	GC-FID	SG
2-Diethylaminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4	24	GC-FID	SG
Diethylenetriamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Di-(2-ethylhexyl) phthalate	5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE	1 - 3	10	200	GC-FID	MCEF
Difluorodibromomethane	1012	DIFLUORODIBROMOMETHANE	0.01-0.2	2.5	10	GC-FID	2 CCT
Difluorodichloromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1	4	GC-FID	2 CCT
Diisobutyl ketone	1300	KETONES I	0.01-0.2	1	10	GC-FID	CCT
Dimethylacetamide	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	0.01-1.0	15	80	GC-FID	SG
Dimethylamine	2010	AMINES, ALIPHATIC	0.01-1.0	3	30	GC-FID	SG
N,N-Dimethylaniline	2002	AMINES, AROMATIC	0.02-1.0	3	30	GC-FID	SG
Dimethylarsinic acid	5022	ARSENIC, ORGANO-	1 - 3	50	1000	IC-HYAAS	PTFE
Dimethylformamide	2004	DIMETHYLACETAMIDE & DIMETHYLFORMAMIDE	0.01-1.0	15	80	GC-FID	SG
1,1-Dimethylhydrazine	3515	1,1-DIMETHYLHYDRAZINE	0.2-1.0	2	100	VIS	BuB (.1 M HCl)
N,N-Dimethyl-p-toluidine	2002	AMINES, AROMATIC	0.02-1.0	20	100	GC-FID	SG
Dimethyl sulfate	2524	DIMETHYL SULFATE	0.01-0.2	0.25	12	GC-ECN	Por P
Dioxane	1602	DIOXANE	0.01-0.2	0.5	15	GC-FID	CCT
Diphenyl	2530	DIPHENYL	0.01-0.5	15	30	GC-FID	Tenax GC
Disulfoton	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Dyes- benzidine-, o-tolidine-, o- dianisidine-	5013	DYES, BENZIDINE-, o- TOLIDINE-, o-DIANISIDINE	1 - 3	150	500	HPLC-UV	PTFE

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Elements	7300	ELEMENTS by ICP	1 - 4	varies	varies	ICP-AES	MCEF
Endrin	5519	ENDRIN	0.5-1.0	12	400	GC-ECD	MCEF & Chrom 102
Epichlorohydrin	1010	EPICHLOROHYDRIN	0.01-0.2	2	30	GC-FID	CCT
EPN	5012	EPN	1 - 2	15	700	GC-FPD	GFF
1,2-Epoxypropane	1612	PROPYLENE OXIDE	0.01-0.2	0.5	5	GC-FID	CCT
Ethanol	1400	ALCOHOLS I	0.01-0.05	0.1	1	GC-FID	CCT
Ethanolamine	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4	24	GC-FID	SG
Ethion; Ethoprop	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
2-Ethoxyethanol	1403	ALCOHOLS IV	0.01-0.05	1	6	GC-FID	CCT
2-Ethoxyethyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Ethyl acetate	1457	ETHYL ACETATE	0.01-0.2	0.1	10	GC-FID	CCT
Ethyl acrylate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Ethyl amyl ketone	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Ethylbenzene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	24	GC-FID	CCT
Ethyl bromide	1011	ETHYL BROMIDE	0.01-0.2	0.5	4	GC-FID	CCT
Ethyl butyl ketone	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Ethyl chloride	2519	ETHYL CHLORIDE	0.02-0.05	0.3	3	GC-FID	2 CCT (lg))
Ethylene chlorohydrin	2513	ETHYLENE CHLOROHYDRIN	0.01-0.2	2	35	GC-FID	PCT
Ethylenediamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Ethylene dibromide	1008	ETHYLENE DIBROMIDE	0.02-0.2	0.1	25	GC-ECD	CCT
Ethylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1	50	GC-FID	CCT
Ethylene glycol dinitrate	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2-1.0	3	100	GC-ECD	Tenax GC
Ethylene oxide	1614	ETHYLENE OXIDE	0.05-0.15	1	24	GC-ECD	PCT w/HBr
Ethylene oxide	3702	ETHYLENE OXIDE by portable GC	> 0.02	NA	80% capac	GC-PID	air bag
Ethylene thiourea	5011	ETHYLENE THIOUREA	1 - 3	200	800	VIS	PVC or MCEF
Ethylenimine	3514	ETHYLENIMINE	0.2	1	48	HPLC-UV	BuB
Ethyl ether	1610	ETHYL ETHER	0.01-0.2	0.25	3	GC-FID	CCT
Ethyl formate	1452	ETHYL FORMATE	0.01-0.2	0.3	10	GC-FID	CCT
Ethyl mercaptan	2542	MERCAPTANS	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Fenamiphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Fibrous glass	7400	ASBESTOS & other FIBERS by PCM	0.5-16	400	varies	PCM	MCEF
Fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Fluorene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Fluorides	7902	FLUORIDES, aerosol & gas	1 - 2	12	800	ISE	MCEF & pad w/ Na_2CO_3
Fluorides	7906	FLUORIDES by IC	1 - 2	1 (sol) 120 (insol)	800	IC	MCEF & pad w/ Na_2CO_3
Fluorotrichloromethane	1006	FLUOROTRICHLOROMETHANE	0.01-0.05	0.3	7	GC-FID	CCT (lg)
Fonofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12	240	GC-FPD	OVS-2

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Formaldehyde	2541	FORMALDEHYDE	0.01-0.1	1	36	GC-FID	XAD-2/HMP
Formaldehyde	3500	FORMALDEHYDE	0.2-1.0	1	100	VIS	PTFE & 2 IMP
Formaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Formaldehyde	5700	FORMALDEHYDE on dust	2	240	1050	HPLC-UV	IOM/PVC
Formic acid	2011	FORMIC ACID	0.05-0.2	1	24	IC	PTFE & SG (washed)
Furfural	2529	FURFURAL	0.01-0.05	1	12	GC-FID	XAD-2/HMP
Furfural	2539	ALDEHYDES, SCREENING	0.05	5	5	GC-FID/MS	XAD-2/HMP
Furfuryl alcohol	2505	FURFURYL ALCOHOL	0.01-0.05	3	25	GC-FID	Por Q
Glutaraldehyde	2532	GLUTARALDEHYDE	0.01-0.08	4	39	HPLC-UV	SG/DNPH
Glycerin mist	0500	PARTICULATES N.O.R.	1 - 2	7	133	Grav	PVC
Glycidol	1608	GLYCIDOL	0.01-1.0	5	100	GC-FID	CCT
Heptanal	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
n-Heptane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4	4	GC-FID	CCT
Hexachlorobutadiene	2543	HEXACHLOROBUTADIENE	0.05-0.2	1	100	GC-ECD	XAD-2
Hexachloro-1,3-cyclopentadiene	2518	HEXACHLORO-1,3-CYCLOPENTADIENE	0.01-0.2	0.25	90	GC-ECD	2 Por T
Hexachloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	3	70	GC-FID	CCT
Hexamethylenediisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5	500	HPLC-ECHD	IMP
Hexanal	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
n-Hexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4	4	GC-FID	CCT
2-Hexanone	1300	KETONES I	0.01-1.0	1	10	GC-FID	CCT
Hydrazine	3503	HYDRAZINE	0.2-1.0	7	100	VIS	BuB
Hydrogen bromide	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG
Hydrogen chloride	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG
Hydrogen cyanide	6010	HYDROGEN CYANIDE	0.05-0.2	2	90	VIS	soda lime
Hydrogen cyanide	7904	CYANIDES, AEROSOL & GAS	0.5-1.0	7	100	ISE	MCEF
Hydrogen flouride	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG
Hydrogen flouride	7902	FLUORIDES, AEROSOL & GAS	1 - 2	12	800	ISE	MCEF & pad w/Na_2CO_3
Hydrogen flouride	7906	FLUORIDES by IC	1 - 2	1	800	IC	MCEF & pad w/Na_2CO_3
Hydrogen sulfide	6013	HYDROGEN SULFIDE	0.1-1.5	1.2	40	IC	PTFE & CCT (lg)
Hydroquinone	5004	HYDROQUINONE	1 - 4	30	180	HPLC-UV	MCEF
Indeno [1,2,3-cd] pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Iodine	6005	IODINE	0.5-1.0	15	225	IC	CCT w/alkali
Iron	7300	ELEMENTS by ICP	1 - 4	5	100	ICP-AES	MCEF
Isoamyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Isoamyl alcohol	1402	ALCOHOLS III	0.01-0.2	1	10	GC-FID	CCT
Isobutyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Isobutyl alcohol	1401	ALCOHOLS II	0.01-0.2	2	10	GC-FID	CCT
Isobutyraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Isocyanates	5521	ISOCYANATES, MONOMERIC	1.0	5	500	HPLC-ECHD	IMP

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Isophorone	2508	ISOPHORONE	0.01-1.0	2	25	GC-FID	PCT
Isopropyl acetate	1454	ISOPROPYL ACETATE	0.02-0.2	0.1	9	GC-FID	CCT
Isopropyl alcohol	1400	ALCOHOLS I	0.01-0.2	0.2	3	GC-FID	CCT
Isopropyl ether	1618	ISOPROPYL ETHER	0.01-0.05	0.1	3	GC-FID	CCT
Isopropyl glycidyl ether	1620	ISOPROPYL GLYCIDYL ETHER	0.01-0.2	1	30	GC-FID	CCT
Isovaleraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Kepone	5508	KEPONE	0.5-1.0	50	600	GC-ECD	MCEF & IMP
Kerosene	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Lead	7082	LEAD by FAAS	1 - 4	200	1500	FAAS	MCEF
Lead	7105	LEAD by HGAAS	1 - 4	1	1500	HGAAS	MCEF
Lead	7300	ELEMENTS by ICP	1 - 4	1250	2000	ICP-AES	MCEF
Lead sulfide	7505	LEAD SULFIDE	1.7 or 2.2	600	1000	XRD	CYC & PVC
Lindane	5502	ALDRIN and LINDANE	0.2-1.0	18	240	GC-ECN	GFF & BuB
Lithium	7300	ELEMENTS by ICP	1 - 4	100	2000	ICP-AES	MCEF
Lithium hydroxide	7401	ALKALINE DUSTS	1 - 4	70	1000	Titration	PTFE
Magnesium	7300	ELEMENTS by ICP	1 - 4	5	67	ICP-AES	MCEF
Malathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	60	GC-FPD	OVS-2
Maleic Anhydride	3512	MALEIC ANHYDRIDE	0.2-1.5	40	500	HPLC-UV	BuB
Manganese	7300	ELEMENTS by ICP	1 - 4	5	200	ICP-AES	MCEF
MBK	1300	KETONES I	0.01-0.2	1	10	GC-FID	CCT
MDI (4,4'-methylene-bisphenyl isocyanate)	5521	ISOCYANATES, MONOMERIC	1.0	5	500	HPLC-ECHD	IMP
Mercury	6009	MERCURY	0.15-0.25	2	100	AAS-cold vap	Hopcalite
Mercaptans	2542	MERCAPTANS	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Mesityl oxide	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Metals in air	7300	ELEMENTS by ICP	1 - 4	varies	2000	ICP-AES	MCEF
Methamidophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Methanol	2000	METHANOL	0.02-0.2	1	5	GC-FID	SG
2-Methoxyethyl acetate	1451	METHYL CELLOSOLVE ACETATE	0.01-0.2	0.2	20	GC-FID	CCT
2-Methoxyethanol	1403	ALCOHOLS IV	0.01-0.05	6	50	GC-FID	CCT
Methyl acetate	1458	METHYL ACETATE	0.01-0.2	0.2	10	GC-FID	CCT
Methyl acrylate	1459	METHYL ACRYLATE	0.01-0.2	1	5	GC-FID	CCT
Methylal	1611	METHYLAL	0.01-0.2	1	3	GC-FID	CCT
Methyl-(n-amyl)-ketone	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Methylarsonic acid	5022	ARSENIC, ORGANO-	1 - 3	50	1000	IC-HYAAS	PTFE
Methyl cellosolve	1403	ALCOHOLS IV	0.01-0.05	6	50	GC-FID	CCT
Methyl cellosolve acetate	1451	METHYL CELLOSOLVE ACETATE	0.01-0.2	0.2	20	GC-FID	CCT
Methyl chloride	1001	METHYL CHLORIDE	0.01-0.1	0.4	3	GC-FID	2 CCT (lg + sm)
Methyl chloroform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.1	8	GC-FID	CCT
Methyl cyanide	1606	ACETONITRILE	0.01-0.2	3	25	GC-FID	CCT
Methyl cyclohexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4	4	GC-FID	CCT
Methylcyclohexanol	1404	METHYLCYCLOHEXANOL	0.01-0.2	1	15	GC-FID	CCT

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Methylcyclohexanone	2521	METHYLCYCLOHEXANONE	0.01-0.05	1	6	GC-FID	Por Q
Methylene chloride	1005	METHYLENE CHLORIDE	0.01-0.2	0.5	2.5	GC-FID	2 CCT
4,4'-Methylenedianiline	5029	4,4'-METHYLENEDIANILINE	1 - 2	10	1000	HPLC-UV	GFF/H_2SO_4
Methyl ethyl ketone	2500	METHYL ETHYL KETONE	0.01-0.2	0.25	12	GC-FID	MS (carbon)
Methyl ethyl ketone peroxide	3508	METHYL ETHYL KETONE PEROXIDE	0.5-0.2	52	520	VIS	IMP
5-Methyl-3-heptanone	1301	KETONES II	0.01-0.2	1	25	GC-FID	CCT
Methyl iodide	1014	METHYL IODIDE	0.01-1.0	15	50	GC-FID	CCT
Methyl isoamyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
Methyl isobutyl carbinol	1402	ALCOHOLS III	0.01-0.2	1	10	GC-FID	CCT
Methyl isobutyl ketone	1300	KETONES I	0.01-0.2	1	10	GC-FID	CCT
Methyl mercaptan	2542	MERCAPTANS	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Methyl methacrylate	2537	METHYL METHACRYLATE	0.01-0.05	1	8	GC-FID	XAD-2
Methyl parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
α-Methyl styrene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	30	GC-FID	CCT
Methyl tert-butyl ether	1615	METHYL tert-BUTYL ETHER	0.1-0.2	2	96	GC-FID	2 CCT (lg)
Mevinphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12	240	GC-FPD	OVS-2
Mineral spirits	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Molybdenum	7300	ELEMENTS by ICP	1 - 4	5	67	ICP-AES	MCEF
Monocrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Monomethylaniline	3511	MONOMETHYLANILINE	0.2-1.0	11	100	GC-FID	BuB/H_2SO_4
Monomethylhydrazine	3510	MONOMETHYLHYDRAZINE	0.5-1.5	3	20	VIS	BuB/HCl
Naphtha (coal tar)	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Naphthalene	1501	HYDROCARBONS, AROMATIC	0.01-1.0	100	200	GC-FID	CCT
Naphthalene	5506	POLYNUCLEAR AROMATIC H/C	2.0	200	1000	HPLC-UV; GC-FID	PTFE & XAD-2
Naphthylamines	5518	NAPHTHYLAMINES	0.2-0.8	30	100	GC-FID	GFF & SG
Nickel	7300	ELEMENTS by ICP	1 - 4	25	1000	ICP-AES	MCEF
Nickel carbonyl	6007	NICKEL CARBONYL	0.05-0.2	7	80	HGAAS	CCT (low Ni)
Nicotine	2544	NICOTINE	1.0	60	400	GC-NPD	XAD-2
Nitric acid	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG (washed)
Nitric oxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025	1.5	6	VIS	MS w/TEA & oxidizer
p-Nitroaniline	5033	p-NITROANILINE	1 - 3	18	350	HPLC-UV	MCEF
Nitrobenzene	2005	NITROBENZENES	0.01-1	10	150	GC-FID	SG
p-Nitrochlorobenzene	2005	NITROBENZENES	0.01-1	1	150	GC-FID	SG
Nitroethane	2526	NITROETHANE	0.01-0.05	1.5	3	GC-FID	2XAD-2
Nitrogen dioxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025-0.2	1.5	6	VIS	MS w/TEA
Nitroglycerin	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2-1.0	3	100	GC-ECD	Tenax-GC
Nitromethane	2527	NITROMETHANE	0.01-0.05	1.2	3	GC-FPD	Chrom 106
2-Nitropropane	2528	2-NITROPROPANE	0.01-0.05	0.1	2	GC-FID	Chrom 106
Nitrosamines	2522	NITROSAMINES	0.2-2.0	15	1000	GC-TEA	Thermosorb/N

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Nitrotoluene	2005	NITROBENZENES	0.01-0.2	1	30	GC-FID	SG
Nitrous oxide	6600	NITROUS OXIDE	NA	NA	80% capac	IR	air bag
Nuisance dusts	0500	PARTICULATES N.O.R.	1 - 2	7	133	GRAV	PVC
n-Octane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4	4	GC-FID	CCT
1-Octanethiol	2510	1-OCTANETHIOL	0.01-0.2	1	15	GC-FPD	Tenax GC
Oil mist (mineral)	5026	OIL MIST, MINERAL	1 - 3	20	500	IR	PVC or MCE
Organophosphorus Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Oxygen	6601	OXYGEN	NA	1	NA	Sensor	portable
Paraquat	5003	PARAQUAT	1 - 4	40	1000	HPLC-UV	PTFE
Parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12	240	GC-FPD	OVS-2
Particulates N.O.R.	0600	PARTICULATES, N.O.R, RESP.	1.7 or 2.2	20	400	Grav.	CYC & PVC
Pentachlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
Pentachloroethane	2517	PENTACHLOROETHANE	0.01-0.2	1	10	GC-ECD	Por R
Pentachlorophenol	5512	PENTACHLOROPHENOL	0.5-1.0	48	480	HPLC-UV	MCEF & BuB
Pentamidine	5032	PENTAMIDINE ISETHIONATE	1 - 2	50	1500	HPLC/FL	PVC/opaque
n-Pentane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.05	2	2	GC-FID	CCT
2-Pentanone	1300	KETONES I	0.01-2.0	1	10	GC-FID	CCT
Petroleum ether/naphtha	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Phenol	2546	CRESOLS and PHENOL	0.01-0.1	1	24	GC-FID	XAD-7
Phenyl ether	1617	PHENYL ETHER	0.01-0.2	1	50	GC-FID	CCT
Phenyl ether-diphenyl mixture	2013	PHENYL ETHER-DIPHENYL MIXTURE	0.01-0.2	1	40	GC-FID	SG
Phenyl glycidyl ether	1619	PHENYL GLYCIDYL ETHER	0.01-1	80	150	GC-FID	CCT
Phenylhydrazine	3518	PHENYLHYDRAZINE	0.2-1.0	25	120	VIS	BuB/HCl
Phorate	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Phosdrin (mevinphos)	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	480	GC-FPD	OVS-2
Phosphine	6002	PHOSPHINE	0.01-0.2	1	16	VIS	SG/$Hg(CN)_2$
Phosphoric acid	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG (washed)
Phosphorus	7300	ELEMENTS by ICP	1 - 4	50	2000	ICP-AES	MCEF
Phosphorus	7905	PHOSPHORUS	0.01-0.2	5	100	GC-FPD	Tenax GC
Phosphorus trichloride	6402	PHOSPHORUS TRICHLORIDE	0.05-0.2	11	100	VIS	BuB/H_2O
Platinum	7300	ELEMENTS by ICP	1 - 4	13	2000	ICP-AES	MCEF
PAH	5506	POLYNUCLEAR AROMATIC H/C	2.0	200	1000	HPLC-FL/UV	PTFE & XAD-2
Polyacrylate	5035	SUPER ABSORBENT POLYMER	1 - 2	50	1500	ICP or AAS	PVC
Polychlorobiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05-0.2	1	50	GC-ECD	GFF & Florisil
Potassium hydroxide	7401	ALKALINE DUSTS	1 - 4	70	1000	titration	PTFE
Propionaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
n-Propyl acetate	1450	ESTERS I	0.01-0.2	1	10	GC-FID	CCT
n-Propyl alcohol	1401	ALCOHOLS II	0.01-0.2	1	10	GC-FID	CCT
Propylene dichloride	1013	PROPYLENE DICHLORIDE	0.01-0.2	0.1	3.5	GC-ECN	PCT
Propylene oxide	1612	PROPYLENE OXIDE	0.01-0.2	0.5	5	GC-FID	CCT

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Pyrethrum	5008	PYRETHUM	1 - 4	20	400	HPLC-UV	GFF
Pyridine	1613	PYRIDINE	0.01-1.0	18	150	GC-FID	CCT
Ribavirin	5027	RIBAVIRIN	1 - 4	5	1000	HPLC-UV	GFF
Ronnel	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	60	GC-FPD	OVS-2
Rotenone	5007	ROTENONE	1 - 4	8	400	HPLC-UV	PTFE
Rubber solvent	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Selenium	7300	ELEMENTS by ICP	1 - 4	5	2000	ICP-AES	MCEF
Silica, amorphous	7501	SILICA, AMORPHOUS	1.7 or 2.2	50	400	XRD	PVC (total) or PVC & CYC
Silica in coal mine dust	7603	SILICA in coal mine dust	1.7 or 2.2	300	1000	IR	CYC & PVC
Silica, crystalline	7601	SILICA, CRYSTALLINE	1.7 or 2.2	400	800	VIS	CYC & MCE or PVC
Silica, crystalline	7602	SILICA, CRYSTALLINE (IR)	1.7 or 2.2	400	800	IR	CYC, & MCE or PVC
Silica, crystalline, respirable	7500	SILICA, CRYSTALLINE, RESP.	1.7 or 2.2	400	1000	XRD	CYC & PVC
Silver	7300	ELEMENTS by ICP	1 - 4	250	2000	ICP-AES	MCEF
Sodium hexafluoro-aluminate	7902	FLUORIDES, aerosol & gas	1 - 2	12	800	ISE	MCEF & pad w/Na_2CO_3
Sodium hexafluoro-aluminate	7906	FLUORIDES by IC	1-2	120	800	IC	MCEF & pad w/Na_2CO_3
Sodium hydroxide	7401	ALKALINE DUSTS	1 - 4	70	1000	Titration	PTFE
Stibine	6008	STIBINE	0.01-0.2	4	50	VIS	SG w/$HgCl_2$
Stoddard solvent	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Strychnine	5016	STRYCHNINE	1 - 3	70	1000	HPLC-UV	GFF
Styrene	1501	HYDROCARBONS, AROMATIC	0.01-1.0	1	14	GC-FID	CCT
Sulfur dioxide	6004	SULFUR DIOXIDE	0.5-1.5	4	200	IC	MCEF & Cell w/Na_2CO_3
Sulfur hexafluoride	6602	SULFUR HEXAFLUORIDE	0.01-0.05	NA	80% capac	GC-ECD	air bag
Sulfuric acid	7903	ACIDS, INORGANIC	0.2-0.5	3	100	IC	SG (washed)
Sulfuryl fluoride	6012	SULFURYL FLUORIDE	0.05-0.1	1.3	10	IC	CCT (lg)
Sulprofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FPD	OVS-2
Super absorbent polymer	5035	SUPER ABSORBENT POLYMER	1 - 3	50	1500	ICP or AAS	PVC
2,4,5-T	5001	2,4-D and 2,4,5-T	1 - 3	15	200	HPLC-UV	GFF
Tellurium	7300	ELEMENTS by ICP	1 - 4	25	2000	ICP-AES	MCEF
Terbufos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12	240	GC-FID	OVS-2
o-Terphenyl	5021	o-TERPHENYL	1 - 3	2	30	GC-FID	PTFE
1,1,2,2-Tetrabromoethane	2003	1,1,2,2-TETRABROMOETHANE	0.2-1.0	50	100	GC-FID	SG
Tetrabutyltin	5504	ORGANOTIN COMPOUNDS	1-1.5	50	500	HPLC/HGAAS	GFF & XAD-2
1,2,4,5-Tetrachlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
1,1,2,2-Tetrachloro-2,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUORO-ETHANE	0.01-0.035	0.5	2	GC-FID	CCT

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
1,1,1,2-Tetrachloro-1,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	0.01-0.035	0.5	2	GC-FID	CCT
1,1,2,2-Tetrachloroethane	1019	1,1,2,2-TETRACHLOROETHANE	0.01-0.2	3	30	GC-FID	PCT
Tetrachloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2	40	GC-FID	CCT
Tetraethyl lead	2533	TETRAETHYL LEAD (as Pb)	0.01-1.0	30	200	GC-PID	XAD-2
Tetraethyl pyrophosphate	2504	TETRAETHYL PYROPHOSPHATE	0.01-0.2	20	48	GC-FPD	2 Chrom 102
Tetrahydrofuran	1609	TETRAHYDROFURAN	0.01-0.2	1	9	GC-FID	CCT
Tetramethyl lead	2534	TETRAMETHYL LEAD (as Pb)	0.01-0.2	15	100	GC-PID	XAD-2
Tetramethyl thiourea	3505	TETRAMETHYL THIOUREA	0.2-1.0	50	250	VIS	IMP/H_2O
Tetranitromethane	3513	TETRANITROMETHANE	0.5-1.0	20	250	GC-FID	IMP/EtAc
Thallium	7300	ELEMENTS by ICP	1 - 4	25	2000	ICP-AES	MCEF
Thiram	5005	THIRAM	1 - 4	10	400	HPLC-UV	PTFE
Tin, organic compds as Sn	5504	ORGANOTIN CPDS. (as Sn)	1-1.5	50	500	HPLC/HGAAS	GFF & XAD-2
Titanium	7300	ELEMENTS by ICP	1 - 4	5	100	ICP-AES	MCEF
o-Tolidine	5013	DYES	1 - 3	150	500	HPLC-UV	PTFE
Toluene	4000	TOLUENE	NA	(15 min)	(8 h)	GC-FID	passive
Toluene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2	8	GC-FID	CCT
Toluene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	8	GC-FID	CCT
2,4 & 2,6-Toluenediamine	5516	2,4- & 2,6-TOLUENEDIAMINE	1.0	30	500	HPLC-UV	IMP
Toluene-2,4-diisocyanate	2535	TOLUENE-2,4-DIISOCYANATE	0.2-1.0	2	170	HPLC-UV	GW coated
Toluene-2,4-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5	500	HPLC-ECHD	IMP
Toluene-2,6-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5	500	HPLC-ECHD	IMP
o-Toluidine	2002	AMINES, AROMATIC	0.02-1.0	10	150	GC-FID	SG
Tribromomethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	4	70	GC-FID	CCT
Tributyl phosphate	5034	TRIBUTYL PHOSPHATE	1 - 3	2	100	GC-FPD	MCEF
Tributyltin chloride	5504	ORGANOTIN COMPOUNDS	1-1.5	50	500	HPLC/HGAAS	GFF & XAD-2
1,2,4-Trichlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
1,1,2-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	2	60	GC-FID	CCT
1,1,1-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.1	8	GC-FID	CCT
Trichloroethylene	1022	TRICHLOROETHYLENE	0.01-0.2	1	30	GC-FID	CCT
Trichloroethylene	3701	TRICHLOROETHYLENE by portable GC	> 0.02	NA	80% capac	GC	air bag
Trichlorofluoromethane	1006	FLUOROTRICHLOROMETHANE	0.01-0.05	0.3	7	GC-FID	CCT
Trichloromethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1	50	GC-FID	CCT
1,2,3-Trichloropropane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.6	60	GC-FID	CCT
Trichylohexyltin hydroxide	5504	ORGANOTIN COMPOUNDS	1-1.5	50	500	HPLC-HGAAS	GFF & XAD-2
1,1,2-Trichloro 1,2,2-trifluoroethane	1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	0.01-0.05	0.1	3	GC-FID	CCT
Triethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5	300	IC	IMP
Triethylenetetramine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Trifluorobromomethane	1017	TRIFLUOROBROMOMETHANE	0.01-0.05	0.1	1	GC-FID	2 CCT (lg+sm)

Chemical	Meth. No.	Method Name	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Trimellitic anhydride	5036	TRIMELLITIC ANHYDRIDE	1.5-2	400	1000	GC-FID	PVC
2,4,7-Trinitrofluoren-9-one	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	1 - 3	100	500	HPLC-UV	PTFE
Triorthocresyl phosphate	5037	TRIORTHOCRESYL PHOSPHATE	1 - 3	2	100	GC-FPD	MCEF
Triphenyl phosphate	5038	TRIPHENYL PHOSPHATE	1 - 3	10	400	GC-FPD	MCEF
Tungsten, soluble/insoluble	7074	TUNGSTEN (soluble/insoluble)	1 - 4	200	1000	FAAS	MCEF
Turpentine	1551	TURPENTINE	0.01-0.2	1	10	GC-FID	CCT
Valeraldehyde	2536	VALERALDEHYDE	0.01-0.04	0.5	10	GC-FID	XAD-2/HMP
Valeraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Vanadium	7300	ELEMENTS by ICP	1 - 4	5	2000	ICP-AES	MCEF
Vanadium oxides	7504	VANADIUM OXIDES	1.7 or 2.2	200	1000	XRD	CYC & PVC
Vinyl acetate	1453	VINYL ACETATE	0.1-0.2	0.75	24	GC-FID	MS (carbon)
Vinyl benzene	1501	HYDROCARBONS, AROMATIC	.01-1	1	14	GC-FID	CCT
Vinyl bromide	1009	VINYL BROMIDE	0.01-0.2	2	10	GC-FID	CCT (lg)
Vinyl chloride	1007	VINYL CHLORIDE	0.05	0.7	5	GC-FID	2 CCT
Vinylidene chloride	1015	VINYLIDENE CHLORIDE	0.01-0.2	2.5	7	GC-FID	CCT
Vinyl toluene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1	24	GC-FID	CCT
VM&P naphtha	1550	NAPHTHAS	0.01-0.2	1.3	20	GC-FID	CCT
Warfarin	5002	WARFARIN	1 - 4	200	1000	HPLC-UV	PTFE
Xylene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	2	23	GC-FID	CCT
2,4-Xylidine	2002	AMINES, AROMATIC	0.02-0.2	3	20	GC-FID	SG
Yttrium	7300	ELEMENTS by ICP	1 - 4	5	1000	ICP-AES	MCEF
Zinc and compounds	7030	ZINC and compounds, as Zn	1 - 3	2	400	FAAS	MCEF
Zinc	7300	ELEMENTS by ICP	1 - 4	5	200	ICP-AES	MCEF
Zinc oxide	7502	ZINC OXIDE	1 - 3	10	400	XRD	PVC
Zirconium	7300	ELEMENTS by ICP	1 - 4	5	200	ICP-AES	MCEF

KEY TO ABBREVIATIONS

Sampling Media/Devices

Ag F	Silver membrane filter
BuB	Bubbler
CCT	Coconut shell charcoal tube
Cell	Cellulose
Chrom	Chromosorb
CYC	Cyclone
DNPH	Dinitrophenylhydrazine HCl
GFF	Glass fiber filter
GW	Glass wool
HMP	2-(Hydroxymethyl)piperidine
IMP	Impinger
IOM	Inspirable dust sampler
MCEF	Mixed cellulose ester filter
MS	Molecular sieve
NITC	1-naphthylisothiocyanate
OVS-2	OSHA versatile sampler (quartz filter/XAD-2)
PCT	Petroleum charcoal tube
Por	Poropak
PTFE	Polytetrafluoroethylene (Teflon) filter
PVC	Polyvinyl chloride filter
SG	Silica gel
TEA	Triethanolamine

Analytical Techniques

AAS	Atomic absorption spectrophotometry
AMP	Amperometric detector
CD	Conductivity detector
DPP	Differential Pulse Polargraphy
ECD	Electron capture detector
ECHD	Electrochemical detector
ECN	Electrolytic conductivity detector
FAAS	Flame AAS
FID	Flame ionization detector
FL	Fluorescence detector
FPD	Flame photometric detector
GC	Gas chromatography
Grav	Gravimetric (filter weight)
HGAAS	Graphite furnace AAS
HPLC	High performance liquid chromatography
HYAAS	Hydride generation AAS
IC	Ion chromatography
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
IR	Infrared spoectrophotometry
ISE	Ion specific electrode
MS	Mass spectrometry
NPD	Nitrogen phosphorus detector
PCM	Phase contrast microscopy
PES	Plasma emission spectrometry
PID	Photoionization detector
PLM	Polarized light microscopy
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
UV	Ultraviolet
VIS	Visible absorption spectrophotometry
XRD	X-ray diffraction
XRF	X-ray fluorescence

NA Not applicable

I. INTRODUCTION

A. PURPOSE AND SCOPE

The NIOSH Manual of Analytical Methods (NMAM) is a collection of air and biological analytical methods which NIOSH has evaluated. NMAM will be updated as methods are developed, evaluated or revised by NIOSH. NMAM is available in looseleaf hard copy form, without binders, from the U.S. Government Printing Office, Washington, DC 20402 (telephone 202/783-3238), and in electronic form from various software companies that have entered into publishing agreements with NIOSH as of the time of this printing:

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420-F Executive Court North
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Telephone: 800/536-0404
FAX: 707/864-2815

Canadian Centre for Occupational Health and Safety (CCOHS)
250 Main Street East
Hamilton, Ontario, Canada L8N 1H6
Telephone: 800/668-4284 or 905/570-8094
FAX: 905/572-2206

The present edition of NMAM replaces previous editions (see page ii for ordering information if previous editions are needed for historical purposes). A few methods from the second edition have not been included in the present edition because of infrequent use at NIOSH (see pp. A-15 through A-28).

These methods are intended to promote accuracy, sensitivity and specificity in industrial hygiene analyses. The scientific literature contains equally accurate methods for many of the substances. There will be situations where users of these methods will need to modify them (e.g., to accommodate interfering compounds from the workplace, to take advantage of special capabilities of the laboratory, or to make possible the analysis of a single sample for several contaminants). When method modifications are made, quality control data showing the reliability of the modified method should be obtained. For example:

- The volume of air sampled on solid sorbents should be reduced in cases of high vapor concentration or high humidity and, in some cases, may be increased above V_{MAX} if such concentrations are relatively low.
- The automation of sample work-up and measurement procedures usually requires some modification of the nonautomated procedure.
- Chromatographic conditions, including choice of column and detector, can be modified to eliminate interferences during measurement.

B. HOW TO USE NMAM

The methods are arranged **alphabetically** by method name, and some method names may refer to a group of related substances. It is possible for you to rearrange the methods **in order of method number** if you find this arrangement more convenient.

1. METHOD FINDER

The easiest and fastest way to locate a method is to refer to the **Method Finder** inside the front cover of the Manual. The Method Finder is an alphabetical listing of common chemical names and their associated methods with information on Compound, Method Number, Method Name, Sampling Rate, Minimum Volume, Maximum Volume, Analytical Technique, and Sampler for quick reference.

2. METHOD NUMBERING SYSTEM

Substances having the same sampler, sample preparation and measurement technique may be grouped together in one method (note that this numbering system is unchanged from the Third Edition):

Method #	Substances
0001-0899	General air samples
0900-0999	Bioaerosols
1000-1999	Organic gases on charcoal
2000-3499	Organic gases on other solid sorbents
3500-3999	Organic gases on other samplers (e.g., liquids, direct-reading)
4000-4999	Organic gases on diffusive samplers
5000-5999	Organic aerosols
6000-6999	Inorganic gases
7000-7999	Inorganic aerosols
8000-8999	Biological samples
9000-9999	Bulk samples

3. INDEXES

There are three indexes in the back of the Manual which can be used in locating methods:

a. Fourth Edition Methods - An index of current NIOSH methods in order of Method number (pp. A-11 through A-14). [**NOTE:** The fourth edition uses the same numbering system as the third edition. This Index also lists the disposition of all third edition methods.]

b. First and Second Edition Method Numbers - An index of the first and second edition "P&CAM" and "S" methods, from which many of the current methods were derived. This index shows the disposition of all of these methods, whether or not they were revised into current methods (pp. A-15 through A-28).

c. Names and Synonyms - An alphabetical listing of all chemical names and synonyms used in the current methods, including Chemical Abstracts Service numbers ("yellow pages", pp. A-29 through A-45).

4. METHOD FORMAT

The methods consist of three major parts:

a. Front page The first page of each method concisely summarizes sampling and measurement parameters, and gives estimates of limit of detection, working range, overall and measurement precision, and interferences. References to other methods are given. New to the fourth edition are: Method Classification, NIOSH Registry of Toxic Effects of Chemical Substances (RTECS) number, and an estimate of Accuracy at the OSHA PEL. (See Figure 1.)

b. Instructions The second page of each method begins with lists of required REAGENTS and EQUIPMENT. Please note that these reflect the conditions under which the methods were evaluated, and that there may be some latitude for variation. Commercial versions of the samplers may differ slightly from the methods. The user of the methods is responsible for assuring accuracy of the results (e.g., to determine that breakthrough and recovery are acceptable for each lot of samplers used). Typical tolerances are:

- Glass tubing used to contain solid sorbents: inside diameter is usually not critical within the range 4 to 6 mm; length should be sufficient to contain the specified mass of sorbent.

- Contents of sorbent tubes: mass of sorbent within ±10% of specification; separators of either glass wool or cleaned polyurethane foam unless otherwise indicated; sorbent mesh size of 20/40 unless sampling efficiency dictates otherwise. Filled sorbent tubes should be sealed to protect from contamination.

The SPECIAL PRECAUTIONS section gives safe practices to be observed during sampling and measurement. Next come the step-by-step instructions for SAMPLING, SAMPLE PREPARATION, CALIBRATION AND QUALITY CONTROL, MEASUREMENT, and CALCULATIONS. Any lengthy instructions for sampler preparation or standardization of stock solutions appear in appendixes to the method. Nomenclature is consistent with the Glossary of Abbreviations, Definitions and Symbols (page A-3).

[**NOTE:** Additional general information relating to sampling and measurement is contained in the chapters on quality assurance and sampling (pp. 6 through 16 and 17 through 32 of these "Blue Pages").]

c. Supporting information Laboratory and field data relating to the method are summarized in the EVALUATION OF METHOD section and on the summary page, along with pertinent references.

NAME OF SUBSTANCE **METHOD #**

FORMULA Molecular Weight Chemical Abstracts Service # RTECS #

Method numbers are the same as those in the 3rd edition. **Evaluation** (Full, Partial, Unrated) is assigned as described on p. 5 of the "blue pages". **Issue date** reflects current version (August 15, 1993) and previous 3rd edition versions, if any.

OSHA : These exposure limit values are
NIOSH: those in effect at the time of
ACGIH: printing of the method.

PROPERTIES: Boiling/melting points, equilibrium vapor pressure, and density help determine the sample aerosol/vapor composition.

SYNONYMS: Common synonyms for the substance, including Chemical Abstracts Service (CAS) numbers; these are all listed alphabetically in the **Index of Names and Synonyms** ("yellow pages" in this Manual).

SAMPLING

SAMPLER: Brief description of sampling EQUIPMENT

FLOW RATE: Acceptable sampling range, L/min

VOL-MIN: Minimum sample volume (L); corresponds to Limit of Quantitation (LOQ) at OSHA PEL

-MAX: Maximum sample volume (L) to avoid analyte breakthrough or overloading

BLANKS: Each set should have at least 2 field blanks, up to 10% of samples, plus 6 or more media blanks in the case of coated sorbents, impinger solutions, or other

ACCURACY

Data are for experiments in which known atmospheres of the substance were generated and analyzed according to the method. Target accuracy is less than 25% difference from actual concentration at or above the OSHA PEL.

MEASUREMENT

TECHNIQUE: The measurement technique used

ANALYTE: The chemical species actually measured

A summary of the measurement EQUIPMENT, SAMPLE PREPARATION, and MEASUREMENT steps appearing on the second page of the method is given here.

CALIBRATION: Summary of type of standards used

RANGE: Range of calibration standards to be used; from **LOQ** to **upper limit of measurement** (Note: More concentrated samples may be diluted in most cases to fall within this calibration range.)

ESTIMATED LOD: Limit of detection (background + 3σ)

PRECISION ($\bar{S}_r$): Experimental precision of spiked samplers

APPLICABILITY: The conditions under which the method is useful, including the working range in mg/m^3 (from the LOQ to the maximum sampler loading) for a stated air volume are given here.

INTERFERENCES: Compounds or conditions which are known to interfere in either sampling or measurement are listed.

OTHER METHODS: Methods from the 2nd edition ("P&CAM" and "S" methods) which are related to this one, as well as similar OSHA and literature methods are keyed to REFERENCES.

Figure 1. Layout of front page of methods.

5. METHOD CLASSIFICATION

Methods in the fourth edition of the NIOSH Manual of Analytical Methods are classified into three Evaluation categories: Full, Partial, and Unrated. Classification is based on the results of laboratory testing and evaluation criteria as described in Chapter E, Development and Evaluation of Methods.

The data from these evaluations are summarized in the EVALUATION OF METHOD section in each method. This section may also contain other corroborating data, e.g., collaborative testing, Proficiency Analytical Testing (PAT) data, or field data from NIOSH Sequences. For Partially Evaluated methods, this section will state which evaluation points were not tested, thus providing the user with information on which to make a reasonable judgment on the quality of the data obtained.

Evaluation: Full

Fully evaluated methods are methods that have been tested and have met all the factors of the NIOSH evaluation protocol as presented in Chapter E.

Evaluation: Partial

Partially evaluated methods are methods that have been subjected to some of the evaluation experiments but have not received a full evaluation (i.e., Short-term Method Development). These may also include methods that were fully tested but did not meet one or two of the evaluation criteria, e.g., some of the earlier-developed methods that do not meet the current $\pm 25\%$ accuracy criterion.

Evaluation: Unrated

Unrated methods have not been tested by NIOSH, but have been developed by a recognized independent source such as the Occupational Safety and Health Administration (OSHA).

6. USER EXPERIENCE WITH THE METHODS

NIOSH seeks to make these methods useful in industrial hygiene analyses. Therefore, the experience of people using the methods is important to us. Suggestions for improvement and questions relating to this Manual are welcome and should be directed to the Manual Coordinator. A comment form has been included in the back of this Manual for this use; it can be mailed or FAXed.

C. QUALITY ASSURANCE

by David L. Smith, CIH; Michele L. Bolyard, CIH; and Peter M. Eller, Ph.D., CIH

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1. ROLE OF LABORATORY QUALITY ASSURANCE PROGRAM

Analytical data are used to make a variety of decisions, i.e., to decide whether a particular chemical agent is present in a workplace atmosphere, whether a hazard to workers' health exists in that atmosphere, or whether a workroom atmosphere complies with applicable standards. Errors in such data can have a variety of costly effects [1]. The consequences of erroneous data may lead to the wrong decision being made as to whether a non-compliance situation exists. If the analytical results are a part of a larger experiment, perhaps the wrong conclusion might be reached or the results might be uninterpretable. If the presence or absence of a particular agent is erroneously reported, a threat to workers' health may be allowed to continue. It is the role of a laboratory's quality assurance program to provide the necessary safeguards to minimize these occurrences and to provide a means of detecting errors when they do occur. There are many good texts and articles addressing the subject of laboratory quality control [2,3,4,5]. The purpose of this chapter is to address some of the aspects of quality control as they relate to industrial hygiene laboratory quality control.

It is not possible to design a quality assurance program to fit all laboratories since no two laboratories serve the exact same purpose or operate in exactly the same manner. Each laboratory must set its own operating procedures and quality control practices, and document them in a Quality Assurance Manual [2,3,5]. This chapter, therefore, will not

to set forth concrete recommendations for implementing a quality assurance program, but rather will present aspects of laboratory quality assurance and quality control which should be addressed by each laboratory.

A successful quality assurance effort cannot be achieved through the efforts of only one individual. A laboratory's quality assurance coordinator needs the assistance and cooperation of all laboratory personnel to be effective. To this end, it is necessary to discourage adversarial relationships between quality control personnel and bench chemists. Analysts must be trained and made aware of the purpose and value of quality assurance functions and, in turn, the quality assurance program must be designed so that its functions are based on sound goals directed toward improving the performance of both the individual analyst and the laboratory as a whole.

Frequently, analytical results are challenged months or years after the analysis is complete. In order to support the original data, an effective, complete, record-keeping system must be maintained. Another chemist must be able to reconstruct the exact treatment to which the samples were subjected solely from a laboratory's records. Furthermore, if the appropriate quality control checks were performed with the analysis and documented, there can be no doubt regarding the results.

2. ORGANIZATION

A laboratory, just as any other organization, should have a clearly defined organizational structure. Responsibilities of each member of the laboratory staff should be in writing and understood by all. In this way, confusion regarding tasks which need to be performed can be avoided.

The specific organizational structure of the laboratory will vary, depending on the laboratory's function. Two functions which relate to quality assurance should be assigned in every laboratory: the quality assurance coordinator and the sample clerk. The size and nature of the laboratory may preclude assignment of a full-time position to these functions; however, a laboratory member should be assigned these duties and it should be understood that they are to have top priority.

a. Quality Assurance Coordinator

The quality assurance coordinator's functions will depend on the size and nature of the laboratory. This professional has overall responsibility for assuring that reported data meet established standards for precision and accuracy and that these results can be supported scientifically by the various quality control checks performed with the analysis. One of the major functions of this individual is to perform audits of the quality control system and to implement changes that eliminate recurring errors [2,3,4,5]. The quality assurance coordinator should not be under the direct supervision of management responsible for day-to-day laboratory operation. In this way, conflicts between the laboratory's dual responsibilities of providing analytical results in a rapid fashion while maintaining quality can be avoided. The quality assurance coordinator should also serve as a resource person for chemists or managers on questions or problems related to quality assurance and should

have a working knowledge of statistics, including quality control charting, and experimental design.

b. Sample Clerk

The sample clerk's functions will also vary, depending on the size and function of the laboratory. As a minimum, the sample clerk is responsible for the receipt and log-in of samples. Field samples should be stored in a secure location under proper conditions (temperature, etc.) until analysis. Logging and tracking of samples in the laboratory is important so that the history of these samples can be documented and processed in a timely manner. The sample clerk may also be given the responsibility of maintaining chain of custody documentation.

3. QUALITY ASSURANCE IN SAMPLING

Quality assurance procedures should not be overlooked by personnel performing field sampling. The field sampling parameters often have more effect on precision and accuracy of the final result than parameters of the measurement [2,4,5,6,7]. Field personnel should become familiar with sampling and measurement methods which they will use. The methods usually specify the proper sampling media to be used, the correct flow rate and sample volume, as well as special precautions on sample handling, shipping and possible interferences.

Sampling equipment must be maintained in reliable working order. It is desirable to have one person or group given responsibility for the care, maintenance and stocking of field sampling equipment. This person or group should periodically inspect and repair all equipment and keep track of the use and location of sampling equipment when it is signed out. Sampling pumps should be calibrated with each use. This calibration should be performed with the sampler in line. Since differences in pressure drop across the sampler will affect flow rate, it may be necessary to perform the calibration with the actual sampler to be used.

The exact sampling time must be known in order to accurately estimate the sampled volume. Recording only the start and stop time assumes that the pump functions properly over the entire sampling period. Occasional spot checks for proper operation should be made throughout the sampling period.

Since many modern analytical techniques are extremely sensitive, special care must be taken to avoid contamination of field samples [8]. Samples must not be stored or shipped with bulk materials which might spill or otherwise present the possibility for contamination. The glassware or other containers used in sampling and shipping should be subjected to any cleaning procedures recommended in the analytical method.

Careful record keeping in the field is also important. Pertinent information such as temperature, humidity, possible interfering compounds, sampling location, etc. should be documented. Special care should be taken in sample labelling and in preparation of paperwork accompanying the samples so that confusion in the laboratory is avoided.

Field blanks are used to estimate contamination which may occur immediately before and after sampling, during shipment, or while awaiting measurement in the laboratory. The nature and number of blanks taken will depend on the method and sampling situation; therefore, field sampling personnel must attempt to determine what sources of contamination are possible in the specific situation at hand. The field blank strategy must then be designed accordingly. Where possible, a written sample protocol should be developed before actual sampling begins [3,4,9,10]. The protocol should contain a description of the environment being sampled; the assumptions made in derivation of the model of that environment; when, where, and how the sampling will be done; and how many samples will be taken. Samplers should be identified by batch or lot number of sampling media.

4. QUALITY ASSURANCE IN MEASUREMENT

Certain quality control checks should be performed with each sample set [2,4] to further support the reported results on actual field samples. The exact number and nature of these checks depend on the specific method and circumstances under consideration and should be thought of as an integral part of the method itself (i.e., a measurement should not be considered completed without the quality control checks also being completed). Each analyst must take an independent responsibility for assuring that the analytical quality control system works. This can be accomplished by using known spiked samples which closely simulate field samples with regard to concentration and interferences. Since the analyst is most familiar with the methods being used and should know what range of recoveries to expect, problems with the system can be detected early. We will attempt to recommend specific quality control checks to be performed with the methods in NMAM; however, our recommendations cannot be expected to cover all situations. The user of these methods should consider adding additional quality control checks as appropriate.

a. Methods

First, and perhaps most important in the area of quality control, a laboratory must have adequate measurement procedures. These methods should be written so that there is no doubt in the analyst's mind of the exact steps which must be performed and so that future references to the work can be as exact as possible. The methods used should be evaluated, where possible (either by the laboratory itself or by some other organization), to verify that the methods perform satisfactorily. Factors which could be evaluated include the recovery of the analyte of interest from both spiked samples and generated samples, the stability of collected samples or possible interferences to accurate use of the method. Methods should be tested for ruggedness so that critical steps in the analysis can be identified. Experimental designs have been published which permit rapid evaluation of a number of factors involved in the analysis (e.g., [11]).

b. Standards

Standard solutions may be for either identification or quantitation of the analyte of interest. The bulk material used for preparation of standards should be of sufficient purity to avoid errors in the identification or quantitation. Where available, Standard Reference Materials (SRMs available from the U.S. National Institute of Standards and Technology)

or other well-characterized standards are useful for assuring that results are consistent with other organizations and agencies [3]. Laboratory reagents and standards should also be properly labelled with contents, and receipt and expiration dates.

For quantitation, sufficient numbers of standards should be prepared so that adequate confidence intervals on reported values can be obtained [3,12]. As a guideline, we recommend that calibration curves be prepared with triplicate points at each of at least five different concentration levels. The standard curve should be prepared so that linearity can be assured over the range of the curve. Also, it is important that the concentration of standard solutions be chosen to bracket the actual samples. In this way, extrapolation outside the range of standards is avoided. The concentration of standard solutions should be chosen to be consistent with the purpose of the sampling. That is, if it is desired to demonstrate whether exposure standards are being met, then the standard curve should be constructed to bracket the concentrations which would be encountered at or near the applicable exposure standard. If it is desired to demonstrate whether a compound is present in the atmosphere being sampled, then the calibration curve should be constructed closer to the limit of detection. During measurement, working standards should be interspersed with field samples. In this way, it should be possible to detect if instrument drift becomes significant. Internal standards are useful for correcting instrument response for the actual amount of sample injected into a chromatograph. The internal standard should be chosen so that its retention time is reasonably close, without peak overlap, to the peak of interest.

c. Blanks (also see page 24)

A particular analysis may involve several types of "blank" measurements including reagent blanks, media blanks or field blanks. Reagent blanks measure the signal contribution from solvents, acids or other reagents used by the laboratory in preparing samples for analysis. Media blanks measure the signal contribution from the collection media (impinger solution, filter, sorbent tube, etc.) and field blanks measure signal contribution of the media plus any contamination which may have occurred during handling, shipping and storage before analysis. The nature and number of blank measurements will depend on the method and circumstances, but the purpose of all blank measurements is to help prevent errors in identification and quantitation of field samples [3].

d. Blind Samples

Blind samples are prepared by someone other than the analyst performing the measurement and are to provide an independent check on the accuracy and precision of the measurement.

If blind samples cannot be prepared with confidence, their use should be avoided. In these cases, confusion may result when discrepancies occur and it will not be possible to say for certain whether the measurement or the blind sample was in error.

The results should be used in conjunction with control charting techniques to identify errors or malfunctions in the system [2,12,13]. To accomplish this goal, quality assurance

personnel should work closely with laboratory personnel to quickly identify and eliminate trouble spots.

It will not always be possible to isolate the source of error in the results of a blind sample. In these instances, it should be recognized that it will not be possible to defend quantitative results for that particular sample set; therefore, reporting of results where these discrepancies occur should be avoided.

e. Recovery Studies

Recovery studies should be performed as a part of the measurement whenever the analyte of interest must be liberated or separated from the sampling media. The analyte of interest should be added to the media at levels consistent with the field samples. These "spiked" samples should then be treated in the same manner as the field samples. Corrections for recovery should be made whenever the measured recovery is significantly different from 100%. Even if recovery has historically been 100%, recovery studies can be useful as additional analytical and calculation checks. It is often helpful for a laboratory to maintain a record of past recovery studies so that current data may be compared for discrepancies. Samples for which estimated recovery is less than 75% should be reported as "semiquantitative."

f. Duplicates

Duplicate preparations of bulk materials are useful as an indication of the uniformity of the bulk material. Duplicate injections or measurements from air samples are of lesser importance since preparations from air samples are generally fairly uniform in nature. True duplicates of air samples are useful as an indication of both the reproducibility of the entire sampling and measurement method and as an indication of the uniformity of the atmosphere being sampled.

5. INTERLABORATORY TESTING

Assignable analytical uncertainty can be considered as consisting of interlaboratory and intralaboratory variability. A knowledge of the magnitude of these two sources of variability is essential in order to interpret and use analytical data properly. Intralaboratory variability can be estimated from the results of analysis of blind samples. Interlaboratory testing requires the cooperation and coordination of a number of independent laboratories [2,11].

Interlaboratory testing can also be useful for defining the relationship of data reported by different laboratories using either the same or different measurement techniques [12,15,16]. Participation in such studies can be useful for uncovering errors in methodology or identifying critical steps in the procedures.

The Proficiency Analytical Testing (PAT) Program operated by the American Industrial Hygiene Association in cooperation with NIOSH is useful for measuring a laboratory's performance on a variety of common industrial hygiene samples, including solvent vapors

on charcoal tubes and metals, asbestos and silica on filters. Participation in this program by laboratories performing industrial hygiene analysis is strongly encouraged.

Similarly, the American Industrial Hygiene Association (AIHA) operates a laboratory accreditation program for industrial hygiene laboratories. Site visits and application reviews can provide a useful review of a laboratory's overall quality assurance system, as well as the adequacy of personnel, facilities and equipment. Appendix E of [2] lists over twenty other proficiency and check sample programs. An extensive listing of laboratories accredited in specific test protocols is also available [17].

6. REPORTING

The detail and nature of the analytical report will depend on the function of the laboratory. As a minimum, the report should include a description or reference to the method used, any deviations or special circumstances encountered with the sample set, estimates of the limits of detection and quantitation, the date of analysis, as well as the results themselves. The report should be signed by the analyst and at least one other person who is responsible for approving the report. The laboratory should adopt a standard report format and attempt to maintain that format with all reports.

The limit of detection (LOD) is defined as the amount of the analyte which can be distinguished from background. The limit of quantitation is that amount of analyte above which the precision of the reported results is better than a specified level. There are numerous methods of determining these quantities and many opinions as to which method is correct. The laboratory should decide on a method for determining these quantities and be consistent to the extent possible in its use. In NMAM, the American Chemical Society definition of LOD (i.e., a sample giving a signal three times the standard deviation of background) is used [4,18].

Sample data should be corrected for recovery or desorption efficiency and for reagent and media blank response. However, field blanks should be treated like field samples (corrected for reagent blanks, media blanks, and recovery). If correction for contamination in the field blanks is necessary, this correction should be performed by the person who submitted the sample.

Data should be reported simply and concisely and in a manner that "their meaning is not distorted by the reporting process [4,12,13]." Attention should be given to the number of significant figures reported. Generally, only the last figure reported should be in doubt.

7. LABORATORY NOTEBOOKS

Laboratory notebooks are used for recording all experimental and analytical notes and data [19]. New notebooks should be logged out to a chemist. The notebook remains the property of the laboratory and should be kept in a central location by the laboratory after it is filled.

Notebooks used in the laboratory should be hard-covered and bound. Use of notebooks with removable pages (e.g., loose-leaf notebooks) should be discouraged. The pages of

the notebook should be numbered and any entries made by an individual other than that to whom the book was assigned should be noted. Some laboratories require that the individual notebook pages be signed by the chemist for legal reasons.

The notebook should contain all information gathered by the chemist pertaining to the sample. Where appropriate, lab number, field number, sequence number and other identifying numbers are noted. Measurements requested, identification of the method, modifications to the method and the sample originator should be included. A description of the sample (whether bulk material, charcoal tube, etc.) should be included. Data on quality assurance aspects of the sample set such as blank values, recovery studies and duplicate determinations should also be included. Formulae used to calculate results and a sample calculation should be shown.

If permanent retention of computer printouts, recorder charts or similar items is deemed necessary, they should be pasted, taped or stapled in the notebook, if practical.

The minimum data entered in the notebook should be sufficient to enable another chemist to derive the same results as the original worker, with no other source of information. In addition to this minimum data, any other facts appropriate and pertinent to the sample analysis are to be entered.

A chemist's notebook is always subject to inspection by his colleagues, supervisors or inspectors from outside the laboratory. Therefore, it is imperative that the notebook be maintained in a professional manner and contain all pertinent information that may be required by other parties, regardless of the particular importance of that information to the chemist. Furthermore, the notebook must be maintained in such a manner that it can withstand challenges as to the validity, accuracy or legibility of its contents.

8. INSTRUMENT MAINTENANCE

Laboratory instrumentation must be maintained in proper operating condition. We have found that in numerous cases the cause for out-of-control quality control samples has been traced to faulty instrument performance. In many of these instances, the operator was unaware that instrument performance had degraded. Performance checks can be useful in documenting instrument performance over time and in detecting deviations. To be of use, performance check procedures should be quick and easy to perform. Appendix C of [2] gives details of suggested performance checks for a variety of instruments. Where appropriate (e.g., balances, microscopes) periodic calibration should be performed and documented. Records of calibration should be recorded in the logbook for that instrument.

An instrument's maintenance history is often valuable in troubleshooting problems with that instrument. The record of instrument maintenance should be maintained in an "instrument logbook" and kept near that instrument or in a recognized location.

Service contracts or maintenance agreements for instrument repair are useful for assuring that instrumentation is serviced by qualified personnel and maintained in proper operating condition.

9. SAMPLE TRACKING

A laboratory should have a mechanism for logging and tracking samples after they are received in the laboratory so that all samples can be processed in the most efficient manner. The exact system used for sample tracking will depend on the size and nature of the laboratory and may range from hand-entry logbooks to sophisticated computer-based systems. The system should include a means of cross-referencing laboratory sample numbers with field sample numbers and it should be possible to determine the chemist, instrument, and other aspects of the sample set from the field number.

Sample tracking systems may also be used to produce management statistics which may aid in forecasting future sample loads or point to problem areas in sample turn-around.

10. QUALITY ASSURANCE RECORDS

Maintenance of quality assurance records aids in recalling details of a particular analysis at a future date. A condensation of quality assurance data can be used as supporting evidence to field personnel should the need arise. Quality assurance records can also be used to track various quality assurance parameters over time (such as desorption efficiency or blank values).

Computerized recordkeeping systems should be backed up periodically. Archive copies of computer data require specialized storage conditions and these archive copies may not be reliable for extended periods of time.

Filing of records should be current and accurate. If rapid retrieval of data is not possible, then maintenance of quality assurance records loses its purpose. The primary purpose is to provide a system to furnish information rapidly regarding the status of specific sample sets.

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D. GENERAL CONSIDERATIONS FOR SAMPLING AIRBORNE CONTAMINANTS

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1. CHOOSING MEASUREMENT METHODS AND SAMPLING MEDIA

As proper advance planning minimizes sampling and measurement costs and labor and contributes to a smooth, successful survey, many things must be considered before collecting field samples [1]. The first step is to define sampling objectives. These may include documenting exposures in particular work settings, determining compliance/non-compliance with existing Federal or local standards or recommended exposure limits, or trying to determine the source of a problem. Sampling parameters that should be defined might include type of sample (area vs. personal), contaminant(s) to be sampled, duration of samples, potential interferences and expected contaminant concentrations (or contaminant concentration of interest). Once these parameters are defined, then the proper analytical method and sampling media can be selected. Other general information needed to plan a survey properly include the number of employees, the sampling strategy plan (discussed later), process flow diagram, material safety data sheets on all process materials, the physical states of the substances to be sampled, and potential hazards involved in collecting and shipping the samples.

An accredited analytical laboratory should be used and it is essential to consult with the analytical laboratory before sampling to ensure that the measurement methods available can meet the defined sampling needs. This step should be an early part of survey planning. The laboratory can also assist in choosing sampling media which are compatible with the sampling needs and the measurement methods available. The

APPLICABILITY section of the individual methods in NMAM can be helpful in choosing which of the available methods is best for a particular situation.

Whether through consultation with the laboratory or through reading the specific measurement method, the sampling media will be specifically identified, e.g., pore size and type of filter, concentration and amount of liquid media required, and specific type and amount of solid sorbent (see Tables 1 and 2 for common types, characteristics and behavior of solid sorbents*). If specific brand name products are called for, no substitutions should be made. Most sampling media are well defined through research and testing; deviations from specifications are undesirable. For example, most organic contaminants are sampled with a dual section tube containing 100 mg front and 50 mg backup sections of 20/40 mesh activated coconut shell charcoal. If larger mesh charcoal or a different type of charcoal were to be used, the sampling capacity and recovery efficiencies for the contaminant of interest might change from that which is specified in the method.

The physical state of the contaminant(s) being sampled may also be a factor in determining the media required. In the case of polyaromatic hydrocarbons (PAHs), for example, the proper sampler consists of a membrane filter to trap particulate matter and a solid sorbent tube to trap the vapors of certain PAHs so that total collection is assured.

The sampling pump used to collect the sample must also be compatible with the sampling needs and the media used. Specifically, the pump must be capable of maintaining the desired flow rate over the time period needed using the sampling media specified. Some pumps may not be able to handle the large pressure drop of the media. This will be true for fine mesh (smaller than 40 mesh) solid sorbent tubes, small pore size filters or when attempting to take a short-term sample on a sorbent tube of a higher than normal pressure drop at a flow rate of 1 L/min or greater. As a rule of thumb, all high flow pumps (1 to 4 L/min) can handle at least 3 kPa (12 inches of water) pressure drop at 1 L/min for 8 hrs. Some pumps can handle up to 7.5 kPa (30 inches of water) pressure drop at flows up to 2 or 3 L/min. Most low flow pumps (0.01 to 0.2 L/min) can handle the pressure drops of available sorbent tubes without problems except that the nominal flow rate may decrease for certain models. All pumps should be calibrated with representative sampling media prior to use. It is good practice to check the pump calibration before and after use each day. As a minimum, calibration should be done before and after each survey.

Table 1. Types and uses of solid sorbents [2]*.

Activated charcoal

By far the most commonly used solid sorbent. Very large surface area:wt. ratio. Reactive surface, high adsorptive capacity. This surface reactivity means that activated charcoal is not useful for sampling reactive compounds (e.g., mercaptans, aldehydes) due to poor desorption efficiency. The high capacity, however, makes it the sorbent of choice for those compounds which are stable enough to be collected and recovered in high yield. Breakthrough capacity is a function of type (source) of the charcoal, its particle size and packing configuration in the sorbent bed.

Silica gel

Less reactive than charcoal. Due to its polar nature, it is hygroscopic and shows a sharp decrease in breakthrough capacity with increasing humidity.

Porous polymers

Lower surface area and much less reactive surface than charcoal. Adsorptive capacity is, therefore, generally lower, but reactivity is much lower as well.

Ambersorbs

Properties midway between charcoal and porous polymers.

Coated sorbents

One of the sorbents upon which a layer of a reagent has been deposited. The adsorptive capacity of such systems usually approaches the capacity of the reagent to react with the particular analyte [3].

Molecular sieves

Zeolites and carbon molecular sieves which retain adsorbed species according to molecular size. A limiting factor is that the water molecule is of similar size to many small organic compounds and is usually many orders of magnitude higher in concentration than the species of interest. This unfavorable situation may result in the displacement of the analyte by water molecules. Drying tubes may be used during sampling to eliminate the effects of humidity [4].

Thermal desorption

May contain several different sorbents in order to collect a wide range of different chemicals [5]. These tubes are generally used in situations where unknown chemicals or a wide variety of organics are present, e.g. in indoor environmental air quality investigations. Analysis is often by gas chromatography/mass spectrometry (GC/MS).

*NOTE: Solid sorbents are used for the collection of vapors only. Aerosols are not collected effectively by most sorbent beds, but may be collected by other components of the sampler (e.g., a prefilter, or the glass wool plugs used to hold the sorbent bed in place).

Table 2. Factors affecting the collection behavior of solid sorbents [2].

Temperature

Since all adsorption is exothermic, adsorption is reduced at higher temperatures. Additionally, if there is a reaction between an adsorbed species and the surface or between two or more adsorbed species (e.g., hydrolysis or polymerization), the rate of such reactions increases at higher temperatures.

Humidity*

Water vapor is adsorbed by polar sorbents; their breakthrough capacity for the analyte is thereby reduced. This effect varies from substantial for more polar sorbents, such as charcoal and silica gel, to a smaller one for Ambersorbs and porous polymers.

Sampling flow rate*

Breakthrough volume of a solid sorbent bed tends to be smaller at higher sampling flow rates, particularly for coated solid sorbents. For sorbents such as charcoal whose breakthrough capacity is significantly reduced by high humidity, lower sampling flow rates may actually result in smaller breakthrough volumes [6].

Concentration*

Breakthrough capacity (mg adsorbed) of solid sorbent bed increases (but breakthrough volume (L of air sampled) decreases) as the concentration of contaminant in air increases [6].

*NOTE: It is important to distinguish between equilibrium (saturation) adsorptive capacity and kinetic (breakthrough) adsorptive capacity of the solid sorbent. Breakthrough capacity is the important characteristic in actual sampling situations; it may be significantly affected by sampling flow rate and relative humidity of the air being sampled and may be significantly less than saturation capacity, which is not dependent on sampling flow rate or relative humidity.

2. FIGURING SAMPLING PARAMETERS

Once the sampling media and measurement method are chosen, then the specific sampling parameters need to be determined [7]. For most methods, this will not pose a problem as the flow rate recommended in the method can be used for the desired sampling period, e.g., 1 to 3 L/min for 8 hrs for most aerosols or 10 to 200 mL/min for 8 hrs for most sorbent tube samples. Generally, the parameters which must be considered are flow rate, total sample volume, sampling time (tied into the two previous parameters), and limit of quantitation (LOQ) (see Glossary of Abbreviations, Definitions and Symbols). Some of these variables will be fixed by sampling needs, e.g., sampling time or by the measurement method of choice (LOQ or maximum sampling volumes). The choice of these variables can best be explained through the use of the following examples.

Examples:

a. **Sampling for Gases and Vapors Using Solid Sorbents**

Given parameters:	Method 1501 for Styrene
Recommended Sample Volume:	5 L
Useful Range of the Method:	85 to 2560 mg/m^3 (20 to 600 ppm)
OSHA PEL:	850 mg/m^3 (200 ppm) - Ceiling
	425 mg/m^3 (100 ppm) - TWA
Recommended Flow Rate:	0.2 L/min
Breakthrough Time:	111 min @ 0.2 L/min and 1710 mg/m^3
Breakthrough Capacity	38 mg

Suppose it is desired to determine both ceiling and TWA exposures of workers exposed to styrene and the concentrations are unknown.

Ceiling Determination: If sampling were done at 0.2 L/min for 30 min and a total sample volume of 6 L collected which is above the 5 L recommended sample volume, would this a problem? Probably not. For instance, in the breakthrough test, a concentration of 2 times the OSHA Ceiling Standard (1710 mg/m^3) was sampled at 0.2 L/min for 111 min (22.2 L) before breakthrough occurred, collecting a total weight of 38 mg of styrene. Of course, this test was conducted in a dry environment with only styrene present. A safety factor of 50% should be allowed to account for humidity effects. Thus, if sampling is done for about 55 min at 0.2 L/min, levels of styrene up to 400 ppm could still be collected without sample breakthrough.

Also to be considered are the other organics present. If a concentration of 200 ppm acetone exists in this environment, then an additional safety factor should be added. An arbitrary 50% reduction in total sampling time or 28 min at 0.2 L/min might be done. This is very close to the original sampling time of 30 min. With the safety factors built in, collecting a 6-L sample should not be a problem. Alternately, the flow could be reduced to 0.1 L/min and be well within the 5-L total volume.

TWA Determination: In this same situation, the goal is to collect 8-hr samples for comparison to the 100 ppm TWA. If sampling was done at 0.05 L/min, then the total sample volume would be 22.5 L, substantially above the 5-L recommended sample volume. If the flow was dropped to 0.02 L/min, then the sample volume would be 9 L. This sample volume might be acceptable if the styrene concentrations are around 100 ppm and no other competing organics are present, e.g., acetone. However, the safer approach would be to collect two consecutive samples at 0.02 L/min for 4 hrs (total sample volume of 4.8 L each).

b. **Pushing a Method to the Limit, Limit of Quantitation**

Given Parameters:	Method 1009 for Vinyl Bromide (VB)
Recommended Sample Volume:	< 10 L @ 0.20 L/min or less
Working Range:	0.3 to 33 ppm (1.3 to 145 mg/m^3) for a 6-L air sample; this equals 8 to 355 μg VB per tube
Limit of Detection:	3 μg VB per tube

In this particular example, let us say that the object is to estimate exposure to vinyl bromide down to 0.1 ppm (0.44 mg/m^3), which is below the working range. In order to collect 8 μg of vinyl bromide (the limit of quantitation) at this concentration, 20 L of air will have to be collected. This volume is substantially above the maximum recommended sample volume of 10 L. Since the recommended sample volume is generally a conservative value used to protect against breakthrough under worst case conditions (i.e., high humidity and high concentrations), considerable leeway exists for the size of the air sample. In this example, the 20-L air samples should be taken at 0.2 L/min or slower, and the possibility of breakthrough should be monitored by observing the relative amounts of analyte on the backup sections of the samples.

The best approach is to consult with the analytical laboratory and then to take a sufficient number of samples to determine the useful limits of the sampler in the particular application. The presence of high relative humidity and other organic solvents will severely reduce the number of active sites available on the sorbent for collection of the contaminant of interest. In pushing a method to the limit, it is often necessary to sample beyond the breakthrough volume, while observing recommended maximum sampling flow rate, in order to obtain the sensitivity to determine the concentration of interest. If this is done, then the risk must be accepted that the method may not work outside the limits tested.

3. BULK SAMPLES

The addition of bulk samples can often make the difference between a successful or unsuccessful sampling effort. This is especially true where there is mixed solvent exposure or unknown dust exposure and for determining silica content of dusts. The primary purpose of bulk samples is to provide the analytical laboratory with a large enough sample for qualitative and sometimes quantitative analysis. The two major types of bulk samples are bulk air and mass bulk (liquid or solid) samples.

a. Bulk Air Samples

Generally, a bulk air sample is defined as a large volume area sample collected for the purpose of qualitative analysis. A good example is multiple solvent exposure where the exact identity of the airborne solvents is unknown, e.g., painting operations. For most organic solvents, a bulk air consists of a charcoal tube (or whatever sorbent is called for) collected at 1 L/min for an hour or more. Although the sample is likely to exhibit breakthrough, this does not matter since one is primarily interested in what substances are present rather than their exact concentrations (the latter aim is accomplished through the separate collection of proper samples). Any questions concerning how or whether or not a bulk air sample is needed should be addressed to the analytical laboratory prior to sampling. In the case of silica, either a bulk air or solid bulk (e.g., a rafter sample) or both are suggested so that enough material will be available to determine free silica content.

b. Bulk Liquids and Solids

Collection of bulk materials may be needed to establish the substances present in the workplace and, in some cases, to establish the relative levels of certain substances present in the raw material. A good example of the latter is the case of mixed solvent exposure when determining if a certain contaminant of interest is present, e.g., benzene. In some cases, a list of 30 solvents may be present (from Material Safety Data Sheets), but it is not certain which ones are present or in what proportions. This example is also true for dusts, as was discussed previously for silica, or for metals which may exist in trace quantities.

In choosing bulk samples, the end goal must be considered: qualitative and/or quantitative analysis. In the case of a painting operation, it is preferred to have the bulk samples separated by contaminants of interest, i.e., solvent fraction separate from the pigment fraction. This allows the laboratory to analyze the different portions of the paints without having to go through a lengthy separation process. In general, the cleaner the bulk, the easier it will be for the laboratory to conduct the analysis. In many cases, the industrial hygienist is interested in a "dirty" bulk. Any information that can be given to the laboratory on what may or may not be present will help speed up the analysis. Advance consultation with the laboratory is desirable.

In choosing bulk dust samples, the sample should be representative of the airborne dust to which the workers are being exposed. Usually this is a settled dust sample collected from rafters or near the workers' job site. In other cases, a process dust sample is chosen to determine the composition of the material before it is airborne. In cases where the choice is not clear, do not follow the adage that "more is better." Bulk samples should be limited in number to optimize the laboratory's time. A good approach, when in doubt as to what bulks are needed, is to collect several but to allow the laboratory to analyze only those needed to answer questions as they arise.

When shipping bulks, care must be taken to preserve the integrity of the samples and to follow established Department of Transportation (DOT) shipping regulations. Only 5 to 10 mL of the liquid or solid is needed, so keep bulk sample sizes small. In general, leak-proof glass containers are best since they will not react with most chemicals; however, polyethylene containers can be used in the majority of cases. A convenient container is a 20-mL scintillation vial with PTFE-lined cap. Specific chemicals for which polyethylene containers should not be used include aromatic compounds, chlorinated hydrocarbons and strong acids. The lids of the containers should be sealed with shrink bands or tape for further assurance against leakage. These containers should be labeled as required by DOT under their regulations, 49CFR Part 171-177. For most materials classified as "Flammable" or "Poisonous," amounts up to 1 quart can be shipped by any carrier. Most bulk dusts are not covered by DOT regulations. Specific restrictions and labelling requirements should be checked prior to shipping any samples.

In the case of volatile bulk samples (and some air samples), consideration should be given to shipping the samples on dry ice or with bagged refrigerant (e.g., "blue ice"). Again, check with the carrier you plan to use as there may be restrictions on the

amount of dry ice they will accept in a package (usually 5 pounds or less is acceptable). Specific labels are usually required when dry ice is used.

4. BLANKS (See also page 10)

Certain numbers of blanks are required by the analytical laboratory for each set of samples to be analyzed. The specific method being used should be consulted concerning the number and type of blanks required. There are two types of sampler blanks: field and media blanks. Field blanks are clean samplers taken to the sampling site, handled in every way as the air samples, except that no air is drawn through them. Media blanks are simply unopened, new samplers which are sent with the samples (these blanks are not usually taken to the field). It is also recommended that additional blind field blanks be sent along with the field samples, labelled as field samples, as a further check on the analysis. Blanks are good insurance to deal with contamination, but the best approach is to avoid sample contamination by being careful. The recommended practice for the number of field blanks is two field blanks for each 10 samples with a maximum of 10 field blanks for each sample set. Approximately five media blanks should also be included. This number should be increased for media which are coated or impregnated with reagent. Again, consult the specific method for the number and type of blanks as these numbers will vary.

Another frequently-used practice is to include blind spiked samples as a quality control check of the analytical laboratory (see page 11). See the following chapter for a detailed discussion of spiking procedures.

5. DIRECT-READING METHODS

The variety of types and costs of direct-reading methods available is large and expanding, including detector tubes (both short- and long-term), aerosol monitors, integrating passive monitors for certain gases and portable instrumentation for gas chromatography or infrared spectroscopy [8]. Many direct-reading instruments now used for personal or area measurements have evolved from laboratory or process control instruments [9].

Some of the considerations (i.e., specificity and sensitivity) for the use of direct-reading methods for quantitative determinations are similar to those already given for classical filter or sorbent methods. In many cases, direct-reading instruments, which are physically small and portable, qualify as personal sampling devices.* These offer the additional advantages over classical methods by reducing labor and analytical costs and may be the methods of choice when instantaneous results are important, even at the expense of some degree of sensitivity or specificity. In general, manufacturers' instructions should be followed in the calibration and use of these devices. Due to the severe conditions to which direct-reading instrument may be subjected, performance checks and preventive maintenance on a periodic

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***NOTE:** A portable instrument is defined as weighing less than 4.5 kg (10 lbs.) and powered by self-contained batteries [10]. For personal monitoring, the instrument configuration should be such that the breathing zone can be monitored. Alarms, both audible and visual, and hard-copy documentation are desirable.

basis or before each use are very important. Many direct-reading instruments are powered by Ni-Cd batteries which can fail to provide a full charge over the full sampling period unless frequently or fully discharged and recharged several times just prior to use. An additional responsibility, that of field calibration of the direct-reading instrument, falls on the field sampling personnel.

6. SAMPLING STRATEGY

To obtain the maximum amount of information during the course of a survey with a minimum amount of samples, a statistical sampling strategy should be developed before conducting any survey [11]. Several pieces of information must be known in advance to plan a sampling strategy, including the size of the workforce to be sampled, the accuracy of the sampling and measurement method to be used and the confidence one wishes to have in predicting the exposure of the workforce.

For example, to determine with 90% confidence that at least one worker from a workplace subgroup will be in the top 10% of the exposures occurring in the group, the number of employees to sample would be chosen from Table 3. Other tables are given in the publication for confidence limits of 95% and for the top 20% of exposures. Again, judicious use of sampling statistics will optimize the number of samples needed.

Table 3. Minimum sample size (n) for including (@ 90% confidence level) at least one high risk employee* [11].

Size of Employee Group (N):	1	2	3	4	5	6	7	8	9	10	11-12	13-14	15-17	18-20	21-24	25-29	30-37	39-49	50	∞
Minimum Number of Measured Employees (n):	1	2	3	4	5	6	7	7	8	9	10	11	12	13	14	15	16	17	18	22

*Exposure in highest 10% of N.

7. SAMPLING TECHNIQUE

The following are suggested general techniques for active sampling using some of the more common samplers. These instructions elaborate on those given in NMAM methods. Consult individual methods for details of sample size.

a. Calibration of Personal Sampling Pumps

The accuracy of determination of the concentration of a toxic substance in air is no greater than the accuracy with which the air volume is measured. Therefore, accurate calibration of the airflow rate through the sampling train is necessary. The frequency of calibration depends on the use, care and handling to which the pump is subjected. In addition, pumps must be recalibrated if they have been abused and after each repair. Ordinarily, pumps

should be calibrated in the laboratory and the field, both before field use and after each field survey.

The choice of a reference instrument will depend on where the calibration is to be performed. For laboratory use, primary standards, such as a spirometer or soap-bubble meter, are recommended [1,2]. Several electronic soap-bubble calibrators and one dry-cell calibrator are commercially available as primary calibrators. Other instruments, such as a wet-test, mass-flow or a dry-gas meter, may be used. The following instructions are for the soap-bubble meter. If another instrument is used, equivalent procedures should be followed.

(1) Set up the apparatus as shown in Figure 1.

(2) Make certain that the rechargeable batteries will power the pump for the entire sampling interval by one of the following methods: 1) run the pump for that length of time, checking for satisfactory operations; 2) test the battery independently of the pump using a current capacity tester [12]. Fully recharge the batteries.

(3) Turn the pump on and moisten the inner surface of the soap-bubble meter with the soap solution. Draw bubbles upward until they travel the entire length of the buret without breaking.

(4) Adjust the pump to the desired nominal flow rate. Check the water manometer. The pressure drop across the sampler should not exceed 2.5 cm Hg (13 inches) of water.

(5) Start a soap bubble in the buret and measure the time, with a stopwatch, that it takes to traverse two calibration marks. For a 1000-mL buret, a convenient calibration volume is 500 mL. Repeat the determination at least twice more. Average the results and calculate the flow rate by dividing the calibration volume by the average time.

(6) Record the following data:
   a. volume measured;
   b. elapsed time;
   c. pressure drop;
   d. air temperature;
   e. atmospheric pressure;
   f. serial number of the pump;
   g. pump model; and
   h. date and name of operator.

(7) If the sampling pump used for sample collection uses a variable area flow meter (rotameter) for flow rate indication, the calibrated flow rate must be adjusted for the actual air pressure and temperature during sampling. The expression for this correction is [13]:

V (Corrected volume, L) = $Q\ t\ (P_c T_s / P_s T_c)^{0.5}$

where: Q = indicated flow rate (L/min)
t = sampling time (min)
P_c = pressure during calibration of sampling pump (kPa or other pressure units)
P_s = pressure of air sampled (same units as P_c)
T_c = temperature during calibration of sampling pump (K)
T_s = temperature of air sampled (K).

This correction is **not** used for non-rotameter sampling pumps.

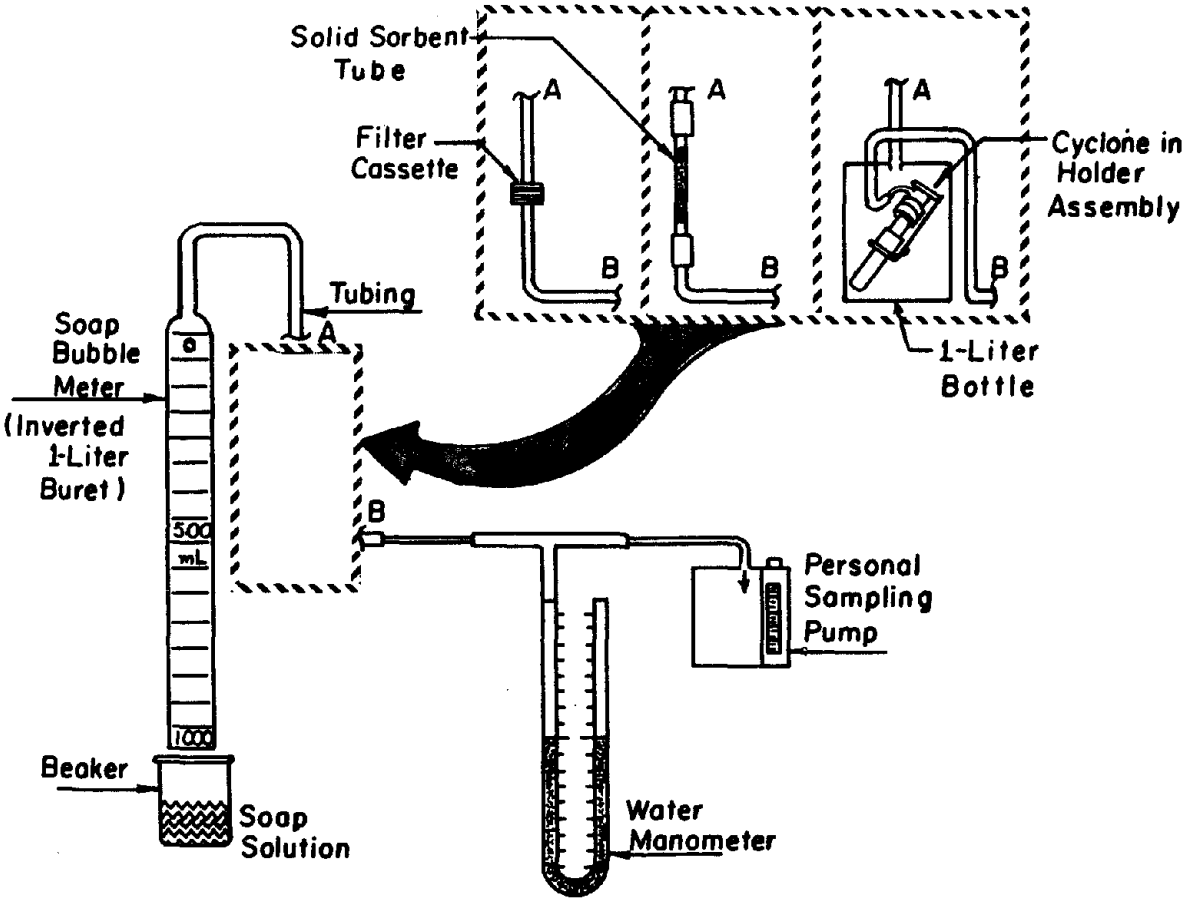

Figure 1. Calibration Apparatus.

b. Sampling Instructions for Solid Sorbent Tube Sampler

Use these instructions for active personal sampling (i.e., pumped sample airflow) for substances which are retained on solid sorbents such as activated charcoal, silica gel, porous polymers, etc.

(1) Calibrate each personal sampling pump at the desired flow rate with a representative solid sorbent tube in line (alternatively, use a flow restrictor to provide a pressure drop equal to that of the average solid sorbent tube). Use a bubble meter or equivalent flow measuring device.

(2) Break the ends of the solid sorbent tube immediately before sampling to provide an opening at least one-half of the internal diameter at each end.

(3) Connect the solid sorbent tube to a calibrated personal sampling pump with flexible tubing with the smaller sorbent section (backup section) nearer to the pump. Do not pass the air being sampled through any hose or tubing before entering the solid sorbent tube. Position the solid sorbent tube vertically during sampling to avoid channeling and premature breakthrough.

(4) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused solid sorbent tubes from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples (e.g., break the ends and seal with plastic caps) but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(5) Take the sample at an accurately known flow rate as specified in the method for the substance and for the specified air volume. Typical flow rates are in the range 0.01 to 0.2 L/min. Check the pump during sampling to determine that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Take two to four replicate samples for quality control for each set of field samples.

(6) Record pertinent sampling data including location of sample, times of beginning and end of sampling, initial and final air temperatures, relative humidity and atmospheric pressure or elevation above sea level.

(7) Seal the ends of the tube immediately after sampling with plastic caps. Label each sample and blank clearly with waterproof identification.

(8) Pack the tubes tightly with adequate padding to minimize breakage for shipment to the laboratory. In addition to the sample tubes and field blanks, ship at least six unopened tubes to be used as media blanks so that desorption efficiency studies can be performed on the same lot of sorbent used for sampling.

(9) Ship bulk samples in a separate package from the air samples to avoid contamination of the samples. Suitable containers for bulk samples are glass with a polytetrafluoroethylene (PTFE)-lined cap, e.g., 20-mL glass scintillation vials.

c. Sampling Instructions for Filter Sampler

Use these instructions for personal sampling of total (respirable and non-respirable) aerosols. Methods requiring these instructions specify FILTER as the sampling method. These instructions are not intended for respirable aerosol sampling.

(1) Calibrate the personal sampling pump with a representative filter in line using a bubble meter or equivalent flow measuring device.

(2) Assemble the filter in the two-piece cassette filter holder. Support the filter by a stainless steel screen or cellulose backup pad. Close firmly to prevent sample leakage around the filter. Seal the filter holder with plastic tape or a shrinkable cellulose band.

(3) Remove the filter holder plugs and attach the filter holder to the personal sampling pump with a piece of flexible tubing. Clip the filter holder to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter holder.

(4) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused filters and filter holders from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples, but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(5) Sample at a flow rate of 1 to 3 L/min until the recommended sample volume is reached. Set the flow rate as accurately as possible (e.g., within ± 5%) using the personal sampling pump manufacturer's directions. Take two to four replicate samples for quality control for each set of field samples.

(6) Observe the sampler frequently and terminate sampling at the first evidence of excessive filter loading or change in personal sampling pump flow rate. (It is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air.)

(7) Disconnect the filter after sampling. Cap the inlet and outlet of the filter holder with plugs. Label the sample. Record pertinent sampling data including times of beginning and end of sampling, initial and final air temperatures, relative humidity and atmospheric pressure or elevation above sea level. Record the type of personal sampling pump used and location of sampler.

(8) Ship the samples to the laboratory as soon as possible in a suitable container designed to prevent damage in transit. Ship bulk material to the laboratory in a glass container with a PTFE-lined cap. Never store, transport or mail the bulk

sample in the same container as the samples or field blanks. In addition to the samples and field blanks, ship five unopened samplers from the same lot for use as media blanks.

d. Sampling Instructions for Filter + Cyclone Sampler

Use these instructions for personal sampling of respirable aerosols (ACGIH definition [14]). Methods requiring these instructions specify CYCLONE + FILTER as the sampling method.

(1) Calibrate the pump to the rate specified by the cyclone (1.7 L/min for the 10-mm nylon cyclone or 2.2 L/min for the Higgins-Dewell cyclone [14]), with a representative cyclone sampler in line using a bubble meter or a secondary flow measuring device which has been calibrated against a bubble meter. The calibration of the personal sampling pump should be done close to the same altitude where the sample will be taken.

(2) Assemble the pre-weighed filter in the two-piece cassette filter holder. Support the filter with a stainless steel screen or cellulose backup pad. Close firmly to prevent sample leakage around the filter. Seal the filter holder with plastic tape or a shrinkable cellulose band.

(3) Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone might be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.

(4) Assemble the two-piece filter holder, coupler, cyclone and sampling head. The sampling head rigidly holds together the cyclone and filter holder. Check and adjust the alignment of the filter holder and cyclone in the sampling head to prevent leakage. Connect the outlet of the sampling head to the personal sampling pump by a 1-m piece of 6-mm ID flexible tubing.

(5) Clip the cyclone assembly to the worker's lapel and the personal sampling pump to the belt. Ensure that the cyclone hangs vertically. Explain to the worker why the cyclone must not be inverted.

(6) Prepare the field blanks at about the same time as sampling is begun. These field blanks should consist of unused filters and filter holders from the same lot used for sample collection. Handle and ship the field blanks exactly as the samples, but do not draw air through the field blanks. Two field blanks are required for each 10 samples with a maximum of 10 field blanks per sample set.

(7) Turn on the pump and begin sample collection. If necessary, reset the flow rate to the pre-calibrated value, using the manufacturer's adjustment procedures. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, observe the filter and personal sampling pump frequently to keep the flow rate within ± 5% of the

target flow rate. The sampling should be terminated at the first evidence of a problem.

(8) Disconnect the filter after sampling. Cap the inlet and outlet of the filter holder with plugs. Label the sample. Record pertinent sampling data including times of beginning and end of sampling, initial and final air temperatures and atmospheric pressure or elevation above sea level. Record the type of personal sampling pump, filter, cyclone used and the location of the sampler.

(9) Ship the samples and field blanks to the laboratory in a suitable container designed to prevent damage in transit. Ship bulk samples in a separate package.

(10) Take two to four replicate samples for every set of field samples to assure quality of the sampling procedures. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber or in the field. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation, s_r, calculated from these replicates should be recorded on control charts and action taken when the precision is out of control.

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E. DEVELOPMENT AND EVALUATION OF METHODS

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1. METHODS DEVELOPMENT AND EVALUATION STRATEGIES

The development and evaluation of analytical methods that are useful, reliable and accurate for most industrial hygiene monitoring problems require the application of some general guidelines and evaluation criteria. This is particularly important when methods are developed by different individuals and organizations (e.g., contractors) and compiled into a single manual. Adherence to guidelines should minimize overlooking potential problems in the methodology during its development, as well as provide cohesiveness and uniformity to the manual that is compiled. Likewise, a generalized set of evaluation criteria should be applied for the evaluation of sampling and analytical methodology.

The methods in this Manual were developed and evaluated by using an established experimental protocol for that specific analyte. Generally, the protocol developed for the joint NIOSH/Occupational Safety and Health Administration (OSHA) Standards Completion Program (SCP) [1,2,3] was used as the basic framework for the methods development protocols. A somewhat broader strategy which incorporates the salient features of the SCP protocol [1,2,3] as well as other protocols used in NIOSH and other methods development work [4,5,6,7,8] will be discussed in this chapter.

The recommended strategy is presented in the following sections. This strategy incorporates both laboratory and field experimentation in developing and evaluating methods. Laboratory generation of test atmospheres of analyte is a necessary and important part of this development and evaluation process. The strategy is relevant for active, as well as passive, sampling systems.

2. DEVELOPING PRELIMINARY INFORMATION

a. Definition of Analyte

Development of analytical methodologies by NIOSH is typically initiated by requests from NIOSH field personnel or other agencies [e.g., OSHA, Mine Safety and Health Administration, Bureau of Mines]. In developing these methodologies, it is important to be sure the method is specific for the analyte (e.g., the OSHA sodium hydroxide standard calls for a method which will determine sodium hydroxide in the presence of sodium salts and other cations).

b. Literature Search

In addition to reviewing the literature for analytical methodologies developed by others, the search should also include defining physical properties, chemical reactions, toxic properties of the analyte as well as analytical reagents used in its determination, and industrial operations and interferences where exposure may occur. OSHA permissible exposure limits (PEL) [9], NIOSH recommended exposure limits (REL) [10], American Conference of Governmental Industrial Hygienists threshold limit values (TLV) [11], Environmental Protection Agency standards and other appropriate sources should be used to establish a target concentration at which the methods development and evaluation work will be conducted.

c. Proposed Method

Findings from the literature search are used to develop proposed analytical methodology. In developing this methodology, the sensitivity of the analytical technique in relation to the target concentration of the analyte in air must be considered, as well as the sample collection scheme. Collection of samples for laboratory analysis is typically accomplished by filtration, adsorption, absorption, or chemical reaction; however, in some cases, "whole air" or "bag" samples are used. Also, it is impractical to develop samplers that are too cumbersome to be worn by workers, that contain chemicals that are too hazardous to be worn by workers, or that require constant attention by the industrial hygienist conducting the sampling. Because of these reasons, bubbler, bag and impinger methods are considerably less desirable than filters, solid sorbents, passive monitors or personal direct-reading instrumentation.

3. LABORATORY TESTING

a. Evaluation of Measurement Parameters

(1) Measurement Range. The useful range of the measurement system must be determined following optimization of the sensitivity and selectivity of the measurement system. This typically includes an estimate of the limit of detection (LOD) and the measurement range. The LOD is defined at the mass of analyte which gives a signal 3 times the standard deviation of the blank signal above the mean blank signal [12]. The limit of quantitation (LOQ) is the larger of: (a) the mass corresponding to the mean blank signal plus 10 times the standard deviation of the blank signal, or (b) the mass above which recovery is greater than or equal to 75%. For OSHA compliance sampling, the analytical range should be sufficient to allow analysis of samples ranging from at least one-half to two times the standard for which the method is being developed (for a nominal sampling volume) without excessive dilution.

(2) Measurement Precision. The measurement precision is determined by pooling the standard deviations found for several points over the measurement range, providing that homogeneity of variance exists [1,2]. A minimum of six determinations at three different concentrations gives 15 degrees of freedom for the precision estimate. The pooled precision should be sufficiently low (better than 7 or 8% relative standard deviation) so that when combined with the imprecision of sampling (e.g., pump error), the total precision is still acceptable [1,2,7].

(3) Measurement Interferences. Potential interferences in the measurement methodology should be investigated and defined. The literature search should be used to help identify substances in workplace environments that would likely be collected with the analyte and could cause erroneous analytical measurements. The measurement conditions should be adjusted to eliminate or minimize these interferences. Interferences which cannot be eliminated should be defined.

b. Evaluation of Sampling Parameters

(1) Recovery From Collection Media. Before investigating the factors affecting analyte collection, it is necessary to verify that the analytical methodology used is accurately determining the quantity of material collected. A means for accomplishing this is fortification (spiking) of the sorbent material (solid sorbent, filter or solution) with a suitable solvent containing dissolved quantities of analyte representative of exposures at 0.1, 0.5, 1 and 2 times the target concentration [6,7] (Section 2.b.); equilibration of analyte and sorbent; followed by desorption or digestion; and analysis. Spiking is normally accomplished by pipetting an analyte containing solvent (preferably less than 10 μL) directly onto the sorbent. This method of spiking has been shown to be comparable to dynamic sampling for a number of organic compounds on charcoal [13]. Direct gas spiking has also been done by injecting gaseous analytes into a gas stream passing through the sampler. In calculating the quantity of analyte necessary for spiking, a sampling time of 8 hours should be used for time-weighted average measurements and 15 minutes for ceiling or short-term exposure limit (STEL) measurements, unless previous experimentation has shown that shorter sampling times

are necessary. For the 0.5, 1 and 2 times the target concentration, recoveries of greater than or equal to 90% are preferred although recoveries greater than or equal to 75% may be acceptable [1,2,3,5,7]. Recoveries greater than or equal to 75% at the 0.1 times the target level are required if validation of the methodology at that level is necessary.

(2) Capacity of Collection Media. Capacity of samplers is usually reported in terms of breakthrough volumes or collection efficiency. Breakthrough volume is determined for solid sorbent tubes, bubblers and impingers by sampling a test atmosphere at 2 times the target value and greater than 80% relative humidity until the sampler effluent reaches an analyte concentration of 5% of the tube influent concentration [3]. The sampler effluent is most easily monitored using direct-reading instrumentation but may also be accomplished with several sampling tubes used consecutively for short sampling times. The efficiency of particulate collection by filtration is also determined using alternate backup sampling devices or similar samplers in series. For passive samplers, capacity is determined by sampling for times varying from 7.5 minutes to 12 hours. Sampler capacity is exceeded when the analyte uptake rate is no longer constant or predictable. Because of potential competition for sorbent sites with other substances that may be present in workplace atmospheres, a safety factor of 0.67 is multiplied with the laboratory-determined capacity and the product is reported as the useful capacity of that sampler [4]. Filters also have a limited capacity which generally is manifested in the increased pressure drop at high loadings. Oils and mists, as well as high loadings of other aerosols, will increase pressure drop across the filter. A maximum loading of 2 mg total dust is recommended to avoid losses owing to mechanical sloughing of the collected aerosol from the filter.

(3) Stability of Collected Analyte. The stability of collected analyte on samplers (storage after sampling) must be determined for all samplers that are returned to laboratories for analysis. Sample storage stability is usually investigated by exposing several samplers to 0.5-1 times the PEL concentrations of analyte and 80% relative humidity. One set of samples (6 to 10 samples per set) is analyzed immediately following exposure, a second set after 1 week room temperature storage. Other sets are analyzed over a period of 30 days [7]. Sampling systems are termed stable if the difference in the means for the immediately analyzed and the stored samples is less than 10%. If samples are not stable for the 30 day period, refrigeration of samples after 7 days storage should be investigated.

(4) Sampling Interferences. Various potential sampling interferences will certainly be encountered under actual use and, consequently, should be investigated during method development. Moisture (humidity) is a potential coadsorbent, the concentration of which may change daily and will certainly be different for different industrial processes and facilities. Moisture and other substances present may also affect the stability of collected gases and aerosols (e.g., hexavalent chromium; see NMAM Method 7600). Other species which are likely to be present in workplace environments and are potential sampling interferences (e.g., competing for sorbent sites) should also be investigated. The extent of interference for these species should be defined.

(5) Overall Precision. The overall precision of sampling and measurement is determined by collecting several samples over the working range of the method. Typically, 6 to 10 samples at each of three (0.5, 1 and 2 times the target value) or four (0.1, 0.5, 1 and 2 times the target value) concentration levels are used to determine a pooled relative standard deviation providing homogeneity of variance exists [1,2,3,7]. The pooled relative standard deviation based on 24 samples (6 samples at each of 4 concentration levels) for unbiased methods must be less than 0.099 for the total analytical error to be less than 25% in at least 95% of the samples analyzed [7].

(6) Overall Bias. The overall bias of sampling and measurement is generally determined from the same samples collected for the overall precision study. The mean concentration determined by the samples must be within 10% of the concentration determined by an independent method. In reporting biases found, the independent method used must be well defined including its known characteristics and limitations (accuracy, precision, interferences, etc.). In addition, any uncorrected analytical bias, in conjunction with the sampling and measurement precision, must meet the ± 25% criterion previously discussed [7].

c. Evaluation of Parameters Specific to Sampler Types

(1) Pressure Drop Across Active Samplers. The pressure drop across active (pumped) samplers must be determined at the flow rate at which these devices will be used. The pressure drop must be sufficiently low that sampling pumps will function properly for the desired sampling period. As noted in 3.b.(2) on the previous page, the pressure drop across membrane filters is a function of total aerosol collected.

(2) Sorbent Stability. Sorbents coated with reactive substrate are finding increased usage because of their specificity for certain analytes. Bubbler and impinger chemistries are also being applied to these solid sampling devices, which are more acceptable to workers. The shelf life of these samplers must be determined since the reagents or derivatizing agents may evaporate from the substrate, atmospheric moisture may be absorbed by the sampling medium or reagent coatings may react with atmospheric gases (CO_2, etc.). The occurrence of any of these possibilities is likely to affect adversely the capacity of the sampler.

(3) Passive Samplers. Passive or diffusional samplers must also be investigated for the effects of reverse diffusion, sampler starvation, monitor orientation and temperature effects [4,5]. Reverse diffusion is checked by exposing two sets of samplers to analyte for some period of time (approximately one-half of a typical work shift, e.g., 4 hours), analyzing one set of samplers after this exposure and exposing the other set of samplers to an analyte-free environment for the same amount of time as the initial exposure. Sampler starvation is typically checked at low (ca. 25 ft/min; 7.6 m/min) and high (ca. 250 ft/min; 76 m/min) face velocities. The effect of sampler orientation on sample collection is determined by exposing samplers to analyte with several samplers positioned parallel and others perpendicular to the direction of airflow. The effect of ambient temperature on sample collection must be determined since diffusion constants are temperature dependent and permeation membranes used in some diffusional samplers are temperature-dependent. Temperature effects are found by determining

recoveries after exposures in low (ca. 10 °C) and high (ca. 40 °C) temperature environments.

(4) Direct-Reading Field Instrumentation. Several of the factors previously discussed are applicable to direct-reading instrumentation (e.g., range, precision, interferences and bias) while others do not directly apply (e.g., capacity and recovery from collection media). Stability of the instrumentation system, more correctly termed reproducibility, includes zero and span drift, background noise and calibration stability. Other factors requiring investigation include instrument warm-up time, frequency of need and ease of field calibration, response time, response linearity, run time with batteries, and specificity. The influence of ambient conditions (temperature and pressure) must be known [14]. During field testing, the effects of spurious radiation (e.g., radio frequency radiation from sealers) should also be investigated.

4. FIELD TESTING

a. Precision

Precision of sampling and measurement in an actual workplace environment is most readily determined by collecting at least 10 replicate samples from a homogeneous atmosphere. This can be accomplished using a field exposure chamber [4]. Overall precision can also be determined by collecting several sets of samples (at least two samples per set). In this instance, the sample sets do not have to be collected from a homogeneous atmosphere; however, a considerably larger number of samples must be collected. Field precision should be compared with laboratory-determined precision. A large increase in field-determined precision over laboratory-determined precision is indicative of uncorrected interfering species present in the workplace environment, the use of a sampling and measurement system that is not rugged, or sampling from an inhomogeneous atmosphere.

b. Bias

Sampling and measurement bias should also be determined in workplace environments [4]. This is also accomplished most easily with a field exposure chamber and requires the use of independent methods for estimating the analyte concentration.

c. Personal Sampler Durability

Sampler durability is a subjective determination that is estimated by conducting personnel sampling. Sample losses due to breakage or leakage of the sampler, worker discomfort because of the sampler, the amount of time required by the industrial hygienist for sampler set-up, monitoring and take-down all should be minimal.

5. USER CHECK AND DOCUMENTATION

As a check on the clarity of new methods, they should be reviewed and submitted to a user check (i.e., the method is used to analyze spiked or generated samples of known concentration by someone other than the researcher who developed it) and to a collaborative

test, if feasible. Also, a backup report should be written detailing the experimentation used in the methods development work.

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F. SPECIAL CONSIDERATIONS FOR BIOLOGICAL SAMPLES

by R. DeLon Hull, Ph.D., NIOSH/DBBS, and Larry K. Lowry, Ph.D.

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1. GENERAL CONSIDERATIONS

Biological monitoring is a rapidly emerging science that is finding increased use, both in the United States and abroad. It is often used in conjunction with environmental monitoring to describe more completely exposures and absorption of chemicals found in the workplace. Specifically, biological monitoring includes the measurement of the absorption of an environmental chemical in the worker. In order to accomplish this measurement, biological specimens are analyzed for the chemical agent, its metabolite or some specific effect on the worker. Some examples include the measurement of blood lead as an assessment of chronic lead exposure, measurement of urinary phenol for assessment of exposure to benzene, and measurement of carboxyhemoglobin in blood as an index of carbon monoxide or methylene chloride exposure. In a broader sense, biological monitoring may include behavioral and performance testing and medical procedures.

Biological monitoring, unlike environmental monitoring, should be considered a medical procedure since, by definition, the specimen comes directly from a human. Therefore, such areas as informed consent, medical-legal ethics and the Federal Privacy Act need to be considered. Additionally, laboratories conducting analyses of human biological samples are subject to the recently promulgated (February 28, 1992) Clinical Laboratory Improvement Amendment of 1988 [1]. These regulations contain requirements for education and training of personnel conducting various analyses, quality control, quality assurance, proficiency testing, and participant test management (i.e., sample submission and handling, test requisition, laboratory records, and reporting test results).

Biological monitoring has been called the ultimate personal sampler because, when properly used, it can assess worker exposure to industrial chemicals by all routes including skin absorption and ingestion. An area often overlooked, however, is the

measurement of actual uptake of environmental agents, and the suitability of biological monitoring to assess inhalation uptake, which is:

(respiratory volume) • (environmental concentration) • (length of exposure).

Another use of biological monitoring is to assess the effectiveness of engineering controls or work practices to limit uptake of environmental chemicals.

Biological monitoring is not without its limitations. A major limitation is the lack of detailed information on the fate of industrial chemicals in humans. Most of the toxicological/pharmacological information available is from experimental animals and not easily applied to humans. Another concern is the apparent wide variability seen in the majority of biological monitoring data. Proper knowledge of the fate of a chemical, its pharmacokinetic properties, specific methodologies and other factors described later can control such variability; however, specific methodology and data interpretation remain an obstacle to widespread use of biological monitoring. Research is underway worldwide to develop more definitive methods and to better define dose-response relationships and suggested limit values.

2. SPECIFIC FACTORS TO BE CONSIDERED WHEN CONTEMPLATING BIOLOGICAL MONITORING

Considerable advance planning is necessary when biological monitoring is contemplated to aid in the selection of the appropriate test and to ensure data that will be meaningful in assessing worker exposure. These factors fall into two areas: (1) the characteristics of the exposure, and (2) the characteristics of the chemical in workers. The type of exposure (i.e., chronic, acute, intermittent), the major route of exposure (i.e., dermal, inhalation, ingestion) and the nature of other workplace chemicals are important considerations when contemplating biological monitoring.

The fate of a chemical in humans is also important. It is necessary to know how the body metabolizes (biotransforms) the chemical, where the analyte of interest is present in measurable quantities (i.e., what sample should be collected) and some knowledge of the pharmacokinetics of the chemical in humans (i.e., when should the specimen be collected). If all of these factors are considered, then a successful biological monitoring program is possible.

3. PRACTICAL CONSIDERATIONS

a. Selection of Methods. A dialog between the occupational health professional familiar with the workplace and a competent laboratory chemist is a requirement for proper method selection. The following areas should be addressed:

(1) Does the survey require rapid, semi-quantitative (non-specific) or specific methodologies?

(2) Do interferences exist from diet, drugs, alcohol, disease states or other workplace chemicals? If so, can these interferences be controlled?

(3) Does the sample matrix affect the analysis? In general, blood serum and urine specimens require different sample preparation and may require separate methodologies to eliminate matrix effects.

(4) Is the limit of detection low enough to differentiate exposed from non-exposed workers? The method may have been developed when exposure limits were higher.

(5) Does the method have guidelines for interpretation of the data or are published guidelines/normals available? If not, can non-exposed workers be used for controls or reference baseline data?

b. Sampling Strategy. Strict attention to sample integrity is essential for quality data. The ideal "perfect" laboratory method and trained analyst cannot produce good results unless:

(1) the correct specimen is collected;

(2) the specimen is collected at the right time after exposure to the toxic substance;

(3) the proper container, with preservative or anticoagulant, is used;

(4) the proper field specimen preparation is used;

(5) the specimen is not contaminated;

(6) the stability of the analyte is assured through proper shipment of the specimen to the laboratory; and

(7) the specimen is properly labeled.

The details of biological sampling are shown in the individual methods. They are important.

c. Quality Assurance. Good data require the utilization of an effective quality control program. Two major areas need attention: (1) laboratory quality control and (2) field quality control.

There are different approaches used in laboratory quality control programs in biological monitoring since few proficiency testing programs are available. Acceptable precision can be maintained for a method by the preparation of a pooled specimen in a biological matrix, aliquoting the pooled specimen into multiple containers, properly preserving the pooled specimens (usually in a freezer) and running a pooled sample with each batch of samples. Quality control charts should be prepared after a minimum of 20 analyses of "pool" and acceptable control guidelines are prepared. When a batch of analyses containing a "pool" value is out of control, results from that entire batch should not be reported until the source of error is corrected.

Accuracy is difficult to substantiate in the absence of proficiency testing programs. Strict attention to such items as standardization, extraction efficiency, recovery, standard stability, reagent and specimen stability, as well as proper instrument calibration, are mandatory. Many gas and liquid chromatographic methods utilize internal standards and results are reported using response factors aiding in instrument quality assurance.

Quality control at the field level can be maintained and the laboratory checked by:

(1) ensuring sample integrity, i.e., proper collection, preservation and shipment procedures;

(2) submitting blind duplicate split samples to the laboratory, with each specimen identified as a normal field sample; and

(3) including "control" specimens from non-exposed workers.

An evaluation of these data and a comparison of "control" population values to published or unpublished historical "control" data will provide the health practitioners with useful information on laboratory quality and data integrity.

4. URINE DATA - HOW SHOULD THEY BE CORRECTED?

There has been some confusion on how urine data collected as a single voiding "spot" sample should be reported. Most urine data from clinical studies are from 24-hour collections and the results are reported as the amount of analyte excreted per 24 hours. However, urine sampling in an industrial environment does not lead to accurate and uncontaminated 24-hour collections. Logistics, as well as sample integrity, become serious problems. As a result, almost all urine specimens collected for biological monitoring purposes are individual voidings or "spot" specimens collected at a pharmacokinetically correct time following exposure to the environmental contaminant.

The major problem with "spot" urine specimens is the dilution of the urine, as influenced by variations in liquid intake and physical work load. A worker who drinks a large volume of liquids may excrete 500 to 800 mL in a single voiding, whereas a worker who is doing heavy work in a hot environment may excrete less than 100 mL over the same time interval. The absolute amount of metabolite in grams may be identical but concentrations will vary widely. Some attempts at correction of data for the dilution of urine would be desirable to "normalize" the data.

In the past, NIOSH and the industrial hygiene community have utilized a specific gravity correction where the concentration of a urinary analyte would be adjusted to some standardized specific gravity. Usually 1.024 was selected as that standard, although the literature also shows 1.016 and 1.018 as "standards."

It is obvious that urine with a specific gravity of less than 1.010 or greater than 1.035 show rather large corrections -- corrections that can change the results by orders of magnitude. Most of these corrections are misleading. Another problem relates to the nature of the specific gravity, i.e., total solids per unit volume. In the case of heavy

metal exposure, urinary protein may increase which, when the specific gravity correction is applied, would lead to a falsely low-corrected concentration.

The medical/clinical community has long favored a "normalization" based on the concentration of a normal urinary constituent, creatinine. The substance, a product of tissue breakdown, is excreted at a relatively uniform rate and the total amount excreted per day is quite constant from day-to-day in a given individual. Results are usually expressed as a ratio of the concentration of the analyte divided by the concentration of creatinine in that same urine specimen. Such units are g analyte/g creatinine or mg analyte/g creatinine, etc.

This correction is gaining wide acceptance in the European community and within occupational health circles. Many NIOSH methods in Volumes 1 through 7 of the Second Edition, as well as the First Edition of this Manual, contained specific gravity corrections, creatinine corrections, both corrections or no corrections.

In order to eliminate the confusion, all methods in NMAM will show "spot" urine data **uncorrected and with the creatinine normalization** in line with widespread usage in the recent literature and in the world community. It should be pointed out that a separate creatinine determination is required. No method is included in this manual as most clinical laboratories perform this analysis on multichannel automated analyzers. Manual methods are readily available and most are based on the original Jaffee alkaline picrate method and revisions or adaptions over the years [2,3].

5. GUIDES TO INTERPRETATION

Interpretation of data is difficult because of the lack of standards or regulations on biological monitoring tests. Results obtained are often dependent on time of collection, specimen integrity, drug or chemical interference, or methodologies. It should be pointed out that finding measurable levels of an occupational chemical in a biological fluid where "normal" people do not have the particular chemical/metabolite carries no adverse health implications in itself. The presence of such chemicals is only an indication of exposure. Further testing or examination of the worker is needed to define health risk.

One recommended approach to data interpretation is to collect specimens from non-exposed control subjects at the workplace and to use this group mean as a baseline to interpret the values from an exposed population. In some cases, a non-exposed control group cannot be obtained from the workplace. In these instances, the use of an outside control group should be considered. Textbooks and literature references are available that quote normal or non-exposed values and some sort of "limit" value [4,5,6,7,8]. However, caution must be used in applying these numbers to a particular laboratory method and sampling strategy. Some guidance to interpretation is included in each method but any suggested value should not be considered as a NIOSH recommended limit.

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G. AEROSOL PHOTOMETERS FOR RESPIRABLE DUST MEASUREMENTS

by Paul A. Baron, Ph.D., NIOSH/DPSE

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1. INTRODUCTION

This discussion will cover direct-reading aerosol photometers that are self-contained (battery-operated) and portable (can be used while carried by one person). There is a variety of direct-reading aerosol monitors using light-scattering detectors. These instruments generally have advantages in reduced weight, improved ruggedness, and continuous readout when compared with other direct-reading aerosol monitors. These instruments can be used to provide accurate dust concentration measurements as described below, though in most situations they are most useful for approximate or relative concentration measurements. Their principle advantage is that of providing real time information.

An aerosol is a group of particles suspended in the air. Aerosols can be introduced into the body primarily through the respiratory system. Total dust measurements indicate concentrations that can enter the nose and mouth of a worker as well as that which can settle on the skin while the respirable fraction of dust is that portion which can reach the lower or gas exchange part of the respiratory system.

The respirable fraction of the dust mass has been defined for sampling purposes by the American Conference of Governmental Industrial Hygienists (ACGIH) as that fraction collected by a device with a penetration curve (Figure 1) fitting the following points [1]:

Particle Size, μm *	% Passing Selector
0	100%
1	97
2	91
3	74
4	50
5	30
6	17
7	9
8	5
10	1

*aerodynamic diameter

There are other definitions of respirable dust [2,3,4] as well as empirical data indicating deposition efficiency of dust in the respiratory system. Historically, the most commonly used respirable dust sampling device in the U.S. is the 10-mm nylon cyclone. At a flow rate of 1.7 L/min, the cyclone passes close to 50% of 4-micrometer aerosol particles. However, it has been shown that the 10-mm cyclone has a somewhat sharper cutoff than the ACGIH curve and, with certain size distributions, may introduce a bias with respect to the ACGIH definition [5].

Aerosols are frequently classified according to their physical form and source. Aerosols consisting of solids (e.g., coal, wood, asbestos) are designated dusts. Aerosols consisting of liquid (e.g., oil, water, solvents) droplets are called mists. Submicrometer aerosols that are formed from condensation or combustion processes are generally called fumes or smokes. Some of these aerosols have a significant vapor pressure and will evaporate when aged. The direct-reading photometer may detect these high vapor pressure aerosols while the reference method for respirable dust (Method 0600) will not.

2. PRINCIPLES OF OPERATION

Light-scattering aerosol monitors (also called nephelometers or aerosol photometers) operate by illuminating aerosol passing through a defined volume and detecting the total light scattered by all the particles in that volume (Figure 2). This discussion will not include single-particle counting photometers that are used to measure lower concentrations such as in clean rooms and give information about individual particles. However, there is an instrument listed below (Portable Dust Monitor from A. P. Buck, Inc.) that uses single-particle counting to estimate mass concentration.

The light source of a photometer can be monochromatic such as a light-emitting diode or laser or a broad-wavelength light source such as a tungsten filament lamp. The choice of light source in different instruments has more to do with the ability to control the light output level than with the wavelength of the output. The detector is generally a solid state photodiode but can be a photomultiplier tube. The detection geometry varies from one instrument to another. These instruments generally use a forward-scattering geometry (i.e., less than 90°). The angle of scattering (theta) is defined with respect to the beam of light passing through the aerosol in the detection volume. The smaller the value of theta the more the detection is weighted toward larger particles.

The amount of light scattered by a particle into the detector is a complex function of the particle size, shape and refractive index. For spherical particles of known refractive index the instrument response can be calculated. However, in general, calibration must be carried out experimentally. An example of instrument response as a function of particle size for spherical particles of two different refractive indices is shown in Figure 1. It can be seen that there is a peak at approximately 0.6 mm and that there is a drop in instrument response to larger particles. For comparison, the ACGIH definition of respirable dust is superimposed on Figure 1 [6]. It can be seen that the size dependent response of the photometer is somewhat similar to the desired response for a respirable sampler.

For quantitative measurements, it is necessary to calibrate with an aerosol similar in refractive index and particle size to the one being measured. This is because aerosols with

different refractive indices can produce photometer responses differing by more than a factor of ten. Since these instruments have specific size-dependent response to particles, the size distribution of dust particles is also important in evaluating the mass response of the instrument for a specific dust.

3. SAMPLING CONSIDERATIONS

a. Safety

Some portable photometers have been designed for intrinsic safety, i.e., for use in potentially explosive atmospheres. This must be checked with the manufacturer to ensure that a specific instrument meets the appropriate intrinsic safety requirements (e.g., Underwriter's Laboratory or Mine Safety and Health Administration).

b. Applications

Photometers generally cannot be used to discriminate between different types of aerosol. The instrument will respond to all types of aerosol present simultaneously in the detection volume. Therefore, measurement of a small amount of a specific aerosol in the presence of a large amount of interfering dust is not feasible with a photometer. For example, if lead fume must be measured in the presence of a large percentage of road dust, the photometer would not be the instrument of choice. However if lead fume were the major aerosol component, use of the photometer would be appropriate for monitoring lead exposure.

At high humidity, water droplets can exist in the air for extended periods of time and be detected by a photometer. These droplets can change size rapidly in response to small changes in humidity. Therefore, care should be taken when measuring aerosols near water sprays and other high humidity locations. It has been found in some cases, such as in cotton mills, that the aerosol produced by dried water sprays can be a significant component of the workplace aerosol.

Aerosol photometers require that the aerosol be carried to the detection volume in some fashion. Because of the inertial and electrical properties of aerosol particles, there may be errors in transporting the aerosol to the detection volume. Most photometers have a sampling pump that draws the aerosol into an inlet, through a length of duct, and to the detector. Some instruments include a preclassifier (cyclone or impactor) to make the overall response more similar to the respirable dust definition. Some photometers rely on air convection or motion of the photometer to bring the aerosol to the detector (passive sampling). In either case, there will generally be some particles that are not detected due to losses in the instrument before they reach the detector. Particles larger than 10 μm are especially likely to be lost. However, these losses will generally be small for smaller particles unless there is high local air velocity or unless the aerosol particles are highly charged.

A list of instruments is provided at the end of this chapter. Other instruments are listed in various references [7,8]. Since instrument development is an active field, it

is suggested that current literature sources and the manufacturers be contacted for the latest information.

4. DATA ACQUISITION AND TREATMENT

a. Calibration

Most photometers are factory-calibrated by comparing the instrument response in a well-defined aerosol to measurements by the gravimetric method (e.g. Method 0600). The instrument response at one or more concentrations is compared with the gravimetric method result. In most cases, the photometer response is modified to read directly in mg/m^3. However, it should be remembered that this calibration is only valid for the specific calibration aerosol and may differ by as much as a factor of ten when used with an aerosol from a different source, different composition, or size distribution. The factory calibration of this type is primarily useful to ensure that the instrument is operating properly and responding the same as other similar instruments. It does not ensure that the photometer will respond accurately to another aerosol.

An aerosol photometer measures a single parameter that is dependent on many variables, e.g., particle size distribution, particle agglomeration, particle refractive index, that can and do change in field situations. Therefore, it is necessary that the aerosol photometer be calibrated in conditions closely approximating the aerosol to be monitored. Calibration is carried out by comparing the time-weighted average photometer readings directly with field measurements using Method 0600. Most photometers do not protect the optical surfaces with a clean air sheath and should be checked frequently for zero drift during calibration and routine monitoring.

b. Operation

Data can be collected in either manual or automated mode. Most direct-reading photometers have a digital or analog readout indicating concentration. This allows manual observation of measured concentration. In this mode the instrument is useful for observing relative concentrations between different locations, for detecting leaks in processes, for evaluating work procedures, etc. Some photometers also have an output port that can be connected to a recorder or other data acquisition system. This allows the instrument to operate unattended while it monitors work processes, filter penetration breakthrough, etc. In some cases, the photometer and the data acquisition system together are sufficiently small that they can be worn by a worker. These photometers can be used to provide a time-dependent profile of exposure over a work period as well as an integrated time-weighted average exposure. In addition, the worker can be made aware of aerosol concentrations while carrying out his tasks so that he can modify work practices to reduce exposure.

It should be noted that the concentration of any contaminant in the air can be highly variable. Therefore, a single measurement of concentration, especially with a direct-reading instrument, should only be considered in the context of other measurements and the environmental conditions.

5. INSTRUMENTS

a. MIE, Inc.

Model RAM-1 Features: Active sampling, with 10-mm nylon cyclone, reference scatterer built in, zero air built in, clean air protection for optics, several time constants for output, dehumidifier available, permissible for explosive atmospheres (optional).

Model MINIRAM Features: Passive sampling, with active sampling attachments (optional) that need a separate pump, automatically calculates running and shift average concentrations, permissible for explosive atmospheres, zero air attachment (optional).

b. MST Measurement Systems, Inc.

Model P-5 Features: Active sampling, labyrinth classifier on inlet, integrating or continuous readout, several measurement periods.

Model PCD-1 Features: Active sampling, respirable dust inlet, programmable parameters include sampling period/alarm concentration/calibration factors, data acquisition built in.

Model PDS-1 Features: Passive sampling, allows personal monitoring, requires separate readout unit or data logger.

c. ppm Enterprises

Model HAM Features: Passive sampling, active sampling attachments (optional), zero air attachment, reference scatterer attachment.

Model Personal Aerosol Monitor Features: Passive sampling, zero air attachment, reference scatterer attachment.

d. Sensidyne, Inc.

Model LD-1 Features: Active sampling, laser light source, 10- or 7-micrometer cut impactor classifier built in, analog and digital readout, one-minute or operator-selected measurement period, reference scatterer, zero air attachment.

e. A. P. Buck, Inc.

Portable Dust Monitor Features: Active sampling, laser diode light source, optional cyclone for respirable sampling, pulse height analyzer for particle sizing information, data logger built in, filter for reference mass built in.

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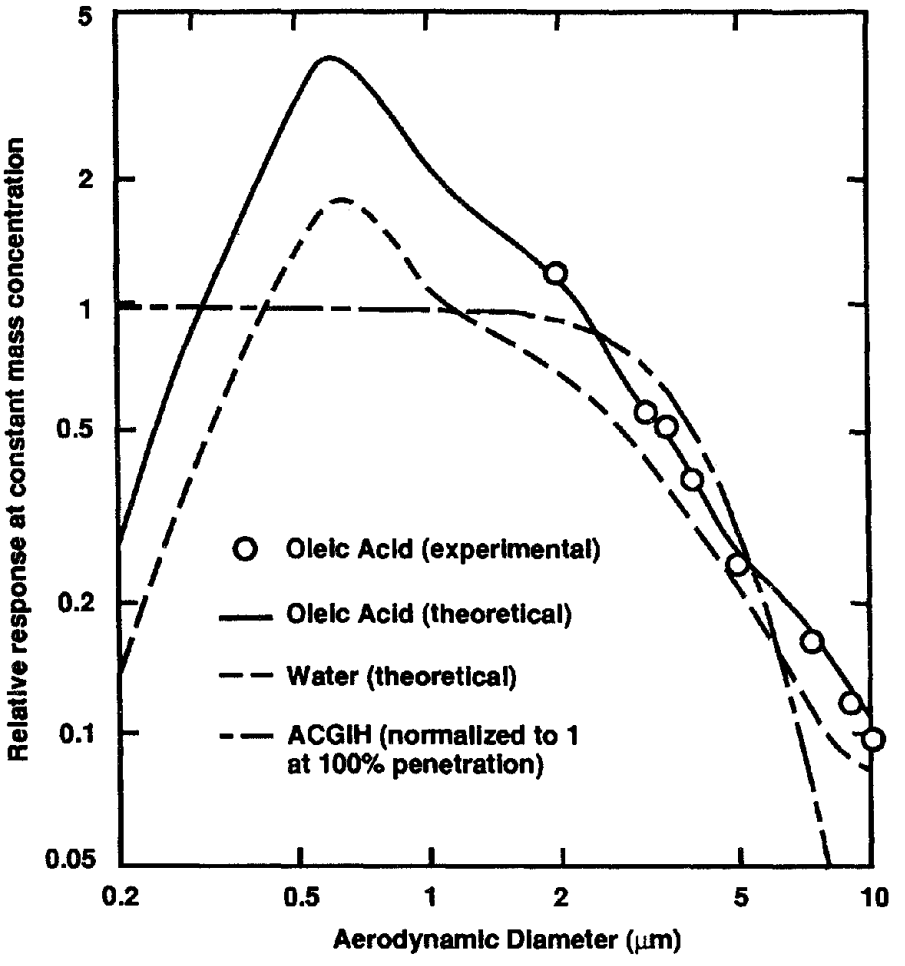

Figure 1. Experimentally determined and theoretically predicted "mass sensitivity" of the GCA RAM-1 to oleic acid and water droplets. Included for comparison is the ACGIH respirable dust penetration curve [1] normalized to one at 100% penetration.

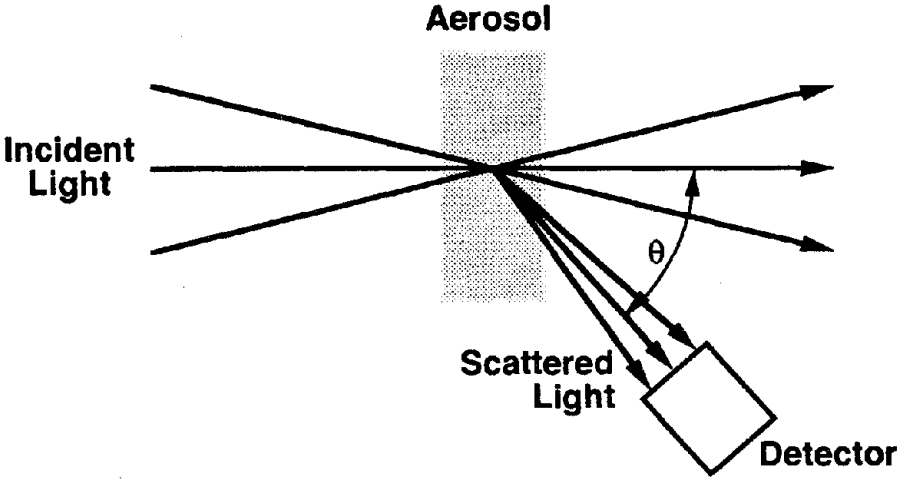

Figure 2. Diagram showing the components of an aerosol photometer.

H. PORTABLE ELECTROCHEMICAL SENSOR METHODS

by W. J. Woodfin, NIOSH/DPSE

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1. INTRODUCTION

Portable electrochemical sensor methods include instruments employing this technology in the determination of oxygen and several toxic gases in the field, using battery-supplied power. They range in size from those small enough to fit into a shirt pocket and weighing less than one pound (0.45 kg) to larger units that weigh as much as six pounds (2.7 kg).

2. PRINCIPLES OF OPERATION

The basis for all electrochemical sensors is the use of a porous membrane (normally PTFE) or capillary system which allows the gas to diffuse into the cell containing the liquid or gel electrolyte and the electrodes (Figure 1). The exact configuration will vary with manufacturers and between different toxic gases. When the gas comes into contact with the electrolyte, a change in electrochemical potential between the electrodes is produced. Associated electronic circuitry then will measure, amplify, and control this electronic signal. Because the reaction is proportional to the concentration (partial pressure) of gas present, the signal is easily translated into parts per million, percent, or ppm-hrs, and read on the readout meter or stored in microprocessor circuits for later readout.

3. SAMPLING CONSIDERATIONS

a. Safety

Some portable electrochemical monitors have been designed for intrinsic safety, i.e., for use in potentially explosive atmospheres. Check with the manufacturer to ensure that a specific instrument meets the appropriate intrinsic safety requirements (e.g., Underwriter's Laboratory or Mine Safety and Health Administration).

b. Applications

Electrochemical sensors are available for, e.g., SO_2, H_2S, NO_2, $COCl_2$, CO and O_2 [1,2,3]. Except for O_2, the widest application for electrochemical sensors has been as alarm/dosimeter systems rather than as continuous monitors. Because of the low power requirements and small size, the electrochemical sensor is ideally suited for use in combination monitors, that is, those that are able to monitor two or more substances at once. Many combination monitors are available, including in one package the sensors for oxygen deficiency, combustible gas, and toxic gas. The oxygen and toxic gas sensors are usually electrochemical. Electrochemical sensors may be located several meters away from the electronics/readout unit in order to facilitate remote or pre-entry monitoring.

Because of the low power requirements of these devices, it is possible for them to be used in lightweight, personal monitor/alarm devices. Electrochemical sensors for oxygen deficiency, H_2S, HCN, and others have been designed into monitor/dosimeter/alarm packages that are small enough to fit into a shirt pocket, that weigh less than one pound (0.45 kg) and that operate continuously for as long as four months without changing the replaceable battery. Also, because of the low power required, it is relatively easy to design them to be intrinsically safe.

c. Environmental Conditions

The environmental conditions (temperature, relative humidity, barometric pressure) of the monitor at the time of calibration should be as near as possible to those that will be encountered during use. Of these three, temperature is most important because changes in temperature are most often encountered in the field and can cause bias in the readings obtained. Even with the temperature compensating circuitry employed in most sensors, some time is required for equilibrium to be reached. If it is not possible to calibrate at the working temperature, the user must allow sufficient time for field equilibration of temperature. Changes in barometric pressure are usually less significant than temperature changes and so are of less concern to the user. Oxygen monitors with pressure compensating circuitry should be employed whenever pressures differing by 5 kPa (0.05 atmosphere) or more from the calibration pressure [1,4] are encountered.

4. DATA ACQUISITION AND TREATMENT

a. Calibration

The most simple example of field calibration of an electrochemical sensor is the oxygen monitor which may be calibrated by placing it in fresh (outdoor) air and adjusting the calibration potentiometer to make the readout meter read 20.9% O_2. To determine if it responds to oxygen deficiency, hold the breath for a few seconds, then slowly exhale, directing the exhaled breath to the sensor. If it is functioning properly, the meter will deflect downscale and the alarm circuit will be activated.

For electrochemical sensors used to monitor other chemicals (e.g. H_2S, CO, NO_2, SO_2), stable cylinders of calibration gases in the concentration range of interest as well as other, less convenient chemical generation systems (e.g., permeation tubes) may be used for calibration. These sensors may also be zeroed in fresh air or zero air from a compressed gas cylinder or clean air prepared by filtration. The frequency of calibration cannot be prescribed exactly, but a good rule is to calibrate at least once a day at the start of a shift. Manufacturers instructions or user experience may dictate more frequent calibration.

Always carry out the calibration procedure for toxic gases in a well-ventilated area, preferably in a fume hood if one is available. Make sure that the calibration procedure itself does not pressurize the sensing cell. This is especially important to observe when pressurized cylinders of standard gases are used for calibration. Overpressurization of the sensor can be avoided by using a pressure regulator on the calibration gas cylinder or by installing a "tee" fitting in the line to reduce the stream to atmospheric pressure. Another method is to fill a bag with gas from the cylinder so that it can be presented to the sensor at atmospheric pressure from the bag. Sensors should be replaced when they can no longer be calibrated or zeroed easily during the routine calibration procedure.

b. Sampling and Measurement Procedure

(1) Toxic Gases

Electrochemical sensors used for toxic gases are normally used as dosimeter/alarms, which means that the electronic circuitry provides a time weighted average (TWA) but not necessarily a continuous readout of the concentration. The alarm circuit is designed to activate whenever the preselected value is reached or exceeded for a predetermined time (or number of counts). On some systems, the TWA value may be obtained from the systems' microprocessor at the end of the shift by attaching it to an accessory printer or plotter designed to display this information. Some units provide a display of the current TWA which can be updated periodically or at the user's command.

(2) Oxygen

Oxygen electrochemical sensors provide either a continuous or on demand display of the present percent oxygen in the atmosphere, and the alarm circuitry is designed to activate at the moment the concentration drops to 19.5% O_2. Some models, designed to be used in hospitals or as area monitors, have both upper and lower alarm levels so that oxygen-enriched atmospheres may also be monitored. Many of these models have output suitable for a strip chart recorder so that a permanent record of the oxygen in the atmosphere may be maintained. The output of these devices is in % O_2. Method 6601 gives a recommended procedure for the use of oxygen monitors.

c. Limits of Performance

(1) Temperature Limits

Most manufacturers of electrochemical sensors specify the lower temperature limits, usually 32 to 50 °F (0 to 10 °C), and upper limits, typically 120 to 140 °F (50 to 60 °C). These do not present a problem for most applications, but the user should be aware that lower temperatures tend to result in longer response times. When used outdoors in cold climates, ambient temperatures should be monitored to assure that the lower limits are not exceeded.

Since many electrochemical sensors are battery-operated, it should be noted that temperature extremes can adversely affect the performance or life of the batteries used in these devices [5,6].

(2) Interferences

Electrochemical sensors designed to measure toxic gases may be non-specific (i.e., cross-sensitive to other compounds). Response specificity is determined by the semi-permeable membrane selected, the electrode material, and the retarding potential (the potential used to retard the reaction of species other than the analyte). Filtering or pre-scrubbing of the sampled atmosphere is also an effective method that has been employed by some manufacturers for some applications. However, not all interferences have been eliminated.

5. MANUFACTURERS

Manufacturers of electrochemical sensors are too numerous to list. For example, there are at least 16 companies that manufacture oxygen monitors with electrochemical sensors. Consult current publications in the field of industrial hygiene and safety for manufacturers of specific sensors [7,8].

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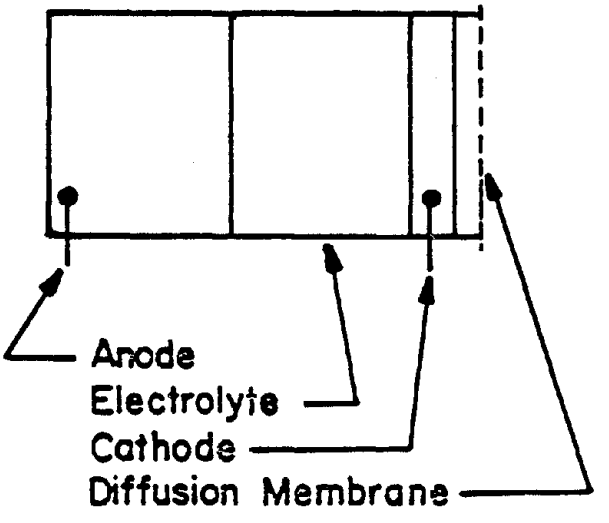

Figure 1. Electrochemical cell schematic.

I. PORTABLE GAS CHROMATOGRAPHY

by Judd C. Posner, Ph.D., NIOSH/DPSE

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1. INTRODUCTION

The term "portable gas chromatograph (GC)" as used here refers to any gas chromatograph not requiring external electrical connections. The portable GC may range in size and portability from a self-contained unit the size of a small suitcase easily carried by one person to a much larger unit requiring auxiliary gas supply and requiring more than one person to transport.

2. PRINCIPLES OF OPERATION

A portable GC consists of, at a minimum, an injection system, a separator (column), and a detector.

a. Injection

There are two basic injection systems: (1) gas-tight syringe through a septum [1] and (2) flushing and filling a sampling loop [2]. The loop is usually filled by means of an on-board pump. Injection is usually accomplished by means of a valve system, either manual or automatic.

The loop system is inherently more accurate, but the volume injected is fixed. However, sample loops are available in a range of volumes. The gas-tight syringe is not as accurate, but injection volumes between 10 μL and 1 mL may be selected as appropriate for concentrations encountered in the field (the lower the concentration,

the larger the injection volume). Both injection systems may require purging to reduce memory effects.

b. Separation

The sample is carried through the column by a carrier gas. Many systems have refillable gas cylinders which must be charged before going to the field. Others may need exterior carrier gas cylinders and regulators. It is important to check the carrier gas requirements in the manual of instructions which goes with the particular portable gas chromatograph. It is also important to consider the appropriate shipping regulations concerning compressed gases.

Columns may be of two types, i.e., packed or capillary. The packed column can accept a larger injection volume, but the capillary column has better separating power. Therefore, the choice of a packed or capillary system depends on the complexity of the atmosphere to be sampled and the desired detection limit. It should also be noted that columns for portable GCs may require special geometries, material of construction and hardware specific to the instrument. The users manual should be consulted for information in this area.

The interaction between the injected sample containing one or more compounds in the vapor phase and a liquid phase present, e.g., on the walls of a capillary column or coated on a diatomaceous earth (solid support) in a packed column results in a separation. The stronger the interaction between the component in the vapor phase and the liquid phase, the more strongly the flow of the component will be retarded by the column, i.e., the longer the retention time, t_r [3].

The use of a heated column system greatly increases the flexibility of the analysis. As in any isothermal situation, there will still be a usable window of retention time. However, the retention time of any peak is a function of the temperature. As a rule of thumb, the retention time doubles for every decrease in column temperature of 30 °C [4]. It is thus possible in many cases to select a temperature at which the peak of interest will have a usable retention time on a particular column.

c. Detectors

After the sample leaves the column, it goes directly to the detector. Detectors vary according to their selectivity, sensitivity, and linearity. The four most commonly used in portable GCs are as follows:

(1) Flame ionization detector (FID) [5] - large linear range; moderate sensitivity; good general detector for organics; low response to CS_2, CO, CO_2, CCl_4; non-selective; requires auxiliary gases (air and H_2).

(2) Photoionization detector (PID) [6] - large linear range; high sensitivity; good general detector for organics and some inorganic gases; generally lower response to some small molecules, i.e., CH_3CN, CH_2Cl_2, CCl_4, CH_3OH and low-M.W.

hydrocarbons; selectivity can be introduced in some systems by using different energy lamps, if available.

(3) Electron capture detector (ECD) [5] - small linear range; high sensitivity; very selective - in general, responds to molecules containing halogen (fluorine, chlorine, bromine, iodine) atoms, cyano groups or nitro groups; minimal response to hydrocarbons, alcohols, ketones, etc.

(4) Thermal conductivity detector (TCD) [5] - good linear range; low sensitivity; general non-selective detector for volatile compounds including all organics, as well as inorganics such as ammonia, CO, SF_6, NO, NO_2, and SO_2.

The choice of detector, and, therefore, in most cases, the instrument, will depend on the chemical to be monitored, the nature of any other contaminants, and the sensitivity required.

d. Limitations

Most portable GCs have no provision for heating the column, detector, or injection port. This limits analyses to the more volatile compounds, and results in variation of retention times with ambient temperature. Also, late-eluting peaks will be poorly formed and will not be very useful for quantitation. This imposes a severe restriction on the number of usable column packings for any given contaminant. It also affects the ability of the system to work well in complex atmospheres, since all quantifiable peaks must have short retention times, and those with long retention times will appear as poorly-defined peaks which may interfere with quantitation of the well-shaped peaks of later injections. Consequently, if contaminants other than the one of interest are known or suspected to be present in the workplace atmosphere, it is essential that these compounds be considered when the selection of a column is made in the laboratory prior to field work.

There is a similar limit to the usable retention time region for a capillary column operated isothermally. Its advantage is that within this usable region it does more efficient separations. Some portable GCs have provision for backflushing the column, which is useful in removing strongly adsorbed compounds which are trapped on the front of the column.

An important point to remember is that an observed retention time does not constitute unequivocal identification of a contaminant; an independent, specific identification must be made to confirm the identity of any peak. However, the knowledge that the compound in question is in use or is likely to be present plus the presence of a peak with the expected retention time is strong evidence for the identity of the contaminant. Thus, some knowledge of the chemicals and the processes in use in the atmosphere to be examined is essential. Retention time on a second column of different retention characteristics is a valuable aid to identification.

Such important parameters as the detector drift with time, retention time variation with temperature, usable battery life, etc., should be determined in the laboratory prior to use in the field.

3. SAMPLING CONSIDERATIONS

a. Safety

The main safety consideration is the use of an FID in areas where a potential explosion hazard may exist. Do not use a detector of this kind in any area where a flame would not be permitted unless the instrument has been rated intrinsically safe. If an electron capture detector is used, the radioactive effluent must be safety vented.

b. Type of sample

In contrast to laboratory-type GCs, portable GCs do not have heated injection ports. Therefore, the sample must be a gas or vapor at room temperature. In general, whether the sample is introduced by means of a loop or a gas-tight syringe, most measurements give essentially instantaneous concentrations. Integrated samples may be taken, if desired, by using gas bags, evacuated gas bottles and the like; in that case, the sample concentration is averaged over the filling time of the sample container. It is important to use only those sample containers in which the analyte is stable.

c. Column Selection

Once the decision to use a portable GC has been made, in most cases, the critical question becomes the selection of the column. The following are some hints to aid in the selection of the column best suited to the analysis to be performed [3]:

(1) Retention time is proportional to column length.

(2) Retention time is proportional to the percent loading of the stationary phase.

(3) Column resolution is proportional to both loading and column length.

(4) Non-polar vapors (e.g., hydrocarbons, halogenated hydrocarbons) are separated most efficiently by non-polar stationary phases; polar vapors (e.g., alcohols, ketones, esters) by polar phases. Information on the polarity and selectivity of stationary phases is available in the form of McReynolds constants which are tabulated in the catalogs of various vendors of GC supplies. A useful discussion of the use of McReynolds constants for column selection appears in the catalog of Applied Science, Inc., 2051 Waukegan Road, Deerfield, IL 60015.

(5) Special columns have been developed for various types of separations. In the catalogs of most suppliers of GC columns there is a section on applications and many of the suppliers will be happy to discuss problems and suggest solutions.

4. DATA ACQUISITION AND TREATMENT

a. Types

Data acquisition may be done automatically or manually depending on the particular design of the portable GC. If the instrument does not have provision for automatic data collection, then, in most cases, the output signal from the GC will have to go to some external data collection and storage device, usually a recorder. In such a display, the area under the peak of interest is proportional to the amount injected. However, peak height, to a reasonable approximation, can be considered proportional to the amount injected. This approximation is only true for measurements performed under identical conditions, i.e., identical column, identical temperature, etc. Thus if there are substantial changes in ambient temperature such as would be encountered, for example, in going from an indoor to an outdoor location, and the GC is operating at ambient temperature (unheated), then the peak height at each location must be related to a standard run under the same conditions.

b. Calibration

As mentioned before, column selection should be done in the laboratory before going into the field. Calibration should be done in the field. There are two reasons for this. First, the potential differences in ambient temperatures between lab and field could lead to errors as mentioned previously. Second, there is almost always drift in the response of detectors with time. Therefore, calibration should always be done as close to the time of actual use as possible. If experience shows that detector drift is significant over the period of time that samples will be taken, then it will be necessary to make frequent injections of standards during the course of the day. Even in the event that drift does not seem to be a problem, occasional injections of standards throughout the period of use is recommended to make certain that the instrument is operating as expected.

Calibration standards may be of two types: commercially available certified gas mixtures or gas bags prepared from a known gas or liquid aliquot of the desired compound plus a carefully metered volume of diluent, usually air or nitrogen. It is strongly advised that the preparation of standards be done in the laboratory as a practice exercise before attempting it in the field, and that the ability to produce accurate bag standards is verified in the laboratory by comparison with a standard concentration.

If the injection system operates by means of a loop, the calibration curve should be of the form of concentration vs. peak height (obtained from the recorder trace). If a gas-tight syringe is used, then the calibration curve is more conveniently of the form of amount (concentration, w/v, times volume injected) or volume (ppm times injection volume) vs. peak height. The range of standards should encompass the expected ambient concentration at the field site. If this is not known, then preliminary samples should be taken to determine the range of expected concentrations. Duplicate injections of each standard should be made and the average value used for the calibration graph. From the data on the precision of the calibration graph, information

about the precision of the measurements and the limits of detection can be obtained using standard statistical methods.

c. Procedure

Once the calibration graph has been generated, the next step is to gather field data. This is done simply by injecting samples of the ambient air periodically into the portable GC and obtaining concentration values by comparison with the calibration graph. The frequency of sample taking is governed by the time necessary for the peak of interest to appear (retention time) plus the time necessary for any other contaminants to elute from the column. As it is seldom possible to know the exact composition of the atmosphere to be sampled beforehand, the time between samples will usually have to be determined in the field.

d. Indications

Portable GCs find their most common use as a tool for the gathering of concentration data during industrial hygiene surveys. They may also be used for real time monitoring of leaks, spills, etc., in order to make a judgment as to whether or not a dangerous concentration may have been reached. Some instruments with microprocessor-controlled acquisition and storage of data may be used to assess trends over extended periods. An important consideration, however, is that portable GCs should not, in general, be used for compliance measurements, nor are they meant as substitutes for the usual analytical methods used for determination of exposure such as those in this Manual. There are basically two reasons for this. First, there is no provision for unequivocally identifying a peak obtained, such as could be done in the laboratory using a GC/mass spectrometer system, and second because the separation step in the portable GC is not, as explained previously, as efficient as that obtainable with a laboratory analytical instrument. It is equally important to point out that the field measurement is inherently much simpler and does not have the problems with incomplete adsorption and desorption, sample storage instability, migration, and breakthrough which some of the compliance methods have. Thus while the field measurement is less exact than would be the case with a laboratory measurement, the overall field sampling and measurement process may be, in fact, more exact.

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NIOSH MANUAL OF ANALYTICAL METHODS

4th EDITION

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A - D

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ACETALDEHYDE by GC 2538

CH_3CHO MW: 44.05 CAS: 75-07-0 RTECS: AB1925000

METHOD: 2538, Issue 1 **EVALUATION: UNRATED** **Issue 1: 15 August 1994**

OSHA : 200 ppm
NIOSH: carcinogen; lowest feasible level
ACGIH: C 25 ppm; suspect carcinogen
(1 ppm = 1.801 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C; BP 20.4 °C; VP 100 kPa (750 mm Hg) @ 20 °C; explosive range 4 to 60% v/v in air

SYNONYMS: acetic aldehyde; ethanal.

SAMPLING

SAMPLER: SOLID SORBENT TUBE [2-(hydroxymethyl)piperidine (2-HMP) on XAD-2, 450 mg/225 mg]

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovery after 21 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 180 to 720 mg/m^3 [2] (3-L samples)

BIAS: 0.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.12 [2]

ACCURACY: ± 23.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of acetaldehyde

DESORPTION: 5 mL toluene, 60 min ultrasonic

INJECTION VOLUME: 1 µL, splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C 1 min; 6 °C/min to 110 °C (hold 2 min) 30 °C/min to 260 °C (hold 1 min)

CARRIER GAS: He, 1 mL/min; makeup 29 mL/min

COLUMN: wide-bore, fused-silica capillary, 15 m x 0.32-mm; 1-µm DB-1301 film

CALIBRATION: standard solutions of acetaldehyde on coated sorbent

RANGE: 4 to 2200 µg per sample [2]

ESTIMATED LOD: 2 µg per sample [1, 2]

PRECISION ($\bar{S}_r$): 0.090 @ 26 to 107 µg per sample [1]

APPLICABILITY: The working range is 0.74 to 407 ppm (1.3 to 730 mg/m^3) for a 3-L air sample.

INTERFERENCES: None identified. An alternative chromatographic column is a 2 m x 6-mm OD x 2-mm ID glass column containing 10% UCON 50-HB-5100 + 2% KOH on 80/100 Chromosorb W-AW.

OTHER METHODS: This is an adaptation of OSHA Method 68 [1], and is a convenient alternative to Method 3507.

REAGENTS:

1. Toluene, chromatographic quality, containing 0.02% (v/v) dimethylformamide or other suitable internal standard.
2. Acetaldehyde*, high-purity. Store in freezer at ca. −20 °C.
3. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
4. Calibration stock solution, 31.2 mg/mL. (APPENDIX A)
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing two sections of 40/60 mesh 2-(hydroxymethyl) piperidine coated on XAD-2 and separated by 2-mm glass-wool plug (front = 450 mg; back = 225 mg). Tubes are commercially available (Supelco, Inc. ORBO-25 or equivalent), or may be prepared (see APPENDIX B).
2. Personal sampling pump, 0.01 to 0.05 L/min. with flexible connecting tubing.
3. Gas chromatograph, capillary column, FID, integrator (page 2538-1).
4. Vials, 7-mL, glass, with PTFE-lined screw caps.
5. Ultrasonic bath or mechanical shaker.
6. Pipets, volumetric, 1- and 5-mL with pipet bulb.
7. Flasks, volumetric, 10- and 25-mL.
8. Syringe, 10 μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Acetaldehyde is toxic if inhaled or if it comes in contact with the eyes or skin [3], and is an animal carcinogen [4]. Exercise appropriate precautions in handling this chemical.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 12 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place front section and front glass-wool plug of the sampler in a vial. Place back section and center glass-wool plug in a separate vial. Discard rear glass-wool plug.
6. Add 5.0 mL to toluene to each vial. Cap each vial tightly.
7. Agitate in an ultrasonic batch for 60 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Place 450-mg portions of coated XAD-2 sorbent, from the same lot as used to collect the air samples, into vials.
   b. Inject known volumes of calibration stock solution or a serial dilution thereof onto the sorbent to obtain acetaldehyde working standards in the range 2 to 2200 μg. Cap vials.
      NOTE: Prepare working standards ca. 16 h before air samples are to be analyzed to ensure that the reaction between acetaldehyde and 2-HMP is complete.
   c. Prepare three media blanks.
   d. Desorb (steps 5 through 7) and analyze (steps 10 and 11) the working standards and media blanks along with the samples and field blanks.

e. Prepare calibration graph, ratio of peak area of analyte/peak area of internal Standard vs. μg acetaldehyde.

9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.
   NOTE: A desorption efficiency study is not usually necessary since standards are prepared on the coated sorbent.

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2538-1. Set air and hydrogen flows on the flame ionization detector to manufacturer's specifications. Inject 1-μL sample aliquot via the splitless injection technique. Retention time = 6.8 min for acetaldehyde under these conditions.
11. Measure peak area. Divide the peak area of analyte by the peak area of the internal standard on the same chromatogram.

CALCULATIONS:

12. Determine the mass, μg, of acetaldehyde found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE 1: If $W_b > W_f/10$, report breakthrough and possible sample loss.
    NOTE 2: Under these conditions, there is typically no detectable acetaldehyde blank level.
13. Calculate concentration, C, of acetaldehyde in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was originally developed and fully validated by OSHA [2] over the range 180 to 720 mg/m^3 per sample. A storage study was done by spiking commercially-available tubes with standard solutions of acetaldehyde [1]. Recovery (26.8 and 107 μg/sample) was 100% after 21 days of refrigerated storage. A migration study was also performed at the above concentrations. After 21 days refrigerated storage, no acetaldehyde was detected on the back sections of the samples. Additional evaluation information is available [2]. Field samples of acetaldehyde were also successfully analyzed by utilizing this method [1]. This method has not been evaluated by NIOSH, except for the storage and migration studies.

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METHOD REVISED BY:

Karen J. Williams.

APPENDIX A: PREPARATION OF CALIBRATION STOCK SOLUTION

Prepare by diluting a known amount of acetaldehyde with toluene:

a. Determine the weight of a sealed 25-mL volumetric flask containing approximately 15 mL of toluene.
b. Place the sealed volumetric flask and a 1-mL pipet in the same freezer used to store the acetaldehyde.
c. After 30 minutes, remove the sealed volumetric flask, 1-mL pipet and the acetaldehyde.
d. Immediately pipet 1.0 mL of acetaldehyde into the cold flask, reseal the flask and allow it to warm to room temperature.
e. Reweigh the flask and subtract the tare weight from the weight of the reweighed flask to determine the weight of acetaldehyde added.
f. Dilute the contents of the flask to the mark with toluene.
g. Store the stock standards in a freezer. Prepare fresh stock standards every 10 days.

APPENDIX B: PREPARATION OF XAD-2 SORBENT COATED WITH 2-HMP

Weigh 125 g of crude XAD-2 adsorbent into a 1-L Erlenmeyer flask. Add about 200 mL of water to the flask and then swirl the mixture to wash the adsorbent. Discard any adsorbent that floats to the top of the water and then filter the mixture using a fritted Buchner funnel. Transfer the adsorbent back to the Erlenmeyer flask and repeat the water wash and the filtration. Air-dry the adsorbent for about 2 min. Transfer the adsorbent back to the Erlenmeyer flask and then add about 200 mL methanol to the flask. Swirl and filter the mixture as before. Transfer the washed adsorbent to a 1-L evaporative flask and remove the methanol using rotary evaporation. Cool the flask to room temperature and add 13 g of 2-HMP and 200 mL of toluene to the flask. Swirl the mixture and then allow it to stand for an hour. Remove the toluene using rotary evaporation. Seal the flask and allow the coated adsorbent to stand overnight at ambient temperature.

Transfer the coated adsorbent to a Soxhlet extractor. Extract the material with toluene for about 24 hours. Replace the contaminated toluene with fresh toluene and continue the extraction for an additional 24 hours. Replace the second aliquot of contaminated toluene with methanol and continue the Soxhlet extraction for 4 hours. Transfer the adsorbent to a weighed 1-L, round-bottomed, evaporative flask and remove the methanol using the rotary evaporation apparatus. Determine the weight of the adsorbent and then add an amount of 2-HMP, which is 10%, by weight, of the adsorbent. Add 200 mL toluene and swirl the mixture. Allow the flask to stand for 1 hour. Remove the toluene using rotary evaporation. If the last traces of toluene are difficult to remove, add about 100 mL of methanol to the flask, swirl the mixture and then remove the solvents using rotary evaporation.

XAD-2 adsorbent treated in this manner will often contain residual formaldehyde derivative levels of about 0.1 μg/150 mg of adsorbent. The formaldehyde blank level and potential acrolein and acetaldehyde chromatographic interferences should be determined at this time. If the formaldehyde blank and/or any interference is determined to be too high, return the lot to the Soxhlet extractor, extract with toluene again and recoat with 2-HMP. This process can be repeated until an acceptable blank and/or level of chromatographic interferences is attained.

The coated adsorbent is now ready to be packed into sampling tubes. The sampling tubes should be stored in the dark and separated by lot number. A sufficient amount of each lot of coated adsorbent should be retained to prepare analytical standards for use with air samples from that lot number.

ACETALDEHYDE by HPLC 3507

CH_3CHO MW: 44.05 CAS: 75-07-0 RTECS: AB1925000

METHOD: 3507, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: carcinogen; lowest feasible
ACGIH: C 25 ppm; suspect carcinogen
(1 ppm = 1.801 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C;
BP 20.4 °C; MP −123 °C;
VP 100 kPa (750 mm Hg; 99% v/v)
@ 20 °C; explosive range 4 to 60% in air

SYNONYMS: ethanal; acetic aldehyde.

SAMPLING		MEASUREMENT	
SAMPLER:	LIQUID IN BUBBLER (midget bubbler containing 15 mL Girard T solution @ pH 4.5)	**TECHNIQUE:**	HPLC, UV
		ANALYTE:	Girard T derivative
FLOW RATE:	0.1 to 0.5 L/min	**SAMPLE PREPARATION:**	dilute 5 mL sample to 100 mL with HPLC mobile phase
VOL-MIN:	6 L @ 200 ppm		
-MAX:	60 L	**INJECTION VOLUME:**	50 µL
SHIPMENT:	seal bubblers to prevent leakage before shipping; protect from light	**COLUMN:**	50 cm x 2-mm ID SS, Zipax SCX
		DETECTOR:	UV @ 245 nm for acetaldehyde
SAMPLE STABILITY:	1 week @ 25 °C in dark [1]	**MOBILE PHASE:**	HPO_4^{2-}/HPO_4^- buffer, 0.75 mL/min
FIELD BLANKS:	2 to 10 field blanks per set	**CALIBRATION:**	standard solutions of acetaldehyde in Girard T reagent
		RANGE:	2 to 60 mg per sample [1]
ACCURACY		**ESTIMATED LOD:**	0.1 mg per sample [1]
RANGE STUDIED:	170 to 670 mg/m^3 [1] (60-L samples)	**PRECISION ($\bar{S}_r$):**	0.024 @ 11 to 43 mg per sample [1]
BIAS:	1.2%		
OVERALL PRECISION ($\hat{S}_{rT}$):	0.053 [1]		
ACCURACY:	± 14.4%		

APPLICABILITY: The working range is 18 to 372 ppm (33 to 670 mg/m^3) for a 60-L air sample. The method is sensitive enough for short-term exposure sampling and can be used to measure lower concentrations by diluting samples to less than the recommended 100 mL.

INTERFERENCES: Other volatile aldehydes and ketones (e.g., acetone, acrolein, benzaldehyde, formaldehyde, furfural, methyl ethyl ketone, and propionaldehyde) compete for the Girard T reagent which should be kept at a two-fold molar excess over aldehyde concentration. Chromatographic conditions may be adjusted to resolve acetaldehyde from other aldehydes [1].

OTHER METHODS: This revises S345 [2]. Method 2538 is an adaptation of OSHA Method 68, which uses solid sorbent collection and GC analysis. Other reported methods for acetaldehyde use collection in 2,4-dinitrophenylhydrazine solution [3,4].

REAGENTS:

1. Acetaldehyde.*
2. Citric acid.
3. Disodium hydrogen phosphate (Na_2HPO_4).
4. Girard T reagent [(carboxymethyl)-trimethylammonium chloride hydrazide] recrystallized from 95% ethanol.
5. Water, distilled, deionized (DD).
6. Ethanol, 95%.
7. Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$).
8. Girard T solution: 5.39 g citric acid, 6.63 g Na_2HPO_4, and 16.77 g Girard T reagent diluted to 500 mL with DD water. Store in annealed flask in the dark. Use within two weeks.
9. HPLC mobile phase: 0.22 M $Na_2HPO_4 \cdot H_2O$, 0.019 M $NaH_2PO_4 \cdot H_2O$ in 20% ethanol. Dissolve and dilute 31.2 g Na_2HPO_4 and 26.2 g $NaH_2PO_4 \cdot H_2O$ to 1 L with DD water. Filter through 5-μm PTFE filter and degas prior to use. Bubble helium through the solution to prevent bacterial growth.
10. Calibration stock solution, 4.32 mg/mL acetaldehyde in 0.2 M Girard T solution. Weight 216 mg freshly-distilled acetaldehyde into 50-mL volumetric flask containing 49 mL Girard T solution. Make to volume with Girard T solution. Use within one day.
11. Helium.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: bubbler, glass, midget, with fritted glass stems, annealed,* with PTFE stoppers for shipping.
2. Personal sampling pump, 0.1 to 0.5 L/min, with trap made from midget bubbler with stem broken off and inert, flexible connecting tubing.
3. High pressure liquid chromatograph, with 245-nm UV detector, integrator, and column (page 3507-1) with 50-μL injection loop or autosampler.
4. Syringe, 2-mL, Luer-lock.
5. Distillation apparatus for preparation of high purity acetaldehyde.
6. Flasks, volumetric, 1-L; 10-, 50-, and 100-mL; and 500-mL, annealed.*
7. Pipets, 0.02- to 1-mL; 5-, 10-, and 15-mL.
8. Marker, glass.
9. Cylinder, graduated, 250-mL.
10. Filter, 5-μm, PTFE, 37-mm, with holder for liquid filtration.
11. Balance, readable to 0.1 mg.

* Heat in an oxidizing atmosphere at 580 °C.

SPECIAL PRECAUTIONS: Acetaldehyde is extremely volatile and a fire hazard. Cool containers of acetaldehyde to ice bath temperature to reduce pressure buildup and open in an exhaust hood only.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler and trap in line.
2. Add exactly 15 mL Girard T solution to each bubbler using a 15-mL pipet. Mark the initial liquid level in the bubbler with a glass marker. Make impinger-to-trap and trap-to-sampling pump connections with flexible inert tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 6 to 60 L.

   NOTE: Higher flow rates will cause frothing of the collection medium. If amount of liquid condensed in the trap is greater than 1 mL, collection efficiency of bubbler may be reduced and sample may be invalid.

SAMPLE PREPARATION:

4. Tap bubbler stem lightly against bubbler body to drain contents into the body. If necessary, bring samples up to the 15-mL mark with distilled water. Swirl bubbler to mix contents well. Do not add solution collected in the trap to the sample.

5. Transfer a 5-mL aliquot to a 100-mL flask and bring to volume with HPLC mobile phase.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.007 to 4 mg acetaldehyde per mL (0.1 to 60 mg acetaldehyde per sample).
   a. Add known amounts of calibration stock solution to Girard T solution in 10-mL volumetric flasks and dilute to the mark. Dilute 5 mL of each of these solutions to 100 mL with HPLC mobile phase. Prepare at least two blanks in the same manner.
   b. Analyze together with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (peak area vs. mg acetaldehyde per sample).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

8. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2507-1. Inject 50-μL sample aliquot with injection loop or autosampler.
   NOTE: If peak area is above the linear range of the working standards, dilute with HPLC mobile phase, reanalyze, and apply the appropriate dilution factor in calculations.
9. Measure peak area.

CALCULATIONS:

10. Determine the mass, mg of acetaldehyde found in the sample (W), and in the average media blank (B).
11. Calculate concentration, C, of acetaldehyde in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S345 was issued on March 16, 1979 [2], and validated over the range 170 to 670 mg/m^3 at 21 °C and 756 mm Hg using a 60-L sample [1,5]. Overall precision, $\hat{S}_{rT}$, was 0.053 with an average recovery of 101.2% representing a non-significant bias. The concentration of acetaldehyde was independently verified by calibrated gas chromatograph. Collection efficiency of a single bubbler was determined to be >0.998 when 61-L air samples were taken at 0.5 L/min in atmospheres containing 670 mg/m^3 acetaldehyde.

REFERENCES:

[1] Backup Data Report, S345, Acetaldehyde, prepared under NIOSH Contract 210-76-0123 (unpublished).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S345, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Kuwata, K., M. Uebori and Y. Yamasaki. J. Chromatog. Sci., 17, 264-268 (1979).
[4] Lipari, F. and S.J. Swarin. J. Chromatog., 247, 297-306 (1982).

[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE; Method S345 was validated under NIOSH Contract 210-76-0123.

ACETIC ACID 1603

CH_3COOH MW: 60.05 CAS: 64-19-7 RTECS: AF1225000

METHOD: 1603, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm
NIOSH: 10 ppm; STEL 15 ppm
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 2.46 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.049 g/mL @ 25 °C;
BP 118 °C; MP 17 °C;
VP 1.5 kPa (11.4 mm Hg) @ 20 °C;
explosive range 5.4 to 16% v/v in air

SYNONYMS: glacial acetic acid; methane carboxylic acid; ethanoic acid

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 20 L @ 10 ppm
-MAX: 300 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 12.5 to 50 mg/m^3 [1] (173-L samples)

BIAS: 5.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.058 [1]

ACCURACY: ± 15.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acetic acid

DESORPTION: 1 mL formic acid; stand 60 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 230 °C
-COLUMN: 130 to 180 °C, 10°/min or 100 °C isothermal

CARRIER GASES: N_2 or He, 60 mL/min

COLUMN: 1 m x 4-mm ID glass; Carbopack B 60/80 mesh/3% Carbowax 20M/0.5% H_3PO_4

CALIBRATION: standard solutions of acetic acid in 88 to 95% formic acid

RANGE: 0.5 to 10 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.007 @ 0.3 to 5 mg per sample [1,3]

APPLICABILITY: The working range is 2 to 40 ppm (5 to 100 mg/m^3) for a 100-L air sample. High (90% RH) humidity during sampling did not cause breakthrough at 39 mg/m^3 for 4.6 hrs [1].

INTERFERENCES: Formic acid contains a small amount of acetic acid which gives a significant blank value. High-purity formic acid must be used to achieve an acceptable detection limit. Alternate columns are 3-m glass, 2-mm ID, 0.3% SP-1000 + 0.3% H_3PO_4 on Carbopack A and 2.4-m x 2-mm ID glass, 0.3% Carbowax 20M/0.1% H_3PO_4 on Carbopack C.

OTHER METHODS: This revises Method S169 [3].

REAGENTS:

1. Formic acid, aqueous 88% to 95%, high-purity (<0.02% acetic acid).*
   NOTE: The acetic acid content varies from lot to lot of formic acid. Test each lot before use.
2. Glacial acetic acid, reagent grade.*
3. Propionic acid, reagent grade.
4. Eluent: Formic acid, 88% to 95%, with 0.1% v/v propionic acid or other suitable internal standard.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube with plastic caps, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 1603-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Care should be taken to avoid skin contact with formic acid and/or acetic acid. These reagents may cause severe burns.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 20 to 300 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 10 mg acetic acid per sample.
   a. Add known amounts of acetic acid to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg acetic acid).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of acetic acid directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg acetic acid recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1603-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with formic acid, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acetic acid found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acetic acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S169 was issued on May 13, 1977 [3], and validated over the range 12.5 to 50 mg/m^3 at 22 °C and 767 mm Hg using a 173-L sample [1,4]. Overall precision, $\hat{S}_{rT}$, was 0.058 with an average recovery of 105.4%, representing a non-significant bias. The concentration of acetic acid was independently verified by a total hydrogen analyzer. Desorption efficiency was 0.96 in the range 2.1 to 8.4 mg per sample. Breakthrough (5% on back section) was never achieved and testing was discontinued after 4.6 hrs when 10.4 mg of acetic acid was collected without breakthrough for a 269-L sample at 90% RH. A user check gave an estimated LOD of 0.01 mg per sample and a desorption efficiency of 1.01 in the range 0.3 to 5 mg per sample [2].

REFERENCES:

[1] Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods," Order No. PB 275-834 from NTIS, Springfield, VA 22161.
[2] User check, UBTL, NIOSH Sequence #4213-K (unpublished, January 31, 1984).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, S169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon, NIOSH/DPSE; S169 originally validated under NIOSH Contract CDC-210-76-0123.

ACETIC ANHYDRIDE 3506

$(CH_3CO)_2O$ MW: 102.09 CAS: 108-24-7 RTECS: AK1925000

METHOD: 3506, Issue 2 **EVALUATION: FULL** **Issue 1: 5 May 1985**
Issue 2: 15 August 1994

OSHA : 5 ppm
NIOSH: C 5 ppm
ACGIH: C 5 ppm
(1 ppm = 4.17 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.080 g/mL @ 15 °C;
BP 139 °C; MP −73 °C;
VP 4 mm Hg @ 20 °C;
explosive range 2.9 to 10.3% v/v in air

SYNONYMS: acetic acid anhydride; acetyl oxide

SAMPLING

SAMPLER:	LIQUID IN BUBBLER (mixed bubbler with 10 mL alkaline hydroxylamine)
FLOW RATE:	0.2 to 1.0 L/min
VOL-MIN:	25 L
-MAX:	100 L
SHIPMENT:	hand delivery or special bubbler cases
SAMPLE STABILITY:	≥ 4 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	9.35 to 37.4 mg/m^3 [1] (100-L samples)
BIAS:	4.9%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.060 [1]
ACCURACY:	± 15.3%

MEASUREMENT

TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
ANALYTE:	acetic anhydride-hydroxylamine-ferric chloride complex
FINAL VOLUME:	50 mL
WAVELENGTH:	540 nm
CALIBRATION:	complexed acetic anhydride standards
RANGE:	0.5 to 4 mg acetic anhydride per sample [2]
ESTIMATED LOD:	0.05 mg acetic anhydride per sample
PRECISION ($\bar{S}_r$):	0.021 @ 1 to 4 mg acetic anhydride per sample [1]

APPLICABILITY: The working range is 1.2 to 10 ppm (5 to 40 mg/m^3) for a 100-L air sample. The upper limit of the range may be extended by diluting the sample with the collection medium prior to color development. The method is sensitive enough for short-term (>5 min) determinations if a 5-cm or longer cuvette is used.

INTERFERENCES: Any substance containing a hydrolyzable carbonyl group, such as esters, acid chlorides, and aldehydes, is an interference. The most likely interference to coexist with acetic anhydride in air is ketene [2,3].

OTHER METHODS: This revises Method S170 [2].

REAGENTS:

1. Hydroxylamine hydrochloride solution. Dilute 200 g $(NH_3OH)Cl$ to 1 L with distilled water in a volumetric flask. Refrigerate in a light-protected container. Discard after two weeks.
2. Sodium hydroxide solution. Dissolve 200 g in distilled water. Cool and bring to volume in a 1-L volumetric flask with distilled water. Store in a polyethylene bottle.
3. Absorbing solution (needed for sampler). Mix equal volumes of the hydroxylamine hydrochloride and sodium hydroxide solutions just prior to use. Do not use after 2 h.
4. HCl:water, 1:1 (v/v). Mix equal volumes of conc. HCl and distilled water.
5. Ferric chloride solution. Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in a 1-L volumetric flask with 1:1 (v/v) HCl:water. Dilute to volume with this mixture.
6. Acetone.
7. Acetic anhydride calibration stock solution. Pipet 10 mL acetic anhydride* into a 100-mL volumetric flask. Make to volume with acetone. The solution must be used within 2 h of preparation.

* See Special Precautions

EQUIPMENT:

1. Sampler: bubbler, standard midget glass, stem containing fritted end with porosity ca. 170 to 220 mm maximum pore diameter with hard, non-reactive stopper (PTFE or glass).
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Splashover tube: glass tube, 5 cm long, 8-mm OD, 6-mm ID, loosely packed with glass wool.
4. Spectrophotometer reading at 540 nm with 5-cm matched cuvettes.
5. Flasks, volumetric, 1-L and 50- and 100-mL.
6. Pipets, graduated, 1-, 5- and 10-mL.
7. Micropipets, 10- to 100-μL.
8. Ice bath.

SPECIAL PRECAUTIONS: Acetic anhydride is readily combustible (flash point = 54 °C) and both the liquid and vapor produce irritation and necrosis of tissues. It may produce allergic sensitization of the skin [4].

SAMPLING:

1. Calibrate the personal sampling pump with a representative sampler in line.
2. Connect a splashover tube between the bubbler and the sampling pump with short pieces of flexible tubing. Do not allow the air being sampled to pass through any tubing or other equipment before entering the bubbler.
3. Pour 10 mL of absorbing solution into bubbler.
   NOTE: Absorbing solution must be prepared just prior to use (see REAGENTS, 3).
4. Sample at an accurately known flow rate between 0.2 and 1 L/min for a sample size of 25 to 100 L. Change sampler every 2 hrs so that the absorbing solution is fresh.
5. After sampling, remove the bubbler stem and tap gently against the inside of the bubbler tube. Wash the stem with 1 to 2 mL absorbing solution and add the wash to the bubbler.
6. Seal the bubbler tightly with a hard, non-reactive stopper and transport the samples by hand. Alternatively, transfer contents of each bubbler to a glass vial, rinsing bubbler with 1 to 2 mL absorbing solution. Cap the vial securely for shipment.

SAMPLE PREPARATION:

7. Transfer sample solution to a 50-mL volumetric flask.
8. Rinse bubbler twice with 1 mL distilled water. Add rinses to the flask.
   NOTE: For samples containing > 4 mg acetic anhydride, dilute an aliquot of the bubbler solution to 50 mL at this step. Apply the appropriate dilution factor in calculations.
9. Pipet 5 mL ferric chloride solution into the flask.
10. In an ice bath, mix equal volumes of sodium hydroxide solution, hydroxylamine hydrochloride solution and ferric chloride solution. Add this solution to bring the solution in the 50-mL volumetric flask to the mark. The purple complex is formed rapidly.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 0.05 to 4 mg acetic anhydride per sample.
    a. Pipet 10 mL absorbing solution into each of six 50-mL volumetric flasks.
    b. Transfer 0 (reagent blank), 10, 20, 40, 80 and 100 μL acetic anhydride calibration stock solution into the flasks.
    c. Add reagents (steps 9 and 10).
    d. Analyze with samples and blanks (steps 12 through 14).
    e. Construct calibration graph (absorbance vs. mg acetic anhydride).

MEASUREMENT:

12. Set spectrophotometer to read at 540 nm.
13. Adjust the baseline to zero with distilled water in both cells.
14. Read absorbance of the sample vs. reagent blank in the reference cell.

CALCULATIONS:

15. Determine the mass, mg, of acetic anhydride in the bubbler, W, and in the average media blank, B, from the calibration graph.
16. Calculate the concentration, C (mg/m^3), of acetic anhydride in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S170 was issued on August 1, 1975 [2], and validated using 100-L air samples over the range 9.35 to 37.4 mg/m^3 at 22 °C and 761 mm Hg [1]. Overall precision, $\hat{S}_{rT}$, was 0.060, with a collection efficiency of 1.00 ± 0.01. The average of concentrations obtained at 20 mg/m^3 for the overall sampling and measurement technique was 2.5% higher than the true concentrations representing a non-significant bias for a limited number of experiments [1]. Sample atmospheres were generated using the apparatus and procedure for epichlorohydrin [5] and a total hydrocarbon analyzer was used to monitor the generated vapor concentrations [1].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S170, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S170, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Diggle, W. M. and J. C. Gage. The Determination of Ketene and Acetic Anhydride in the Atmosphere, Analyst, 78, 473 (1953).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[5] Documentation of the NIOSH Validation Tests, op. cit., S118.

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE.

ACETONE

See KETONES I (Method 1300) for procedure

ACETONE CYANOHYDRIN 2506

$(CH_3)_2C(OH)CN$ MW: 85.11 CAS: 75-86-5 RTECS: OD9275000

METHOD: 2506, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: C 1 ppm/15 min
ACGIH: no TLV
(1 ppm = 3.48 mg/m^3)

PROPERTIES: liquid; d 0.932 g/mL @ 19 °C;
BP 95 °C; MP −19 °C
VP 110 Pa (0.8 mm Hg) @ 20 °C

SYNONYMS: 2-cyano-2-propanol; 2-methyllactonitrile; 2-hydroxy-2-methylpropanenitrile

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Porapak QS, 100 mg/ 50 mg)

FLOW RATE: 0.2 L/min

VOL-MIN: 0.3 L @ 1 ppm
-MAX: 12 L

SHIPMENT: in refrigerated container @ 0 °C

SAMPLE STABILITY: at least 5 days if stored at @ 0 °C immediately following collection

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.33 to 16.7 mg/m^3 [1] (3-L samples)
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	0.093 [1]
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPH, NP (THERMIONIC) DETECTOR

ANALYTE: acetone cyanohydrin

DESORPTION: 1 mL ethyl acetate; ultrasonicate 60 min

INJECTION VOLUME: 5 μL, 1 μL flush

TEMPERATURE-INJECTOR: 100 °C
-DETECTOR: 100 °C
-COLUMN: 70 °C

CARRIER GASES: N_2, 33 mL/min

COLUMN: PTFE, 2 m x 3.2-mm ID, packed with 5% OV-17 on 40/60 mesh Chromosorb T (APPENDIX)

CALIBRATION: solutions of acetone cyanohydrin in ethyl acetate

RANGE: 1 to 50 μg per sample

ESTIMATED LOD: 0.1 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.042 [1]

APPLICABILITY: The working range is 0.1 to 4.8 ppm (0.33 to 17 mg/m^3) for a 3-L air sample. However, coadsorbed water vapor will decompose the analyte unless the samples are refrigerated immediately after collection.

INTERFERENCES: Acetone, methyl methacrylate and methanol do not interfere with the analysis. Methacrylamide does not elute from the column under the conditions given above. The gas chromatograph must be modified to eliminate contact of analyte with heated glass or metal surfaces.

OTHER METHODS: This method was originally designated P&CAM 340 [2].

REAGENTS:

1. Desiccant, bagged, for field use.
2. Acetone cyanohydrin, 98% or better.*
3. Ethyl acetate, chromatographic quality.
4. Silicone oil (OV-17).
5. Coated Chromosorb-T, 40/60 mesh, for GC stationary phase (APPENDIX).
6. Calibration stock solution, ca. 1.8 mg/mL. Inject 2.0 μL acetone cyanohydrin into 1.0 mL ethyl acetate. Compute the actual concentration from analyte density.
7. Nitrogen, purified.
8. Hydrogen, purified.
9. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; two sections (front = 100 mg; back = 50 mg) of pre-extracted 50/80 mesh Porapak QS held in place and separated by silanized glass wool plugs. Tubes are commercially available (SKC, Inc. #226-59-09, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, NPD, integrator and column (page 2506-1 and APPENDIX).
5. Vials, 2-mL, glass, PTFE-lined crimp caps.
6. Ultrasonic bath, water.
7. Syringe, 10-μL, readable to 0.1 μL.
8. Pipet, 1-mL, with pipet bulb.
9. Spatula.

SPECIAL PRECAUTIONS: Acetone cyanohydrin is extremely toxic; it is readily decomposed by water to form hydrogen cyanide and acetone. Perform all work with the analyte in a hood. Avoid dermal contact with acetone cyanohydrin. It is readily absorbed through the skin and will decompose in the body, with release of HCN, to induce cyanosis [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size between 0.3 and 12 L.
4. Cap the samplers with PTFE tape and plastic (not rubber) caps. Pack the samplers in a plastic bag containing bagged refrigerant. Ship in a refrigerated container at 0 °C.

SAMPLE PREPARATION:

5. Bring the samples to room temperature before uncapping. Remove the end caps from the sorbent tube.
6. Remove the front glass wool plug. Place it in a vial along with the front (larger) sorbent section. Transfer the separating glass wool plug along with the back sorbent section to a separate vial.
7. Add 1.0 mL ethyl acetate to each vial. Attach crimp cap to each vial.
8. Agitate the samples in an ultrasonic waterbath for 60 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.1 to 50 μg acetone cyanohydrin per sample.
   a. Add aliquots of calibration stock solution or a serial dilution thereof to 1.0 mL ethyl acetate in 2-mL vials. Attach crimp cap to each vial.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area vs. μg acetone cyanohydrin).

10. Determine desorption efficiency (DE) at least once for each lot of samplers used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of calibration stock solution or a serial dilution thereof directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze together with working standards and blanks (steps 12 and 13).
    e. Prepare a graph of DE vs. μg acetone cyanohydrin recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2506-1. Inject sample aliquot manually using solvent flush technique, or auto sampler. t_r = 3.2 min under these conditions.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the sample solution with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of acetone cyanohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of acetone cyanohydrin in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD [1]:

Calibration curve: Over the range 2.5 to 250 ng acetone cyanohydrin injected (0.5 to 50 μg per sample), the correlation coefficients of NPD response with mass injected ranged from 0.998 to 0.999 for peak height and from 0.990 to 0.996 for peak area.

Recovery of spiked samples after storage for one week at room temperature was ≥98% over the range 0.5 to 50 μg per sample. Independent verification of sample concentrations generated dynamically was not possible. The method was evaluated by evaporating 1, 10 or 50 μg of analyte from U-tubes onto the sorbent tube. Three liters of humid air (RH = 80%) were then drawn through the tube at 0.2 L/min for 15 min. Two sets of six samples at each level were generated. One set of six samples at each level were stored for one day at room temperature. The other sample sets were stored for five to seven days at 0 °C. Recovery was ≥ 89% (s_r = 10.6%). Experiments also showed that storage of 1 or 10 μg samples collected as above, but stored at ambient temperature for four days, gave recoveries of 62 to 80%.

A maximum of 2% mass breakthrough to the backup section was obtained when 10 to 100 μg aliquots of analyte were evaporated from U-tubes into a stream of humidified air (RH = 80%) onto the sorbent at 0.2 L/min for 60 min. Recovery from the primary sorbent section for all samples was ≥ 92%.

REFERENCES:

[1] Glaser, R. and P. Fey. Development of a Quantitative Sampling and Analytical Method for Acetone Cyanohydrin in Air (1981), available as Order No. PB 83-139-444 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 340, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-141 (1981).
[3] Criteria for a Recommended Standard...Occupational Exposure to Nitriles, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-212 (1978).

METHOD WRITTEN BY:

Robert Glaser, NIOSH/DPSE.

APPENDIX: COLUMN PREPARATION AND GC MODIFICATION

1. Stationary phase preparation:

   Weigh 10 g Chromosorb T into a glass Petri dish or small bowl. Dissolve 0.5 g OV-17 in 50 mL acetone; pour this solution over the Chromosorb T. Using a small spatula, slowly stir the stationary phase into the solution while evaporating the solvent away under a stream of nitrogen. Avoid crushing the soft Chromosorb T. A portion of the coated Chromosorb T will adhere to the glass; do not attempt to recover this material. Continue to stir the support into the solution until the solvent has completely evaporated. After the solvent has evaporated, allow the coated Chromosorb T to dry completely under the nitrogen stream. Refrigerate the coated Chromosorb T at 0 °C until it is packed into the GC column.

2. Column preparation, GC modification:

   Although the column dimensions are 2 m long x 3.2-mm ID, a longer piece of PTFE tubing (2.3 m) should be used in order to allow fitting to the chromatograph. Measure the length of the injector zone from the injector port to the point of column attachment in the oven. Push a plug of silanized glass wool this distance (about 10 to 20 cm) into the front (injector) end of the column. Add the packing material from the other end of the column under vacuum to a point about 1 cm before the detector end of the column. A 2-m column requires ca. 5 g of packing material. Seal the detector end of the column with a 0.5-cm plug of silanized glass wool. If it is necessary to replace transfer lines (see below), do not fill the column completely; leave about 1 cm open at the detector end after insertion of the glass wool. Use plastic (nylon, PTFE, etc.) compression fittings to connect the column to the instrument. Slide the injection port compression fittings onto the column directly over the silanized glass wool plug. Remove the septum retainer fitting, the septum, and the injector liner from the GC injection port. Push the empty end of the column through the oven side of the injection port to the point where it is just flush with the external port opening. If the column is made from thin-walled PTFE tubing, do not tighten the compression fitting over the soft column packing; otherwise, the Chromosorb T may be crushed and a plug may develop that will block carrier flow. Trim any column overhang away from the outer edge of the injection port. It may be necessary to slide a small piece of oversize glass or PTFE tubing over the column into the injection port in order to center the column with the septum retainer fitting. Be careful not to block any holes drilled in the port for carrier flow. Gently tighten the compression fitting around the column over the glass wool plug. Replace the septum and septum retainer fitting.

Because the analyte is thermally labile, it must not contact hot metallic or glass surfaces in the gas chromatograph. To eliminate this contact, push the end of the column into the detector port up to the detector itself. If the design of the instrument does not permit the column to be pushed up to the detector, the transfer line from the end of the column to the detector must be replaced with low dead-volume PTFE tubing. Use a 1.6-mm ID x 3.2-mm OD x 1 cm long PTFE plug to seal the detector end of the column. Determine the length of transfer line needed from the column end fitting to the bottom of the detector jet. Force a piece of 1.6-mm OD PTFE tubing equal to this length plus the length of the PTFE plug, through the center to the back end of the plug. Insert the PTFE plug, back end first, into the opening at the detector end of the column. Push the compression fitting over the column where the PTFE plug was inserted. Attach the column to the chromatograph, pushing the transfer line as close as possible to the bottom of the detector jet. Gently tighten the compression fitting around the column. Once the column has been installed in the instrument, pressurize it with nitrogen. Check the column for a flow of 33 mL/min. Check the compression fittings for leaks; gently tighten them as necessary. After it has been determined that there is flow through the column, condition it at 125 °C for 1 to 2 hrs. A diagram of a column where the transfer line has been replaced is shown in Figure 1.

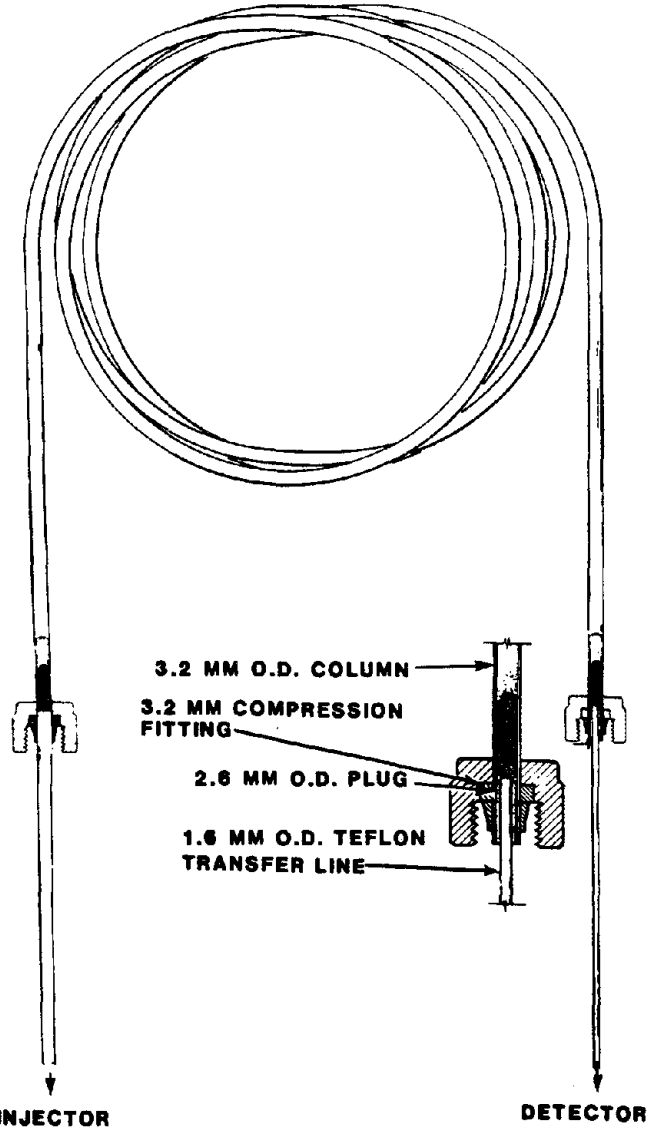

Figure 1. All-PTFE gas chromatograph system used for the determination of acetone cyanohydrin.

ACETONITRILE

CH_3CN MW: 41.06 CAS: 75-05-8 RTECS: AL7700000

METHOD: 1606, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 40 ppm
NIOSH: 20 ppm
ACGIH: 40 ppm, STEL 60 ppm
(1.0 ppm = 1.68 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.783 g/mL @ 20 °C; BP 82 °C; VP 12 kPa (89 mm Hg; 12% v/v) @ 25 °C explosive range 4.4 to 16% v/v in air

SYNONYMS: methyl cyanide; cyanomethane; ACN.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L @ 40 ppm
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 31.4 to 140.2 mg/m^3 [1] (10-L samples)

BIAS: 4.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.072 [1]

ACCURACY: ± 15.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acetonitrile

EXTRACTION: 5 mL benzene; stand 30 min

INJECTION VOLUME: 5.0 µL

TEMPERATURE-INJECTOR: 270 °C
-DETECTOR: 285 °C
-COLUMN: 180 °C

CARRIER GAS: N_2 or He, 50 mL/min

COLUMN: stainless steel, 1.2 m x 8-mm O.D., packed with 50/80 mesh Porapak Q

CALIBRATION: solutions of acetonitrile in benzene

RANGE: 0.2 to 2 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.047 [1]

APPLICABILITY: The working range is 12 to 120 ppm (20 to 200 mg/m^3) for a 10-L air sample. Large (400 mg/200 mg) charcoal tubes are necessary for collection of the analyte since breakthrough volume is low with smaller charcoal tubes. The method was used in a NIOSH health hazard evaluation where an estimated limit of detection of 0.01 mg per sample was reported [2]. The capacity of the charcoal for the analyte has not been determined under conditions of high relative humidity [1].

INTERFERENCES: None identified.

OTHER METHODS: This is Method S165 [3] in a revised format.

REAGENTS:

1. Acetonitrile, chromatographic quality.
2. Benzene, chromatographic quality.*
3. Calibration stock solution, 70 mg/mL. Add 700 mg (0.894 mL) acetonitrile to a 10-mL volumetric flask. Dilute to the mark with benzene.*
4. Nitrogen, purified.
5. Hydrogen, pre-purified.
6. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 9.0 cm long, 8 mm OD, 6-mm ID; two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 400 mg, back = 200 mg), separated by a 3-mm section of urethane foam and held in place with plugs of silanized glass wool, flame-sealed at both ends; plastic caps for tube. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1606-1).
4. Vials, glass, 10-mL, PTFE-lined crimp caps.
5. Syringes, 10- to 50-μL, readable to 0.1 μL; 1.0-mL, readable to 0.01 mL.
6. Volumetric flasks, 10-mL
7. Pipets, delivery-type, 5.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen. Perform all work with this solvent in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 5.0 mL benzene to each vial. Attach crimp cap to each vial.
   NOTE: If desorption efficiency is acceptable, toluene may be substituted for benzene.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 2 mg acetonitrile per sample.
   a. Add known amounts of calibration stock solution to benzene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg acetonitrile).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg acetonitrile recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1606-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with benzene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of acetonitrile found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acetonitrile in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S165 was issued on August 1, 1975 [3]. Synthetic atmospheres of the analyte in dry air were generated dynamically at 22 °C and 762 torr by the vapor pressure saturation/air dilution technique [1]. The concentrations ranged from 31.4 to 140.2 mg/m^3; these were verified by total hydrocarbon analyzer. Mean recovery was 105%. Breakthrough of the 400-mg front sorbent section occurred after sampling 140 mg/m^3 for 190 min at 0.196 L/min (37.2 L). The desorption efficiency, over the range 0.346 to 1.383 mg per sample, averaged 81%. A DE correction factor was used to compute the total recovery of the collected samples. Recovery of the analyte after long-term storage on the sorbent was not evaluated.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S165, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Health Hazard Evaluation Report HHE 81-359-1058 (1981).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S165, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

Robert Glaser, NIOSH/DPSE; S165 originally validated under NIOSH Contract CDC-99-74-45.

(1) HF; (2) HCl; (3) H_3PO_4; (4) HBr; (5) HNO_3; (6) H_2SO_4 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 7903, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) hydrofluoric acid; hydrogen fluoride
(2) hydrochloric acid; hydrogen chloride
(3) phosphoric acid; ortho-phosphoric acid; meta-phosphoric acid
(4) hydrobromic acid; hydrogen bromide
(5) nitric acid; aqua fortis
(6) sulfuric acid; oil of vitriol

SAMPLING

SAMPLER: SOLID SORBENT TUBE (washed silica gel, 400 mg/200 mg with glass fiber filter plug)

FLOW RATE: 0.2 to 0.5 L/min

VOL-MIN: 3 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 21 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 12 to ± 23%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: F^-, Cl^-, PO_4^{3-}, Br^-, NO_3^-, SO_4^{2-}

DESORPTION: 10 mL 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3

INJECTION LOOP VOLUME: 50 µL

ELUENT: 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3; 3 mL/min

COLUMNS: HPIC-AS4A anion separator, HPIC-AG4A guard, anion micro membrane suppressor [2]

CONDUCTIVITY SETTING: 10 µS full scale

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: see EVALUATION OF METHOD

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: The working range is ca. 0.01 to 5 mg/m³ for a 50-L air sample (see EVALUATION OF METHOD). This method measures the total concentration of six airborne anions. The corresponding acids may be collected on a single sampler and determined simultaneously. Formic acid has been determined by this method [3].

INTERFERENCES: Particulate salts of all the acids will give a positive interference. Chlorine or hypochlorite ion interfere with chloride determination and bromine interferes with bromide. Silica gel will collect ca. 30% of the free Cl_2 and Br_2 in an atmosphere [4]. Acetate, formate and propionate have elution times similar to F^- and Cl^-. If these anions are present, use a weak eluent (e.g., 5 mM $Na_2B_4O_7$) for greater resolution.

OTHER METHODS: This is P&CAM 339 in a revised format [5]. Alternate methods are 7902 for fluoride and P&CAM 268 for sulfate [6].

REAGENTS:

1. $NaHCO_3$, reagent grade.
2. Na_2CO_3, reagent grade.
3. Distilled, deionized water, filtered through 0.45-μm membrane filter.
4. Eluent: bicarbonate/carbonate buffer solution (1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3). Dissolve 0.5712 g $NaHCO_3$ and 0.7631 g Na_2CO_3 in 4 L filtered deionized water.
5. Calibration stock solutions, 1 mg/mL (as the anion). Dissolve salt in filtered deionized water.
   a. Fluoride: 0.2210 g NaF/100 mL.
   b. Chloride: 0.2103 g KCl/100 mL.
   c. Phosphate: 0.1433 g KH_2PO_4/100 mL.
   d. Bromide: 0.1288 g NaBr/100 mL.
   e. Nitrate: 0.1371 g $NaNO_3$/100 mL.
   f. Sulfate: 0.1814 g K_2SO_4/100 mL.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11 cm x 7-mm OD, containing a 400-mg front section and 200-mg backup section of washed silica gel, flame-sealed ends with plastic caps. Front section is retained with a glass fiber filter plug. Urethane plugs separate and retain the backup section. Tubes are commercially available (Supelco ORBO 53 or equivalent) or may be prepared according to APPENDIX.
2. Personal sampling pump, 0.2 to 0.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, HPIC-AG4A anion separator and HPIC-AG4A anion micro membrane suppressor, conductivity detector, integrator and strip chart recorder.
4. Waterbath: hotplate with beaker of boiling water.
5. Centrifuge tubes, 15-mL, graduated, plastic, with caps.*
6. Syringes, 10-mL, polyethylene with luer tip.
7. Filters, luer tip, with membrane filter, 13-mm, 0.8-μm pore size.
8. Micropipettes, disposable tips.
9. Volumetric flasks, 50- and 100-mL.*
10. Laboratory timer.
11. Bottles, polyethylene, 100-mL.
12. Auto sampler vials (optional).

* Thoroughly clean glassware with mild detergent, rinse thoroughly with deionized water, to minimize anion blank values.

SPECIAL PRECAUTIONS: Acids, particularly HF, are extremely corrosive to skin, eyes, and mucous membranes. HF will attack glass. Plastic labware is recommended.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.5 L/min for a total sample size of 3 to 100 L.
   NOTE: Do not exceed 0.3 L/min when sampling for HF.

SAMPLE PREPARATION:

4. Score sampler with a file in front of primary sorbent section.
5. Break sampler at score line. Transfer glass fiber filter plug and front sorbent section to a 15-mL graduated centrifuge tube.

NOTE: Particulate salts of the volatile acids (HCl, HB, HF, and HNO_3), if present in the air sample, will collect on the glass fiber filter plug. To estimate the concentration these salts, analyze the plug separately from the front sorbent section.

6. Place backup sorbent section in separate centrifuge tube. Discard urethane plugs.
7. Add 6 to 8 mL eluent to each centrifuge tube. Heat in boiling waterbath for 10 min.
   NOTE: Eluent used for desorption should be from same batch as the eluent used in the chromatograph to avoid carbonate/bicarbonate peaks near F^- and Cl^-.
8. Allow to cool, dilute to 10.0-mL volume with eluent.
9. Cap the centrifuge tube and shake vigorously.
10. Pour sample into 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards covering the range 0.001 to 0.3 mg of each anion per sample.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark.
    b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    c. Analyze working standards together with samples and blanks (steps 12 through 14).
    d. Prepare a calibration graph for each anion [peak height (mm or μS) vs. concentration (μg per sample)].

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 7903-1, according to manufacturer's instructions.
13. Inject 50-μL sample aliquot. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging system valves or columns.
14. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Determine the mass, μg, of anion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
16. Calculate concentration, C, of acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot F}{V}, \text{ mg/m}^3.$$

where: F (conversion factor from anion to acid) = 1.053 for HF; 1.028 for HCl; 1.032 for H_3PO_4; 1.012 for HBr; 1.016 for HNO_3; and 1.021 for H_2SO_4.

EVALUATION OF METHOD:

The method was evaluated for hydrochloric, hydrobromic, nitric, phosphoric and sulfuric acids by laboratory generation of mixed acids [1]. Data for the individual analytes are:

Acid	Range Studied (mg/m^3)	Range Studied (μg/sample)	(%)	Measurement Precision ($\bar{S}_r$)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)	Estimated LOD [2] (μg per sample)
HF [7]	0.35 - 6	0.5 - 200	0.7	0.053	0.116	±23.4	0.7
HCl [8]	0.14 - 14	0.5 - 200	0.3	0.025	0.059	±11.9	0.6
H_3PO_4 [1]	0.5 - 2	3 - 100	−0.9	0.029	0.096	±19.7	2.0
HBr [1]	2 - 20	3 - 960	2.0	0.056	0.074	±16.5	0.9
HNO_3 [1]	1 - 10	3 - 500	2.0	0.018	0.085	±18.7	0.7
H_2SO_4 [1]	0.5 - 2	3 - 100	2.4	0.028	0.087	±19.4	0.9

The method was field-evaluated at two electroplating facilities using side-by-side silica gel tubes and bubblers. The method was evaluated for hydrofluoric acid in 1983 using the silica gel tubes and impingers [7]. Recovery based on impinger collection was 106% with $\hat{S}_{rT}$ of 0.116. The capacity of the silica gel sampler for HF was 820 μg. This is equivalent to an 8-h sample at two to three times the OSHA PEL. Samples were stable for at least 21 days at 25 °C. Updated analytical columns have been used by NIOSH for analytical sequences [2].

REFERENCES:

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[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, P&CAM 268, U.S. Department of Health and Human Services, (NIOSH) Publication No. 82-100 (1982).

[7] Cassinelli, M. E. "Laboratory Evaluation of Silica Gel Sorbent Tubes for Sampling Hydrogen Fluoride," Am. Ind. Hyg. Assoc. J., 47(4):219-224 (1986).

[8] Cassinelli, M. E. and P. M. Eller. Ion Chromatographic Determination of Hydrogen Chloride, Abstract No. 150, American Industrial Hygiene Conference, Chicago, IL (1979).

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

APPENDIX: SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities upon analysis by ion chromatography, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7-mm OD, 4.8-mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).

TABLE 1. GENERAL INFORMATION.

Acid and M.W.	CAS RTECS	EXPOSURE LIMITS OSHA	NIOSH	ACGIH	PROPERTIES mg/m³ = 1 ppm @ NTP	Physical State	MP (°C)	BP (°C)	Sp. Gr. (liq.)	VP @ 20 °C kPa (mm Hg)
HF (20.01)	7664-39-3 MW7875000	3 ppm	3 ppm; 6 ppm STEL	C 3 ppm;	0.818	gas	-83.1	19.5	0.987	>101 (>760)
HCl (36.46)	7647-01-0 MW4025000	C 5 ppm	C 5 ppm	C 5 ppm	1.491	gas	-114.8	-85.0	1.194	>101 (760)
H_3PO_4 (97.99)	7664-38-2 TB6300000	1 mg/m³	1 mg/m³;* STEL 3 mg/m³	1 mg/m³; STEL 3 mg/m³	(aerosol)	liquid	21.0	260	1.7	0.0038 (0.03)
HBr (80.92)	10035-10-6 MW3850000	3 ppm	C 3 ppm	C 3 ppm	3.31	gas	-88.5	-66.8	2.16	>101 (>760)
HNO_3 (63.01)	7697-37-2 QU5775000	2 ppm	2 ppm; STEL 4 ppm	2 ppm; STEL 4 ppm	2.58	liquid	-42.0	83	1.50	0.39 (2.9)
H_2SO_4 (98.08)	7664-93-9 W55600000	1 mg/m³	1 mg/m³*	1 mg/m³ STEL 3 mg/m³	(aerosol)	liquid	3.0	290	1.84	<0.0001 (<0.001)

*Group I Pesticide

ACROLEIN

$H_2C=CHCHO$ MW : 56.07 CAS: 107-02-8 RTECS: AS1050000

METHOD: 2501, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm; STEL 0.3 ppm; Group I Pesticide
ACGIH: 0.1 ppm, STEL 0.3 ppm
(1 ppm = 2.29 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8389 g/mL @ 20 °C; BP 52.5 °C; MP −88 °C; VP 28.5 kPa (214 mm Hg; 28% v/v) @ 20 °C; explosive range 2.8 to 31% v/v in air

SYNONYMS: 2-propenal; acrylicaldehyde; acrylaldehyde; allylaldehyde.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 13 L @ 0.1 ppm
-MAX: 48 L

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks and 10 media blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 1.50 mg/m^3 (24-L samples)

BIAS: 7.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.111 [1]

ACCURACY: ± 29%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NITROGEN-SPECIFIC DETECTOR

ANALYTE: 9-vinyl-1-aza-8-oxabicyclo[4.3.0]nonane

DESORPTION: 2 mL toluene; ultrasonic bath for 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C for 8 min; 20 °C/min; hold @ 200 °C for 11 min

CARRIER GAS: Helium, 30 mL/min

COLUMN: 2 m x 2-mm glass, 5% SP-2401-DB on Supelcoport (100-120 mesh)

CALIBRATION: acrolein spiked on coated sorbent

RANGE: 3 to 36 µg per sample

ESTIMATED LOD: 2 µg per sample

PRECISION ($\bar{S}_r$): not determined

APPLICABILITY: The working range is 0.05 to 0.2 ppm (0.13 to 0.5 mg/m^3) for a 24-L air sample. For STEL measurements, the limit of the method is 0.9 ppm for a 15-min sample at 0.1 L/min.

INTERFERENCES: None known. Peaks for acetaldehyde and formaldehyde oxazolidines may be observed in the chromatogram, but they are resolved from the acrolein peak. Capacity of the sampler is reduced if sampling in air containing acids [1].

OTHER METHODS: This method was developed to give improved sample stability and to provide for ease of personal sampling compared to P&CAM 118 [2] and P&CAM 211 [2], which have not been revised.

REAGENTS:

1. Toluene, chromatography quality.
2. Acrolein,* freshly distilled under N_2 to remove stabilizer. Store at 0 °C.
3. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until pure by GC analysis. Store in dessicator.
4. XAD-2 (Amberlite - Rohm and Haas) or equivalent. Extract 4 h in soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
5. Calibration stock solution, 1.0 μg/μL. Add 11.9 μL acrolein to a septum-capped 10-mL volume of toluene.

* See Special Precautions

EQUIPMENT:

1. Sampling tube: glass tube, 10 cm x 4-mm ID, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop ca. 2.2 inches of water (756 Pa) at 0.10 L/min. Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Vials, 4-mL, with septum and plastic screw caps.
4. Ultrasonic bath.
5. Pipettes, volumetric, 1- and 2-mL, with pipet bulb.
6. Flasks, volumetric, 10-mL.
7. Pipettes, disposable, 2-mL.
8. Syringes, 10-μL (readable to 0.1 μL) and 25- and 50-μL.
9. Gas chromatograph, nitrogen-specific detector, integrator and column (page 2501-1).
10. File.

SPECIAL PRECAUTIONS: Acrolein is an acute irritant and a potential fire hazard (flash point = −17.8 °C); work with this compound only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Score with a file and break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 1.5 to 48 L.

   NOTE: Sampling rate is limited by the speed of reaction of acrolein with the sorbent coating. Sampling at rates above 0.10 L/min could cause appreciable acrolein breakthrough, possibly invalidating the sample.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place glass wool plug and rear sorbent section in a 4-mL vial.
6. Transfer front section with the remaining glass wool plugs to a second 4-mL vial.
7. Add 2.0 mL of toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials by placing them in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six standards covering the range of the samples.
   a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from 10 unused samplers (media blanks).
   b. Inject aliquots of the calibration stock solution into the vials at six different levels and allow to stand overnight at room temperature. Prepare two standards at each level.
   c. Desorb (steps 7 and 8) and analyze together with samples and blanks (steps 10 and 11).
   d. Prepare calibration graph (peak area or height vs. concentration of acrolein, μg/mL).
      NOTE: The calibration procedure used in this method does not require a desorption efficiency (DE) correction to be made. If DE is needed, see the APPENDIX.

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2501- 1. Set air and hydrogen flows on the nitrogen specific detector to manufacturer's specifications. Inject 1-μL sample aliquot.
11. Measure peak area or peak height. Acrolein derivative t_r = 3.6 min and t_r for 2-(hydroxymethyl)piperidine = 10.7 min for these conditions.

CALCULATIONS:

12. Read the μg/mL of acrolein found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph and multiply by the desorption volume, 2 (mL). Calculate concentration, C (mg/m^3), of acrolein in the air volume sampled, V (L):
    NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary.

$$C = \frac{(W_f + W_b) \cdot 2}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated over the range of 0.12 to 1.5 mg/m^3 using 24-L samples. Average desorption efficiencies were ca. 1.0 for all levels studied. Mean recovery was 107%, representing an insignificant bias in the method [1]. Concentration of the generated acrolein vapor was independently verified by a modification of P&CAM 211 by Shell Development Co. [3]. No breakthrough was observed for an 8-h sample at 0.10 L/min (48 L) of a 4.5 mg/m^3 of acrolein at 80% RH. The method has been used by three separate analysts at NIOSH and no intralaboratory bias was observed. Measurement precision ($\bar{S}_r$) was not determined. Overall accuracy was ± 29%; therefore, the method does not meet the ± 25% criterion for a valid method.

REFERENCES:

[1] Kennedy, E.R., O'Connor, P.F., Gagnon, Y.T. "Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography," Anal. Chem. 56(12):2120-2123 (1984).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 118 and 211, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Shell Development Company Analytical Department. Determination of Acrolein in Air, Bubbler/Colorimetric Method, SRC 11A11/79, Shell Development Company Westhollow Research Center.

METHOD WRITTEN BY:

Eugene R. Kennedy, Ph.D. and Paula Fey O'Connor, NIOSH/DPSE.

APPENDIX:

SORBENT PREPARATION

Add 1 g of the purified 2-(hydroxymethyl)piperidine in 50 mL of toluene for each 9 g of extracted XAD-2 sorbent . Allow this mixture to stand for 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze using steps 6 through 11. No blank peak is expected for acrolein although a blank for formaldehyde and acetaldehyde may be observed.

DESORPTION EFFICIENCY

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure outlined in this method. The following procedure can be used to determine DE, if necessary:

a. Using a 10-μL syringe and the calibration stock solution inject four sampling tubes at each of five levels. Open several blank tubes but add no acrolein to them. Cap all the tubes.
b. Using the 10-μL syringe, spike the calibration stock solution into 4-mL vials containing 2 mL of toluene and 10 mg of purified 2-(hydroxymethyl)piperidine. Prepare four replicate vials at each of the five concentrations used in step a.
c. Allow the spiked tubes, spiked standard solutions and blank tubes to stand overnight at ambient temperature to assure complete reaction. Desorb and analyze the spiked and blank tubes according to steps 4 through 11. Analyze the spiked solutions according to steps 10 and 11.
d. To calculate the recovery, compare the blank-corrected peak areas or heights of the acrolein peak found in the spiked tubes (Q_r - B) to the peak area or height of the acrolein peak found in the spiked solutions (Q_a).

$$DE = \frac{(Q_r - B)}{Q_a}.$$

e. Prepare a graph of DE vs. mg acrolein recovered.

$CH_2=CHCN$ MW : 53.06 CAS: 107-13-1 RTECS: AT5250000

METHOD: 1604, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 ppm; C 10 ppm (skin)
NIOSH: carcinogen; 1 ppm; C 10 ppm/15 min; Group I Pesticide (skin)
ACGIH: carcinogen; 2 ppm (skin)
(1 ppm = 2.17 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.806 g/mL @ 20 °C; BP 77.2 °C; VP 11 kPa (83 mm Hg 11% v/v) @ 20 °C; explosive range 3 to 17% v/v in air

SYNONYMS: 2-propenenitrile; vinyl cyanide; AN.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3.5 L @ 2 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 100 mg/m^3 [1,2] (20-L samples)

BIAS: − 4.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1,2]

ACCURACY: ± 14.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acrylonitrile

DESORPTION: 1 mL 2% (v/v) acetone in CS_2; stand 30 min

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 200 °C
-COLUMN: 85 °C

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: 3-m x 3-mm stainless steel, 20% SP-1000 on 80/100 Chromosorb WHP

CALIBRATION: standard solutions of distilled acrylonitrile in hexane

RANGE: 15 to 1000 µg per sample [1]

ESTIMATED LOD: 1 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.06 @ 16 µg per sample [1]

APPLICABILITY: The working range is 0.7 to 46 ppm (1.5 to 100 mg/m^3) for a 10-L air sample. This method is applicable to 15-minute ceiling measurements. NIOSH has sampled for acrylonitrile at acrylic and electric plants.

INTERFERENCES: None known. An alternate chromatographic column is a fused silica capillary, 30 m x 0.32-mm, coated with 0.5 µm DB-WAX or 1 µm DB-5.

OTHER METHODS: This revises NIOSH Method S156 [1,3] and Method 1604 (dated 2/15/84). P&CAM 202 has been dropped because of poor sensitivity (LOD 0.1 mg per sample) [4]. Marano et al. [5] have shown that the use of a nitrogen selective detector (NPD) increases the sensitivity and specificity of the analysis.

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Acetone, chromatographic quality.
3. Hexane, reagent grade.
4. Eluent: 2% acetone (v/v) in carbon disulfide.*
5. Acrylonitrile, stabilized.* Stable at least one month at 4 °C.
6. Acrylonitrile, freshly distilled.*
7. Calibration stock solution, 4 μg/μL. Add 50 μL freshly distilled acrylonitrile to 10 mL hexane. Stable one week at 4 °C.
8. Helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1604-1).
4. Micro-distillation apparatus for vacuum distillation of acrylonitrile.
5. Vials, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-μL and other sizes as needed, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a severe fire and explosion hazard (flash point = −30 °C). Acrylonitrile is explosive, flammable, toxic, and a suspect carcinogen [3]. Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3.5 to 20 L.
4. Cap the samplers pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
   NOTE: An internal standard, e.g., 0.1% (v/v) benzene or n-hexane, may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 1 to 1000 μg acrylonitrile per sample.
   a. Add known amounts of calibration stock solution, or a serial dilution thereof, to eluent in 10-mL volumetric flasks and dilute to the mark with eluent (2% acetone in CS_2).

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area vs. μg acrylonitrile).
NOTE: Compare the peak areas of the working standards with a 0.1 mg/mL reference standard prepared from stabilized (undistilled) acrylonitrile in hexane. When the concentration of the working standards starts to decrease, prepare new working standards.

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. μg acrylonitrile recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1604-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE 1: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
NOTE 2: Under these conditions t_r for acrylonitrile is ca. 8.5 min.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of acrylonitrile found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of acrylonitrile in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S156 [2] was validated at levels of 0.48, 0.95, and 1.91 mg per sample, using samples of acrylonitrile prepared both by sampling standard atmospheres generated by calibrated syringe drive and by spiking standard solutions in hexane on to the charcoal [6].

After the OSHA standard for acrylonitrile was lowered to 2 ppm, the method was evaluated by NIOSH at levels of 8.6 and 16.6 μg per sample (desorption solvent 2% acetone in CS_2), using samples from gas bag atmospheres and by spiking the charcoal with standard solutions of acrylonitrile in hexane [1]. At the higher levels (> 16 μg), the recoveries of acrylonitrile averaged 94% and the $\bar{S}_r$ was 0.06. At the lower level (8.6 μg), the recovery for the two sets of samples prepared from standard atmospheres averaged 79% with a $\bar{S}_r$ of 0.14. The sample set prepared by spiking charcoal at the lower level had a recovery of 94%. The parity between the recoveries of samples obtained from test atmospheres and from liquid spikes at the lower level suggested a possible problem with accuracy at this level [1]. Samples were found to be stable for at least seven days at room temperature [1,6]. Several breakthrough studies have been reported. At 80% relative humidity, breakthrough occurred after 184 minutes (36.7 L) sampling 8 mg/m^3 at 0.2 L/min [7]. Breakthrough did not occur after sampling dry air at 92 mg/m^3 at 0.2 L/min for 4 hours [6].

REFERENCES:

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[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Criteria for a Recommended Standard...Occupational Exposure to Acrylonitrile, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-116 (1978); revised Mar, 1978 as part of NIOSH testimony at OSHA hearing.
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 202, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Marano, R.S., Levine, S.P. and T.M. Harvey. Trace Determination of Subnanogram Amounts of Acrylonitrile in Complex Matrices by Gas Chromatography with a Nitrogen Selective Detector. Anal. Chem., 50, 1948 (1978)
[6] Documentation of the NIOSH Validation Tests, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[7] OSHA Report, Acrylonitrile Method 37, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (May, 1982).

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE; S156 originally validated under NIOSH Contract CDC-99-74-45.

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 1400, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS AND SYNONYMS: (1) ethanol: ethyl alcohol.
(2) isopropyl alcohol: 2-propanol.
(3) tert-butyl alcohol: 2-methyl-2-propanol.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min (≤0.05 L/min for ethyl alcohol)

	(1)	(2)	(3)
VOL-MIN:	0.1 L	0.3 L	1.0 L
-MAX:	1 L	3 L	10 L

SHIPMENT: cooled

SAMPLE STABILITY: unknown, store in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 14%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% 2-butanol in CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250-300 °C
-COLUMN: 65-70 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 2 m x 4-mm ID, 0.2% Carbowax 1500 on 60/80 Carbopack C or equivalent

CALIBRATION: solutions of analyte in eluent (internal standard optional)

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [2]

APPLICABILITY: The working ranges are 16 to 1000 ppm ethanol (30 to 1900 mg/m^3) for a 1-L air sample; 4 to 400 ppm isopropyl alcohol (10 to 1000 mg/m^3) for a 3-L air sample; and 1 to 100 ppm t-butyl alcohol (3 to 300 mg/m^3) for a 10-L air sample. This method employs a simple desorption and may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling efficiency. The methods were validated using a 3 m x 3-mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S56, S65 and S63 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) 2-butanol and 0.2% v/v n-undecane, 0.1% v/v ethyl benzene, or other suitable internal standard.
2. Analyte, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (Blue Ice, or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1400-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 1 L (ethanol), 0.3 to 3 L (isopropyl alcohol) or 1.0 to 10 L (t-butyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely with bagged refrigerant for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1400-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S56, S65 and S63 were issued on January 17, 1975 [3], and validated using 1-, 3- and 10-L air samples, respectively, of atmospheres generated in dry air by calibrated syringe drive from absolute ethanol, 2-propanol and t-butyl alcohol [1]. No stability studies were done. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision ($\hat{S}_{rT}$)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision ($\bar{S}_r$)
			mg/m³	mg per sample			
S56	0.065	103.6	900 to 3300	1 to 4	1.6 L	0.79*	0.027
S65	0.064	96.7	505 to 1890	1 to 5	6.0 L	0.93*	0.033
S63	0.075	100.3	165 to 600	1.5 to 6	17.0 L	0.91*	0.018

*Over the range studied. Each laboratory must do their own DE determinations.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, (NIOSH) Publication No. 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-S (unpublished, November 3, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S56, S65 and S63, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

TABLE 1. PROPERTIES

Compound	Formula	mg/m^3 = 1 ppm @ NTP	M.W.	Density @ 20 °C (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
Ethanol	CH_3CH_2OH; C_2H_6O	1.883	46.07	0.789	78.5	5.6 (42)
Isopropyl alcohol	$CH_3CH(OH)CH_3$; C_3H_8O	2.46	60.09	0.785	82.5	4.4 (33)
tert-Butyl alcohol	$(CH_3)_3COH$; $C_4H_{10}O$	3.03	74.12	0.786	82.4; MP = 25.6 °C	4.1 (31)

TABLE 2. GENERAL INFORMATION.

COMPOUND	EXPOSURE LIMITS (ppm) OSHA	NIOSH	ACGIH	CAS#	RTECS#
Ethanol	TWA 1000	1000	1000	64-17-5	KQ6300000
Isopropyl alcohol	TWA 400	400 500 STEL	400 500 STEL	67-63-0	NT8050000
tert-Butyl alcohol	TWA 100	100 150 STEL	100	75-65-0	EO1925000

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 1401, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS and SYNONYMS:
(1) n-butyl alcohol: 1-butanol; n-Butanol; Propyl carbinol
(2) sec-butyl alcohol: 2-butanol; methyl ethyl carbinol; 2-hydroxybutane.
(3) isobutyl alcohol: 2-methyl-1-propanol; isopropyl carbinol; IBA.
(4) n-propyl alcohol: 1-propanol; ethyl carbinol.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

	(1)	(2)	(3)	(4)
VOL-MIN:	2 L	2 L	2 L	1 L
-MAX:	10 L	10 L	10 L	10 L

SHIPMENT: routine

SAMPLE STABILITY: unknown; store in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 15%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% 2-propanol in CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250-300 °C
-COLUMN: 75 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: glass, 3 m x 2-mm ID, 10% SP-1000 on 80/100 mesh Chromosorb WHP, or equivalent

CALIBRATION: solutions of analyte in eluent (internal standard optional)

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [2]

APPLICABILITY: This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: The methods were validated using a 3 m x 3-mm ID stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used.

OTHER METHODS: This method combines and replaces Methods S66, S53, S64 and S62 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) 2-propanol and 0.2% (v/v) n-undecane, 0.1% (v/v) hexane or other suitable standard.
2. Analyte.
3. DE stock solution, 100 mg/mL. Prepare solutions of each analyte in heptane.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back - 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1401-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L (2 to 10 L for sec-butanol and isobutyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of DE stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1401-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S66 (n-butyl alcohol), S53 (sec-butyl alcohol), S64 (isobutyl alcohol), and S62 (n-propyl alcohol) were issued on January 17, 1975, and validated using 10-L air samples of atmospheres generated by injection of the pure alcohol into dry air using a calibrated syringe drive [1]. No stability studies were done. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision ($\hat{S}_{rT}$)	Recovery (%)	Range Studied mg/m³	Range Studied mg per sample	Breakthrough @ 2X OSHA in Dry Air	Avg. DE	Measurement Precision ($\bar{S}_r$)
S66	0.065	100.0	170 to 610	1.5 to 6	35 L	0.89	0.021
S53	0.066	107.2	270 to 850	2.2 to 9	15 L	0.92	0.028
S64	0.073	100.0	180 to 620	1.5 to 6	31 L	0.85	0.023
S62	0.075	103.5	225 to 835	2.5 to 10	19 L	0.89	0.016

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-X (unpublished, November 3, 1983).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

George Williamson, NIOSH/DPSE; S53, S62, S64 and S66 originally validated under NIOSH Contract 99-74-45.

TABLE 1. PROPERTIES

Compound	Formula	mg/m^3 = 1 ppm @ NTP	M.W.	Density (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$; $C_4H_{10}O$	3.03	74.12	0.810 @ 20°C	117	0.56 (4.2)
sec-Butyl alcohol	$CH_3CH(OH)CH_2CH_3$; $C_4H_{10}O$	3.03	74.12	0.808 @ 20°C	99.5	1.7 (13)
Isobutyl alcohol	$(CH_3)_2CHCH_2OH$; $C_4H_{10}O$	3.03	74.12	0.806 @ 15°C	108	1.2 (9)
n-Propyl alcohol	$CH_3CH_2CH_2OH$; C_3H_8O	2.46	60.09	0.805 @ 20°C	97	2.0 (15)

TABLE 2. GENERAL INFORMATION

			Exposure Limits (ppm)		
COMPOUND	CAS#	RTECS#	OSHA	NIOSH	ACGIH
n-Butyl alcohol	71-36-3	EO1400000	100 TWA	C 50 (skin)	C 50 (skin)
sec-Butyl alcohol	78-92-2	EO1750000	150 TWA	100 TWA; 150 STEL	100 TWA
Isobutyl alcohol	78-83-1	NP9625000	100 TWA	50 TWA	50 TWA
n-Propyl alcohol	71-23-8	UH8225000	200 TWA	200 TWA; 250 STEL (skin)	200 TWA; 250 STEL (skin)

Table 1 MW: Table CAS: Table 2 RTECS: Table 2

METHOD: 1402, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS and SYNONYMS:	(1) allyl alcohol:	2-propen-1-ol; 2-propenol; vinyl carbinol.
	(2) diacetone alcohol:	4-hydroxy-4-methyl-2-pentanone; 2-methyl-2-pentanol-4-one.
	(3) cyclohexanol:	hexalin; hydralin; hydroxycyclohexane; anol.
	(4) isoamyl alcohol:	3-methyl-1-butanol; isobutylcarbinol; isopentyl alcohol.
	(5) methyl isobutyl carbinol:	MIBC; 4-methyl-2-pentanol; methyl amyl alcohol.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: unknown; store in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 20%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 5% 2-propanol in CS_2; 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250-300 °C
-COLUMN: 80-120 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2-mm ID, 10% SP-1000 on 80/100 mesh Supelcoport or equivalent

CALIBRATION: solutions of analyte in eluent (internal standard optional)

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [2]

APPLICABILITY: The working range is 1 to 10 mg/m^3 for allyl alcohol (other analytes range from 45 to 140 mg/m^3 at low end and 175 to 680 mg/m^3 at high end of working ranges) for a 10-L air sample. This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling capacity. The methods were validated using a 3 m x 3-mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S52, S55, S54, S58 and S60 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic) with 5% (v/v) 2-propanol and 0.1% (v/v) hexane, 0.2% (v/v) n-pentadecane or other suitable internal standard.
2. Analyte.
3. n-Heptane.
4. DE stock solution, allyl alcohol, 12 mg/mL in n-heptane.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back - 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1402-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte or DE stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1402-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S52 (allyl alcohol), S55 (diacetone alcohol), S54 (cyclohexanol), S58 (isoamyl alcohol) and S60 (methyl isobutyl carbinol) were issued on January 17, 1975 [3], and validated using 10-L air samples of atmospheres generated in dry air by calibrated syringe drive from the pure substances [1]. No stability studies were done. Precision and recovery were as shown below, representing non-significant bias in each method:

Method [1,3]	Overall Precision ($\hat{S}_{rT}$)	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision ($\bar{S}_r$)
			mg/m^3	mg per sample			
S52	0.111	98.8	1.8 to 8.4	0.02 to 0.1	>48 L	0.90	0.023
S55	0.104	91.8	140 to 510	1.1 to 4.7	>48 L	0.78	0.054
S54	0.080	98.9	95 to 380	1 to 4	>48 L	0.99	0.015
S58	0.077	107.6	195 to 680	1.8 to 7	34 L	0.99	0.020
S60	0.080	101.8	45 to 175	0.5 to 2	>48 L	0.99	0.035

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #3990-V (unpublished, November 4, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

TABLE 1. PROPERTIES

Compound	Formula	mg/m^3 = 1 ppm @ NTP	MW	Density (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
Allyl alcohol	$CH_2=CHCH_2OH$; C_3H_6O	2.37	58.08	0.854 @ 20°C	96-97	2.3 (17)
Diacetone alcohol	$(CH_3)_2C(OH)CH_2COCH_3$; $C_6H_{12}O_2$	4.75	116.16	0.931 @ 25°C	167.9	0.1 (0.8)
Cyclohexanol	$C_6H_{12}O$	4.09	100.16	0.962	161; MP = 24	0.13 (1.0)
Isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$; $C_5H_{12}O$	3.60	88.15	0.813 @ 15°C	132	3.7 (28)
Methyl isobutyl carbinol	$(CH_3)_2CHCH_2CH(OH)CH_3$; $C_6H_{14}O$	4.18	102.18	0.802	132	0.4 (3)

TABLE 2. GENERAL INFORMATION

			EXPOSURE LIMITS (ppm)		
COMPOUND	CAS#	RTECS#	OSHA	NIOSH	ACGIH
Allyl alcohol	107-18-6	BA5075000	2 TWA; (skin)	2 TWA; 4 STEL (skin) (Group I Pesticide)	2 TWA; 4 STEL (skin)
Diacetone alcohol	123-42-2	SA9100000	50 TWA	50 TWA	50 TWA
Cyclohexanol	108-93-0	GV7875000	50 TWA	50 TWA (skin)	50 TWA (skin)
Isoamyl alcohol	123-51-3	EL5425000	100 TWA	100 TWA; 125 STEL (skin)	100 TWA; 125 STEL
Methyl isobutyl carbinol	108-11-2	SA7350000	25 TWA; (skin)	25 TWA; 40 STEL (skin)	25 TWA; 40 STEL (skin)

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1403, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS and SYNONYMS:
(1) 2-methoxyethanol: methyl cellosolve; ethylene glycol monomethylether; EGME
(2) 2-ethoxyethanol: cellosolve; ethylene glycol monoethylether, EGEE
(3) 2-butoxyethanol: butyl cellosolve; ethylene glycol monobutylether, EGBE

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

	(1)	(2)	(3)
VOL-MIN:	6 L	1 L	2 L
-MAX:	50 L	6 L	10 L

SHIPMENT: routine

SAMPLE STABILITY: unknown; store in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: ± 17%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 5% methanol in CH_2Cl_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250-300 °C
-COLUMN: (1) 95 °C; (2) 140 °C (3) 145 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2-mm ID, 10% SP-1000 on 80/100 mesh Chromosorb WHP, or equivalent

CALIBRATION: solutions of analyte in eluent (internal standard optional)

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 to 0.02 mg per sample [1]

APPLICABILITY: This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity may reduce sampling capacity. The methods were validated using a 3 m x 3-mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S79 [2], S361 [3], and S76 [2]. Butyl cellosolve and butyl cellosolve acetate are included in OSHA Method 83. Cellosolve and cellosolve acetate are included in OSHA Method 79. Both of these OSHA methods are very similar to Method 1403.

REAGENTS:

1. Eluent: methylene chloride with 5% (v/v) methanol and 0.2% (v/v) 1-heptanol, 0.1% (v/v) ethyl benzene or other suitable internal standard.
2. Analyte.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1403-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Methylene chloride is a carcinogen [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 6 to 50, 2-methoxyethanol; 1 to 6, 2-ethoxyethanol; 2 to 10, 2-butoxyethanol.
   NOTE: Maximum flow rate for 2-methoxyethanol and 2-butoxyethanol is 0.2 L/min.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1403-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S79 (2-methoxyethanol), S361 (2-ethoxyethanol) and S76 (2-butoxyethanol) were issued on February 14, 1975 [2,5], March 17, 1978 [3,6,7], and February 14, 1975 [2,5], respectively, and validated using, respectively, 50-, 6- and 10-L air samples of atmospheres generated by calibrated syringe drive. Storage stability of these alcohols was not determined. Precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision ($\hat{S}_{rT}$)	Recovery (%)	Range Studied mg/m³	Range Studied mg per sample	Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision ($\bar{S}_r$)
S79 [1,4]	0.068	93	44 to 160	2 to 8	128 L*	0.98	0.008
S361 [2,5,6]	0.059	107	340 to 1460	2 to 7	>10 L**	1.02	0.009
S76 [1,4]	0.060	92	124 to 490	1 to 5	>44 L*	0.99	0.009

*Dry air.
**90% RH.
The method was also successfully checked for spiked samples of 2-butoxyethyl acetate [8].

REFERENCES:

[1] User check, UBTL, NIOSH Sequence #3990-Z (unpublished, November 3, 1983).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] Ibid, V. 5, S361, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] NIOSH Recommendations for Occupational Safety and Health, U.S. Department of Health and Human Services (NIOSH) Publ. 92-100 (January, 1992).
[5] Documentation of the NIOSH Validation Tests, S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[6] Backup Data, S361, available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
[7] NIOSH Research Report, Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Dept. of Health and Human Services Publ. (NIOSH) 80-133 (1980).
[8] User Check, DataChem Laboratories, NIOSH Sequence #6960-J,K (unpublished, August 15, 1990).

METHOD REVISED BY:

George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contracts 99-74-45 and 210-76-0123.

TABLE 1. GENERAL INFORMATION

Compound CAS# RTECS#	Exposure Limits (ppm) OSHA	 NIOSH	 ACGIH	Formula	mg/m^3 = 1 ppm @ NTP	MW	Density @ 20 °C (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
2-Methoxyethanol 109-86-4 KL5775000	25 (skin)	0.1 (skin)	5 (skin)	$HOCH_2CH_2OCH_3$	3.11	76.09	0.966	124	0.8 (6)
2-ethoxyethanol 110-80-5 KK8050000	200 (skin)	0.5 (skin)	5 (skin)	$HOCH_2CH_2OCH_2CH_3$	3.68	90.12	0.931	135	0.5 (4)
2-butoxyethanol 111-76-2 KJ8575000	50 (skin)	5 (skin)	25 (skin)	$HOCH_2CH_2O(CH_2)_3CH_3$	4.83	118.17	0.902	171	0.11 (0.8)

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 2539, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS: acetaldehyde; acrolein; butyraldehyde; crotonaldehyde; formaldehyde; furfural; heptanal; hexanal; isobutyraldehyde; isovaleraldehyde; propionaldehyde; valeraldehyde.
SYNONYMS: Table 1

SAMPLING

SAMPLER: SOLID SORBENT TUBE (10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOLUME: 5 L

SHIPMENT: @ 25 °C or lower

SAMPLE STABILITY: at least 1 week @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID & GC/MS

ANALYTE: oxazolidine prepared from aldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless; split vent time 30 sec

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 6 °C/min to 100 °C for 2 min; 30 °C/min to 260 °C

CARRIER GAS: He, 0.5 mL/min; makeup flow, 29 mL/min

COLUMN: capillary, 15 m x 0.32-mm, 1.0-µm film 6% cyanopropyl-phenyl, DB-1301 or equivalent

CALIBRATION: standard solutions of aldehydes spiked on sorbent

RANGE AND PRECISION: not determined

ESTIMATED LOD: 2 µg aldehyde per sample

APPLICABILITY: This is a screening technique to determine the presence of aldehydes and should not be used for quantitation. Further confirmation of aldehyde identification should be performed by gas chromatography/mass spectrometry (See Table 2 for structural ion data). Methods for quantitation of some aldehydes listed in this method are available in the NIOSH Manual of Analytical Methods (See OTHER METHODS). All aldehydes tested have been detected by this method in bulk field samples.

INTERFERENCES: High-boiling naphtha mixtures, such as kerosene and mineral spirits may have components with retention times similiar to the oxazolidines and may be interferences in the gas chromatographic analysis. A second column (DB-5, DB-WAX) may be needed to separate some of the earlier C_3-C_4 aldehydes from excess HMP reagent.

OTHER METHODS: This method incorporates sampling technology used in NIOSH methods 2501 (acrolein), 2541 (formaldehyde), 2529 (furfural), 2531 (glutaraldehyde) [1], and 2526 (valeraldehyde), and OSHA methods 68 (acetaldehyde) and 52 (acrolein/formaldehyde) [2].

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas or equivalent).
4. Formaldehyde,* 37% (w/v) solution in water.
5. Formaldehyde stock solution, 1 μg/μL (see APPENDIX A).
6. Acetaldehyde*.
7. Acrolein*.
8. Propionaldehyde*.
9. Butyraldehyde*.
10. Isobutyraldehyde*.
11. Crotonaldehyde*.
12. Valeraldehyde*.
13. Isovaleraldehyde*.
14. Hexanal*.
15. Heptanal*.
16. Furfural*.
17. Sulfuric acid, 0.02 N.
18. Sodium hydroxide, 0.01 N.
19. Sodium sulfite, 1.13 M.
20. Water, deionized, then distilled.
21. Hydrogen, prepurified.
22. Air, filtered, compressed.
23. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID; flame-sealed ends and plastic caps, containing two sections of 40/60 mesh, 2-(hydroxymethyl)piperidine-coated XAD-2 (front = 120 mg; back = 60 mg: see APPENDIX A) retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 kPa (5.7 mm Hg). Tubes are commercially available (Supelco, Inc. ORBO-23 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator and column (page 2539-1). GC/MS system for confirmation.
4. Ultrasonic bath.
5. Vials, glass, 1-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-mL.
7. Pipets, volumetric, 1-mL with pipet bulb
8. Syringes, 10-μL (readable to 0.1-μL), 25-, and 50-μL.
9. File.
10. Beakers, 50-mL.
11. pH meter.
12. Magnetic stirrer.
13. Burets, 50-mL.
14. Flasks, round-bottomed, 100-mL.
15. Soxhlet extraction apparatus.
16. Vacuum oven.
17. Distillation apparatus.

SPECIAL PRECAUTIONS: Aldehydes can irritate the mucous membranes and act on the central nervous system [3]. Certain aldehydes are also suspect carcinogens. Work with these compounds only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. For general screening, sample at 0.01 to 0.05 L/min for a maximum sample volume of 5 L.
   NOTE: Aldehydes react with the 2-(hydroxymethyl)piperidine to form an oxazolidine derivative in the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Owing to the lower reactivities of some aldehydes, sampling even at 0.02 L/min may cause breakthrough because of incomplete reaction.

SAMPLE PREPARATION:

4. Score each sampler with a file in front of the first sorbent section.

5. Break sampler at score line. Remove and place front glass wool plug and front sorbent section in a vial. Transfer back section with remaining glass wool plugs to a second vial.
6. Add 1.0 mL toluene to each vial. Crimp cap tightly onto each vial.
7. Agitate vials in an ultrasonic bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

8. Prepare qualitative oxazolidine standard samples.
   a. Prepare aldehyde standard stock solutions.
      NOTE: Aldehydes can oxidize to other compounds on exposure to air. This will introduce bias into the method, so use of freshly-opened bottles of aldehydes is recommended.
      (1) Inject an aliquot of formaldehyde stock solution directly onto the sorbent.
      (2) Take special care with acetaldehyde because of its volatility. To prepare acetaldehyde standard solutions, weigh a 10-mL capped volumetric flask containing about 5 mL toluene. With a cooled pipette, transfer about 1 mL of acetaldehyde into the weighed flask, recap and reweigh. Dilute to the mark.
      (3) For the other aldehydes, add measured aliquots (ca. 12 μL) of each to toluene in 10-mL volumetric flasks and dilute to the mark. From the density of each aldehyde, determine the amount of each aldehyde present in each solution (ca. 1 μg/μL).
   b. Inject 10 μL of the standard aldehyde solutions separately onto blank tubes from the same lot as the field samples.
   c. Analyze (steps 4 through 7 and 10 through 12) along with blanks for qualitative identification of derivative peaks by retention times.
9. Determine limit of detection (LOD) for individual aldehydes by GC/FID with standards covering the range 0.5 to 10 μg per sample. Do this once, when first setting up the method to determine approximate sensitivities for the various aldehyde derivatives. Subsequently, analyze only low-level formaldehyde standard samples with each set of samples as an internal check that the analytical system is working.
   a. Weigh 120-mg portions of unused sorbent from media blanks into vials. Keep at least three 120-mg portions of this sorbent for determination of the background levels of each aldehyde.
   b. Add 0.5- to 10-μL aliquots of the individual aldehyde standard solutions to obtain standard samples in the range 0.5 to 10 μg per 120 mg portion of sorbent. Cap vials and allow to stand overnight at room temperature.
   c. Desorb the standard samples of aldehydes (steps 6 and 7) and analyze (steps 10 through 12) along with blanks.
   d. Determine lowest spike to be detected (peak area greater than three times the background or lowest standard observable) to estimate LOD for each aldehyde.
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.

MEASUREMENT:

10. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2539-1. Inject 1-μL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene.
11. Compare retention times of unknown peaks in samples to the retention times for the oxazolidines as determined by the qualitative standard samples. (See Appendix B for sample chromatogram).
    a. Analyze samples with GC retention times matching any oxazolidine by GC/MS using the same GC columns and conditions if possible. Alternate columns such as a DB-WAX (formaldehyde, acetaldehyde, propanal) or DB-1 (remaining aldehydes) may also be used for GC/MS confirmation depending on which aldehyde is suspected.

b. Determine the presence of oxazolidines by monitoring for specific ions known to be present in the derivative spectra. See Table 2 for characteristic ion table and Appendix C for reference mass spectra. Retention times by GC/MS must also match authentic oxazolidine standards.

NOTE 1: This method may also sample aldehydes other than those listed. The presence of these other aldehydes can be confirmed by examination of the mass spectral data and observation of peaks at m/e 126 and at the molecular ion minus one mass unit. The molecular ion for a particular aldehyde is equal to the molecular weight of the original aldehyde plus 97. Fragmentation patterns are also important for the identification of the oxazolidines.

NOTE 2: The absence of some C_3-C_5 aldehydes, such as propionaldehyde, isobutyraldehyde and crotonaldehyde, does not necessarily mean that these compounds are not present in the air sampled. These compounds are not efficiently trapped by the sorbent, and will readily breakthrough the sampler sorbent beds.

NOTE 3: Higher molecular weight aldehydes, such as isovaleraldehyde, hexanal and heptanal, probably will be more efficiently collected on the sorbent owing to their lower vapor pressure. Thus, absence of these compounds in sample results may be indicative of the absence of these compounds in the environment sampled.

12. Report the presence of a particular aldehyde if:
    a. There is a detectable peak by GC-FID at the correct retention time for that aldehyde derivative.
    b. The correct mass spectrum for the derivative is obtained by GC/MS at the proper retention time.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 3rd ed., P.M. Eller, Ed., DHHS (NIOSH) Publication No. 84-100 (1984).

[2] Occupational Safety and Health Administration, "OSHA Analytical Method Manual," American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1985).

[3] Kennedy, E. R., P. F. O'Connor, Y. T. Gagnon. Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography. Anal. Chem., 56, 2120-2123 (1984).

[4] Kennedy, E. R., Y. T. Gagnon, J. R. Okenfuss, A. W. Teass. The Determination in Air of Selected Low-molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography. Appl. Ind. Hyg., 3, 274-279 (1988).

METHOD WRITTEN BY:

Ardith A. Grote and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

TABLE 1. GENERAL INFORMATION

Compound (Synonyms)	Formula	MW	d(g/mL) @ 20 °C	BP(°C)	Exposure Limits (ppm) OSHA	NIOSH	ACGIH	VP(mm Hg) (@ 20 °C)
Formaldehyde (formic aldehyde; formalin; CAS #50-00-0 RTECS LP8925000	CH_2O	30.03	--	-19.5	3; C 5; P 10/30 min	Carc.[a]; 0.016 C 0.1 Group I Pesticide	C 0.3 Suspected Carcinogen	20 (-88°C)
Acetaldehyde (acetic aldehyde; ethyl aldehyde; CAS #75-07-0 RTECS AB1925000	C_2H_4O	44.05	0.788 (@ 16°C)	21	200	Carc.[a] 18 ppm LOQ	100 150 STEL	740
Propionaldehyde (propanal;. CAS # 123-38-6) RTECS UE0350000	C_3H_6O	58.08	0.807	49	--	--	--	258
Acrolein (2-propenal; allyl aldehyde; CAS #107-02-8) RTECS AS1050000	C_3H_4O	56.06	0.839	52.5	0.1	0.1 0.3 STEL Group I Pesticide	0.1 0.3 STEL	210
Butyraldehyde (butanal; CAS # 123-72-8) RTECS ES2275000	C_4H_8O	72.10	0.802	75	--	--	--	92
Isobutyraldehyde (2-methylpropanal dimethylacetaldehyde; CAS #78-84-2) RTECS NQ4025000	C_4H_8O	72.10	0.794	64	--	--	--	170
Crotonaldehyde (2-butenal; ß-methyl acrolein; CAS # 123-73-9) RTECS GP9625000	C_4H_6O	70.09	0 853	104	2	2	2	30
n-Valeraldehyde (pentanal; CAS # 110-62-3) RTECS YV3600000	$C_5H_{10}O$	86.13	0.810	102	no standard	50	50	50
Isovaleraldehyde (3-methylbutanal; isopentanal; CAS # 590-86-3) RTECS ES3450000	$C_5H_{10}O$	86.13	0.785	92	--	--	--	50
Hexanal (caproaldehyde; CAS # 66-25-1) RTECS MN7175000	$C_6H_{12}O$	100.16	0.834	131	--	--	--	10
Heptanal (enanthal; CAS #111-71-7) RTECS MI6900000	$C_7H_{14}O$	114.18	0.809 (@ 30°C)	153	--	--	--	3
Furfural (2-furancarboxaldehyde; CAS # 98-01-1) RTECS LT7000000	$C_5H_4O_2$	96.08	1.16 (@ 25°C)	162	5 (skin)	--	2 (skin)	

[a] - Carcinogen

TABLE 2. MASS SPECTRAL DATA FOR ALDEHYDE DERIVATIVES OF 2-(HYDROXYMETHYL)PIPERIDINE (HMP)

	HMP DERIVATIVE		
Aldehyde	Formula	Base Peak m/z	Other Characteristic Ions m/z
Formaldehyde	$C_7H_{13}NO$	97	126, 127*
Acetaldehyde	$C_8H_{15}NO$	126	140, 141*
Propionaldehyde	$C_9H_{17}NO$	126	154, 155*
Acrolein	$C_9H_{15}NO$	126	152, 153*
Butyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Isobutyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Crotonaldehyde	$C_{10}H_{17}NO$	126	166, 167*
Valeraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Isovaleraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Hexanal	$C_{12}H_{23}NO$	126	196, 197*
Heptanal	$C_{13}H_{25}NO$	126	210, 211*
Furfural	$C_{11}H_{15}NO_2$	192	95, 163, 193*

* indicates molecular ion.

APPENDIX A:

SORBENT PREPARATION (optional if commercially prepared tubes are used):

Extract Amberlite XADS-2 for 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight. Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 kPa (1 mm Hg) at ambient temperature for ca. 1 h. To determine the amount of background for each batch, extract several 120-mg portions of the coated sorbent with toluene and analyze (steps 6 through 12). No blank peak is expected for any aldehydes other than formaldehyde and possibly acetaldehyde.

SYNTHESIS OF ALDEHYDE OXAZOLIDINES:

Place a solution of purified 2-hydroxymethylpiperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 20 mL portions of toluene to rinse residual 1-(hydroxymethyl)piperidine from the container used for weighing. Add anhydrous magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 10 mole of aldehyde in 10 mL of toluene to the 2-hydroxymethylpiperidine solution dropwise with stirring over 1 h. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene and excess aldehyde from the solution at reduced pressure by rotary evaporation.

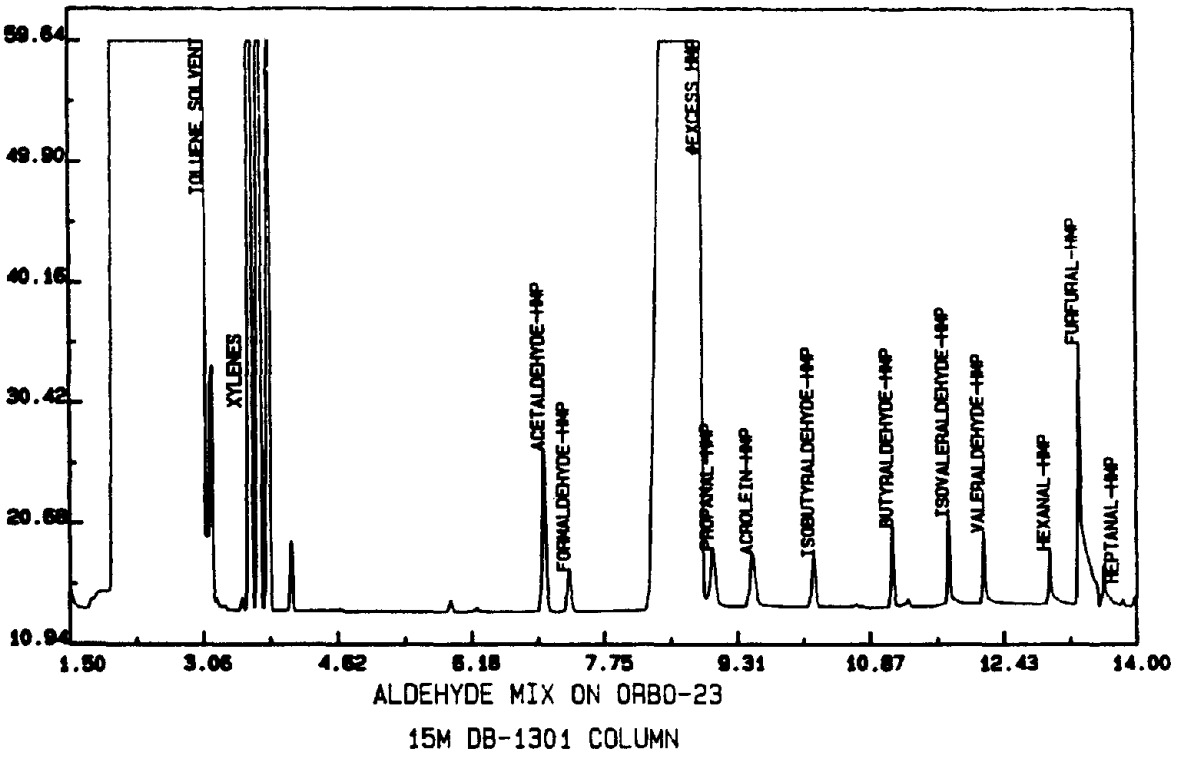
PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL):

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL stock formaldehyde solution. The pH should be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid ≅ 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0 \times (N_a \cdot V_a - N_b \cdot V_b)}{V_s}.$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_s = volume of formaldehyde stock solution (10.0 mL).

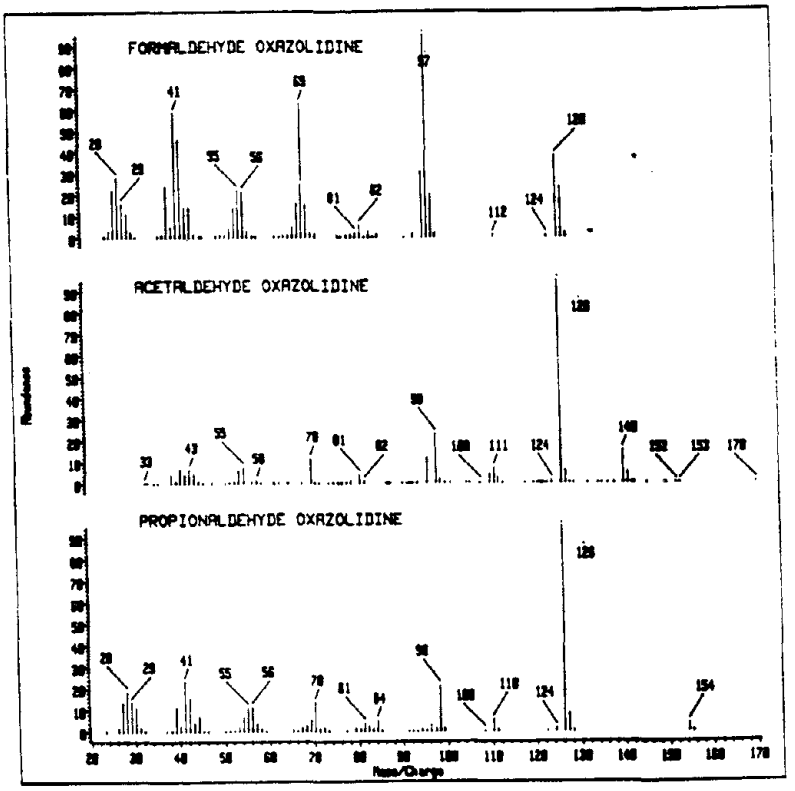
APPENDIX B: Sample chromatogram of aldehyde oxazolidines on DB-1301 column using conditions listed on page 2539-1.

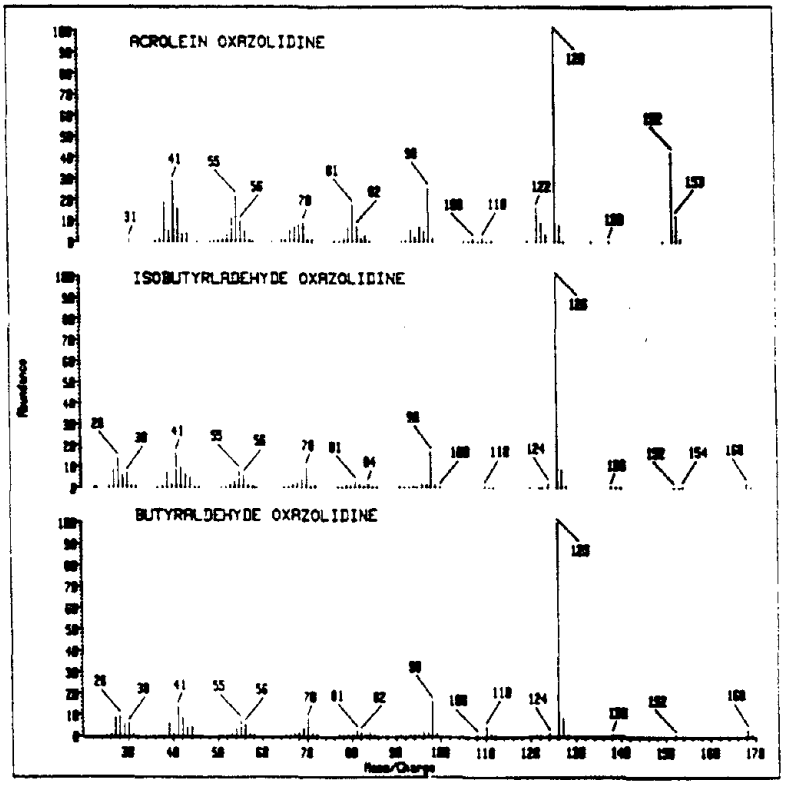


ALDEHYDE MIX ON ORBO-23

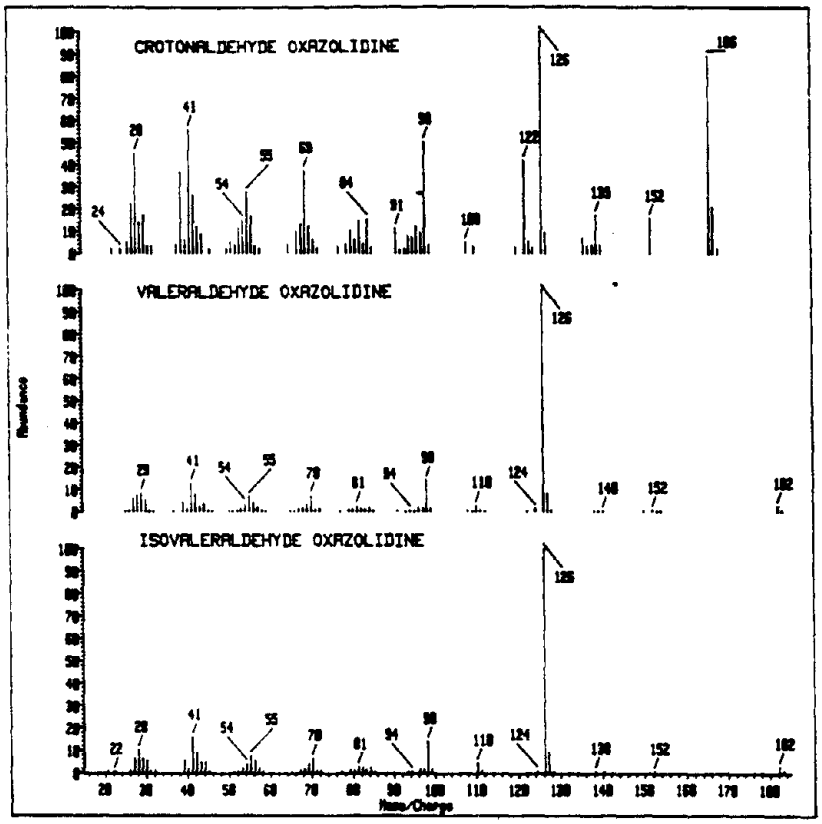
15M DB-1301 COLUMN

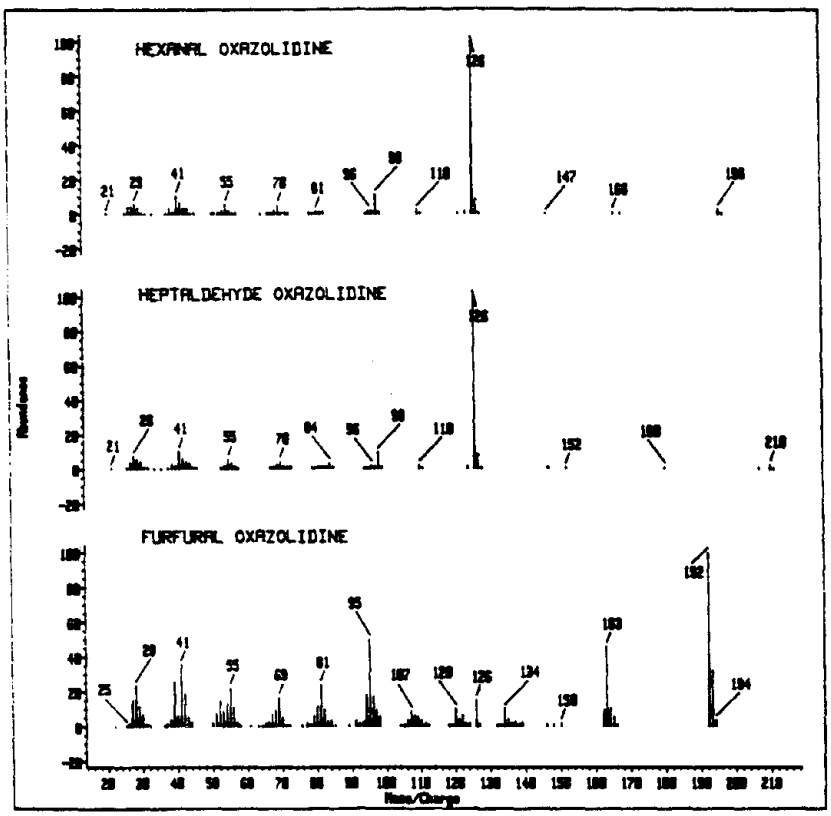
APPENDIX C: Reference mass spectra of oxazolidines of aldehydes individually spiked onto ORBO-23 tubes. GC/MS conditions: HP 5890 gas chromatograph interfaced (direct) to HP 5970 mass-selective detector (70eV); 30-m DB-1 column, 0.25-mm I.D., 1.0-μm film; 70 °C for 1 min, 15 °C/min to 300 °C; interface temperature, 280 °C; injector, 250 °C, 1 μL splitless injection; scan 20-400 amu.





APPENDIX C: (Continued)





$C_{12}H_8Cl_6$ MW: 364.93 CAS: 309-00-2 RTECS: IO2100000

METHOD: 5502, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.25 mg/m^3 (skin)
NIOSH: 0.25 mg/m^3 (skin); carcinogen; Group I Pesticide
ACGIH: 0.25 mg/m^3 (skin)

PROPERTIES: solid; MP 104 °C; VP 0.008 Pa (6 x 10^{-6} mm Hg; 0.12 mg/m^3) @ 20 °C;

SYNONYMS: Aldrin: Octalene; aldrite; aldrosol; HHDN

SAMPLING

SAMPLER: FILTER AND BUBBLER (glass fiber + 15 mL isooctane)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 18 L @ 0.25 mg/m^3
-MAX: 240 L

SHIPMENT: transfer bubbler solutions and filters in scintillation vials; pack carefully

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.15 to 0.5 mg/m^3 [1];

BIAS: − 0.44%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.092 [1]

ACCURACY: ± 16.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTOR

ANALYTE: Aldrin or Lindane

FILTER EXTRACTION: isooctane

INJECTION VOLUME: 15 µL

TEMPERATURE-FURNACE: 750 to 770 °C
-TRANSFER: 225 °C
-VENT: 205 to 260 °C
-COLUMN: 160 to 190 °C

GASES-H_2 (furnace): 150 to 160 mL/min
-N_2 (carrier): 140 mL/min

COLUMN: glass, 1.2 m x 3-mm OD; 5% SE-30 on 80/100 mesh acid-washed DMCS Chromosorb W or equivalent

CALIBRATION: solution of analyte in isooctane

RANGE: 5 to 135 µg per sample

ESTIMATED LOD: 3 µg per sample

PRECISION ($\bar{S}_r$): 0.012 [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 of Aldrin or Lindane for a 90-L air sample. Evaporation of isooctane from the bubbler necessitates refilling the bubbler frequently.

INTERFERENCES: None identified.

OTHER METHODS: This method combines and replaces S275 [2] and S290 [2]. Lindane has also been sampled with a filter-solid sorbent train [3].

REAGENTS:

1. Aldrin, reagent grade.*
2. Lindane, reagent grade.*
3. Isooctane, chromatographic grade.
   NOTE: Needed for field use in sample collection.
4. Benzene, reagent grade.*
5. Calibration stock solution,10 mg/mL. Dissolve 0.1 g accurately weighed Aldrin or Lindane in 1:5 (v:v) benzene:isooctane; dilute to 10 mL. Stable at least one week.
6. Hydrogen, prepurified.
7. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filter, organic binder-free (e.g., Gelman Type A/E), 37-mm, held without backup pad in a two-piece polystyrene cassette filter holder connected in series with a midget bubbler containing 15 mL of the collection medium.
   NOTE: a. Do not use filter holders made of Tenite.
   b. Place glass tube, 5 cm x 6-mm ID, plugged with glass wool between the exit cover of the bubbler and the inlet of the personal sampling pump to avoid splashover or solvent condensation.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Vial, scintillation, with PTFE-lined cap, graduated at 15 mL.
4. Gas chromatograph with electrolytic conductivity detector, quartz reduction furnace, in-line vent upstream of furnace, integrator and column (page 5502-1).
5. Syringes, 5-, 10- and 25-μL, for making standard solutions and GC injections.
6. Volumetric flasks.
7. Pipets, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen; work with it only in a hood.

Aldrin and Lindane are toxic when absorbed through the skin [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Add 15 mL isooctane to the bubbler.
3. Sample at an accurately known flow rate of 0.2 to 1 L/min (e.g., 0.5 L/min for 1 to 6 h) for a total volume of 18 to 240 L.
   NOTE: Check liquid level in the bubbler every 15 min. Maintain between 10 and 15 mL isooctane in the bubbler throughout the sampling period with a volume at the end of sampling of about 10 mL.
4. Remove the bubbler stem and tap it gently against the inside wall of the bubbler to transfer solvent from the stem to the bubbler.
5. Transfer contents of the bubbler to a vial. Rinse the bubbler with 2 mL isooctane. Add the rinse to the vial.
6. Transfer the glass fiber filter to the same vial using tweezers.
7. Cap the vial and pack carefully for shipment.

SAMPLE PREPARATION:

8. Adjust the volume of solution in the vial to 15 mL.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six solutions covering the range 3 to 135 μg Aldrin or Lindane per sample.
   a. Add calibration stock solution with a microliter syringe to 15 mL isooctane in a vial.
   b. Analyze the working standards together with samples and blanks (steps 10 through 13).
   c. Prepare calibration graph (peak area vs. μg Aldrin or Lindane). Analyze three additional quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

10. Set gas chromatograph to manufacturer's specifications and to conditions given on page 5502-1.
11. Mix the contents of the scintillation vial thoroughly.
12. Inject 15 μL sample aliquot using solvent flush technique or autosampler.
    NOTE: Open vent valve for 20 sec, beginning with time of injection, to prevent the solvent peak from entering the furnace.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg, of Aldrin or Lindane found in the sample (filter plus bubbler), W, and average media blank (filter plus bubbler), B, from the measured peak areas and the calibration graph.
15. Calculate the concentration, C (mg/m^3), of Aldrin or Lindane in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Methods S275 (Aldrin) and S290 (Lindane) were issued on February 27, 1976, and March 26, 1976, respectively [2]. The substances used to generate test atmospheres at 25 °C and 760 mm Hg in dry air were Aldrite emulsifiable concentrate (64% Aldrin) and Ortho-Lindane Borer and Leaf Miner Spray [1]. Collection efficiencies and analytical method recoveries were 1.00 for both substances in the range 22 to 90 μg per sample. Sample filters extracted in isooctane immediately and stored one week at ambient conditions gave recoveries of 103% and 102%, respectively. Overall precision, $\hat{S}_{rT}$, was 0.092 for Aldrin and 0.086 for Lindane. No significant bias was found for either substance.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S275 and S290, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, V. 3, S275 and S290, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Hill, R.H. and J.E. Arnold. Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).
[4] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., ATSDR; S275 and S290 originally validated under NIOSH Contract CDC-99-74-45.

ALKALINE DUSTS 7401

NaOH, KOH, LiOH, and basic salts	MW : 40.00 (NaOH); 56.11 (KOH)	CAS: 1310-73-2 1310-58-3	RTECS: WB490000 (NaOH) TT2100000 (KOH)

METHOD: 7401, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 mg/m^3 (NaOH)
NIOSH: C 2 mg/m^3/15 min (NaOH); Group I Pesticide
ACGIH: C 2 mg/m^3 (NaOH)

PROPERTIES: basic, hygroscopic, caustic solids and aerosols; VP not significant

SYNONYMS: alkali; caustic soda; lye; sodium hydroxide; potassium hydroxide

SAMPLING

SAMPLER: FILTER (1-μm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 70 L @ 2 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.76 to 3.9 mg/m^3 [1] (360-L samples)
BIAS:	5.6%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.062 [1]
ACCURACY:	± 16.2%

MEASUREMENT

TECHNIQUE: ACID-BASE TITRATION

ANALYTE: OH^- (alkalinity)

EXTRACTION: 5.00 mL 0.01 N HCl, 15 min under nitrogen with stirring

TITRATION: 0.01 N NaOH under nitrogen, endpoint by pH electrode

CALIBRATION: 0.01 N NaOH standardized with 0.01 N HCl

RANGE: 0.14 to 1.9 mg (as NaOH) per sample [1]

ESTIMATED LOD: 0.03 mg per sample (as NaOH) [1] (7 x 10^{-4} moles of alkalinity)

PRECISION ($\bar{S}_r$): 0.033 @ 0.38 to 1.5 mg NaOH per sample [1]

APPLICABILITY: The working range is 0.4 to 5.4 mg/m^3 for a 360-L air sample. The method measures total alkalinity of alkali hydroxides, carbonates, borates, silicates, phosphates, and other basic salts, expressed as equivalents of NaOH.

INTERFERENCES: Carbon dioxide in the air may react with alkali on the filter to produce carbonates but does not interfere when titrated. The carbonates will produce the equivalent amount of strong alkali that was consumed on the filter [1]. Acid aerosols may neutralize the sample, if present, producing a negative interference.

OTHER METHODS: This revises Methods S381 [2] and P&CAM 241 [3].

REAGENTS:

1. Sodium carbonate, primary standard grade.
2. Hydrochloric acid stock solution, 0.1 N. Standardize with sodium carbonate primary standard.
3. Dilute hydrochloric acid, 0.01 N. Dilute 10.0 mL 0.1 N stock HCl to 100 mL in a volumetric flask with distilled water.
4. Water, distilled, CO_2-free. Boil and cool under N_2 or bubble nitrogen through distilled water for 30 min. Store with an Ascarite trap.
5. Nitrogen, compressed.
6. Sodium hydroxide, 50% w/v.* Dissolve 50 g NaOH in CO_2-free distilled water and dilute to 100 mL.
7. Stock sodium hydroxide, 0.1 N. Dilute 8 mL 50% NaOH to 1.0 L with CO_2-free distilled water. Store under Ascarite or other CO_2-absorbing trap.
8. Working sodium hydroxide solution, 0.01 N. Dilute 10 mL stock (0.1 N NaOH) to 100 mL with CO_2-free distilled water.
9. Standard buffer solutions, pH 4 and 7.

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter (Millipore, Fluoropore or equivalent), 1.0-μm pore size, supported by a cellulose backup pad in a cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. pH meter with pH electrode and recorder.
4. Titration vessel, 150 to 200 mL beaker, flask or jar with cover containing openings for the pH electrode and N_2 inlet and outlet.
5. Stirrer, magnetic, and stir bar.
6. Glass rod, ca. 5-mm diameter and 10 cm long to hold filter under liquid surface in titration vessel.
7. Pipets, 5- and 10-mL.
8. Volumetric flasks, 100-mL and 1-L.
9. Burets, 50-mL, readable to 0.1 mL.
10. Tweezers.

SPECIAL PRECAUTIONS: NaOH solutions are corrosive to tissue [4]. Handle with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 70 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer the sample filter to a titration vessel with tweezers. Place the filter face down in the titration vessel.
4. Place the end of a glass rod in the center of the filter to maintain the filter below the liquid surface during the analysis.
5. Cover the titration vessel, add 5.00 mL 0.01 N HCl, start the magnetic stirrer and N_2 purge (ca. 0.1 L/min).
6. Allow to stand 15 min (with stirring).

CALIBRATION AND QUALITY CONTROL:

7. Calibrate the pH meter with pH 4 and pH 7 buffer solutions.
8. Standardize aliquots of the 0.1 N HCl stock solution with sodium carbonate in triplicate [3].
   a. Dry 3 to 5 g primary standard grade Na_2CO_3 at 250 °C for 4 h. Cool in a desiccator.
   b. Weigh ca. 2.5 g Na_2CO_3 to the nearest mg. Dissolve and dilute to exactly 1 L with CO_2-free distilled water. The concentration is ca. 0.05 N Na_2CO_3.
   c. Place 5.00 mL 0.05 N Na_2CO_3 solution into a titration vessel and titrate potentiometrically to a pH of 5.

d. Remove electrodes, rinse them into the titration vessel, and bubble N_2 gas through contents of the titration vessel for 3 to 5 min to remove dissolved CO_2.
e. Proceed with the titration to the inflection point.
f. Calculate the normality of the stock HCl solution:

$$N_{HCl} = \frac{(\text{ g } Na_2CO_3 \text{ weighed })(\text{ mL } Na_2CO_3 \text{ solution used in titration })}{(\text{ 52.99 })(\text{ mL HCl used })}$$

9. Standardize the working (ca. 0.01 N) NaOH solution against the standardized HCl solution by following steps 8.c. and 8.e, substituting the standardized HCl stock solution for the Na_2CO_3 solution and the 0.01 N NaOH solution for the 0.1 N HCl solution. Calculate the normality of the NaOH titrating solution.

$$\underline{N}_{NaOH} = (N_{HCl})(\text{mL HCl used})/(\text{mL NaOH used})$$

10. Prepare at least three spiked media blank samples to check analytical recoveries at levels expected on the field samples.

MEASUREMENT:

11. Back-titrate the excess HCl in the samples, blanks and spiked blank solutions with the standardized NaOH solution while maintaining the N_2 purge.
12. Observe the pH meter. Calculate the endpoint (mL of 0.01 N NaOH used).

CALCULATIONS:

13. Using the normality (N) and volumes of NaOH in the titration of the sample ($V_{NaOH\text{-}s}$) and average blank filter ($V_{NaOH\text{-}b}$), and the volume of air sampled, V(L), calculate the concentration, C (mg/m^3), of alkalinity (as NaOH with equivalent weight = 40.0):

$$C = \frac{(V_{NaOH\text{-}b} - V_{NaOH\text{-}s}) \cdot N \cdot 4 \times 10^4}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S381 [1] was issued on July 8, 1977, and was validated using generated atmospheres of NaOH over the range 0.76 to 3.9 mg/m^3 using a 360-L sample [1,6]. Overall precision, $\hat{S}_{rT}$, was 0.062 with an average recovery of 105%, representing an insignificant bias. The NaOH concentration was independently verified by analyzing additional samples for sodium by atomic absorption spectrophotometry. An overall average collection efficiency of greater than 99% was found by sampling 1 to 360 L in an atmosphere of 7.50 mg/m^3 (NaOH) using backup Fluoropore filters and also by collecting two 615-L samples using backup impingers filled with water.

REFERENCES:

[1] Backup Data Report No. S381, Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, available as Order No. PB 275-838 from NTIS, Springfield, VA 22161 (July 8, 1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S381, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Ibid, V. 1, P&CAM 241, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[4] Criteria for a Recommended Standard...Occupational Exposure to Sodium Hydroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-105 (1975).

[5] Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, American Water Works Association and Water Pollution Control Federation (1981).

[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE; S381 originally validated under NIOSH Contract No. 210-76-0123.

ALLYL ALCOHOL

See ALCOHOLS III (METHOD 1402) for procedure

ALLYL CHLORIDE 1000

$CH_2 = CHCH_2Cl$ MW : 76.53 CAS: 107-05-1 RTECS: UC7350000

METHOD: 1000, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1 ppm
NIOSH: 1 ppm; STEL 2 ppm
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 3.13 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.938 g/mL @ 20 °C; BP 45 °C; MP −135 °C; VP 39.3 kPA (295 mm Hg) @ 25 °C; explosive range 3.3 to 11% v/v in air

SYNONYMS: 3-chloro-1-propene; 1-chloro-2-propene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 16 L @ 1 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.8 to 7.2 mg/m^3 [1] (100-L samples)

BIAS: 6.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [1]

ACCURACY: ± 16.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: allyl chloride

DESORPTION: 1 mL benzene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 185 to 200 °C
-DETECTOR: 250 °C
-COLUMN: 160 to 200 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6-mm OD; 50/80 mesh Porapak Q or equivalent

CALIBRATION: standard solutions of allyl chloride in benzene

RANGE: 0.05 to 1.5 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.023 [1]

APPLICABILITY: The working range is 0.16 to 3 ppm (0.5 to 10 mg/m^3) for a 100-L air sample. The method is applicable to short term samples taken at 1 L/min. The upper limit of loading depends on the concentrations of allyl chloride and other substances in the air, including water vapor.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S116 in a revised format [2].

REAGENTS:

1. Benzene, chromatographic quality.*
2. Allyl chloride.
3. Hexane.
4. Calibration stock solution, 7.5 μg/μL. Dilute 75 mg allyl chloride (80.0 μL at 20 °C) to 10 mL with hexane.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1000-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Benzene is a suspected human carcinogen. All work should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 16 to 100 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL benzene to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 1.5 mg allyl chloride per sample.
   a. Add known amounts of calibration stock solution to benzene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg allyl chloride).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg allyl chloride recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1000-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with benzene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of allyl chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of allyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S116 was issued on May 9, 1975 [2], and validated over the range 1.8 to 7.2 mg/m^3 at 25 °C and 759 mm Hg using a 100-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.071 with average recovery 105.5%, representing a non-significant bias. The concentration of allyl chloride was independently verified by direct gas chromatography. Desorption efficiency was 0.943 in the range 0.15 mg to 0.6 mg allyl chloride per sample. Breakthrough (5% on back section) occurred between 210 and 240 min when sampling an atmosphere containing 7.56 mg/m^3 allyl chloride at 0.94 L/min at 0% RH.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, NIOSH, S116, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S116, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE; originally validated under NIOSH Contract CDC-99-74-45.

ALLYL GLYCIDYL ETHER 2545

$CH_2=CHCH_2OCH_2CH(O)CH_2$ MW: 114.14 CAS: 106-92-3 RTECS: RR0875000

METHOD: 2545, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 10 ppm
NIOSH: 5 ppm; STEL 10 ppm (skin)
ACGIH: 5 ppm; STEL 10 ppm (skin)
(1 ppm = 4.67 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.970 g/mL @ 20 °C; BP 154 °C; VP 0.63 kPa (4.7 mm Hg, 0.62%) @ 25 °C

SYNONYMS: 1-allyloxy-2,3-epoxypropane; ((2-propenyloxy)methyl)oxirane; AGE

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Tenax GC; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1.5 L @ 5 ppm
-MAX: 8 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 19 to 87 mg/m^3 [1] (3-L samples)

BIAS: −1.3% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ±12.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: allyl glycidyl ether

DESORPTION: 2 mL diethyl ether, 30 min

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 280 °C
-COLUMN: 150 °C

INJECTION VOLUME: 2 μL

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 3.2-mm ID x 6.1 m, packed with 10% FFAP on 100/120 mesh Supelcoport

CALIBRATION: standard solutions of allyl glycidyl ether and internal standard in diethyl ether

RANGE: 30 to 300 μg per sample

ESTIMATED LOD: 10 μg per sample

PRECISION ($\bar{S}_r$): 0.034 [1]

APPLICABILITY: The working range is 2 to 20 ppm (10 to 100 mg/m^3) for a 3-L air sample. An appropriate capillary column may be used for better resolution and sensitivity.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S346 [2] in a revised format.

REAGENTS:

1. Allyl glycidyl ether*, reagent grade.
2. Diethyl ether*, anhydrous, containing approximately 0.1 mg/mL isoamyl alcohol or other suitable internal standard.
3. Hexane.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 10 cm long, 8-mm OD, 6-mm ID; flame-sealed ends with plastic caps, containing two sections of 35/60 mesh Tenax GC (front = 100 mg; back = 50 mg) separated by a urethane foam plug. A silanized glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1.0 L/min air flow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 2545-1).
4. Vials, 5-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Flasks, volumetric, 10-mL.
7. Pipets, 2-mL.

SPECIAL PRECAUTIONS: Allyl glycidyl ether is flammable (flash point = 57 °C) and a moderate skin and severe eye irritant [3]. Diethyl ether is a serious fire and explosion hazard (flash point = −45 °C) and may form explosive peroxides during storage. All work with these compounds must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 1.5 to 8 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL diethyl ether to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 10 to 800 μg allyl glycidyl ether per sample.
   a. Add a known amount of allyl glycidyl ether to diethyl ether in 10-mL volumetric flask and dilute to the mark. Use serial dilutions as needed for smaller concentrations.

b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of allyl glycidyl ether peak area to internal standard peak area vs. μg allyl glycidyl ether per 2 mL).

9. Determine desorption efficiency (DE) at least once per year for each lot of Tenax GC used for sampling in the range of interest. Determine for three samplers at each of five concentrations plus three media blanks.
   a. Transfer front sorbent section of media blank sampler to a 5-mL vial.
   b. Inject known amount (1 to 10 μL) of allyl glycidyl ether or standard solution of allyl glycidyl ether in hexane directly into sorbent in vial with a microliter syringe.
      NOTE: Standard solutions for DE determination should not contain internal standard.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg allyl glycidyl ether recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2545-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with diethyl ether, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak areas. Divide peak area of allyl glycidyl ether by peak area of internal standard for each chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of allyl glycidyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    Note: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of allyl glycidyl ether in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S346 was issued on January 21, 1977 [2] and was validated over the range 19 to 87 mg/m^3 for 3-L air samples from dynamically generated test atmospheres [1]. The average recoveries ranged from 98.2 to 99.5%. The allyl glycidyl ether concentrations were independently calculated from analyte delivery rate and air dilution ratios. Breakthrough was observed after sampling 12 L from a test atmosphere containing 87 mg/m^3 of allyl glycidyl ether at 90% relative humidity. Desorption efficiency ranged from 101% to 89.8% for loadings of 67 to 269 μg allyl glycidyl ether per sample. A storage stability study gave average recoveries of 96.9% for 7-day storage versus 98.1% for 1-day storage.

REFERENCES:

[1] Backup Data Report for Allyl Glycidyl Ether, No. S346, prepared under NIOSH Contract No. 210-76-0123.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S346, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE. Method S346 was originally validated under NIOSH Contract No. 210-76-0123.

ALUMINUM and compounds, as Al

Al MW: 26.98 (Al); 101.96 (Al_2O_3) CAS: 7429-90-5 (Al); 1344-28-1 (Al_2O_3) RTECS: BD0330000

METHOD: 7013, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: see table 1
ACGIH: see table 1

PROPERTIES: ductile metal; valence 3; MP 660 °C

SYNONYMS: vary depending upon the compound; alumina (Al_2O_3)

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not evaluated

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: aluminum

ASHING: conc. HNO_3, 6 mL; 140 °C

FINAL SOLUTION: 10% HNO_3, 10 mL
1000 μg/mL Cs

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 309.3 nm

BACKGROUND CORRECTION: none used

CALIBRATION: Al^{3+} in 10% HNO_3

RANGE: 50 to 5000 μg per sample [1]

ESTIMATED LOD: 2 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.03 [1,2]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 100-L sample. This is an elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure. Aliquots of the samples can be analyzed separately for approximately four additional metals.

INTERFERENCES: Cesium at 1000 μg/mL controls ionization in the nitrous oxide-acetylene flame [3]. Iron and HCl at greater than 0.2% (w/w) decrease the sensitivity. Vanadium or H_2SO_4 require 1% (w/w) La as a releasing agent [4].

OTHER METHODS: This is Method P&CAM 173 for Al [1] in a revised format. Method 7300 (ICP-AES) is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 μg Al/mL. Commercially available or dissolve 1.000 g Al wire in minimum volume of (1+1) HCl using small drop of Hg as catalyst. Dilute to 1 L with 1% (v/v) HCl.
4. Cs solution, 50 mg/mL. Dissolve 73.40 g $CsNO_3$ in 100 mL water; dilute to 1 L.
5. Nitrous oxide.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and aluminum hollow cathode lamp.
4. Regulators, two-stage, for N_2O and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Micropipets, 5 to 500 μL.*
8. Hotplate, surface temperature 100 to 140 °C.

* Clean with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: Alumina (Al_2O_3) will not be dissolved by this procedure. Lithium borate fusion is necessary to dissolve alumina. The following sample preparation gave quantitative recovery for soluble aluminum compounds (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassettes and transfer the samples and blanks to separate clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 10% HNO_3.
7. Place the beakers on a hotplate and allow to go to a small liquid volume (ca. 0.5 mL).
8. When sample is dry, rinse walls of beaker with 3 to 5 mL 10% HNO_3. Reheat for 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 10-mL volumetric flask containing 0.2 mL 50 mg/mL Cs solution. Dilute to volume with 10% HNO_3.
   NOTE: If vanadium or sulfuric acid are present, add 1% (w/w) La as a releasing agent [1,3].

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts, covering the range 0 to 500 mg Al per sample, of calibration stock solution to 100-mL volumetric flasks containing 2.0 mL 50 mg/mL Cs solution and dilute to volume with 10% HNO_3.

11. Analyze the working standards together with the samples and blanks (steps 16 and 17).
12. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
13. Aspirate a standard for every 10 samples to check instrument drift.
14. Check recoveries with at least one spiked media blank per 10 samples.
15. Use method of additions occasionally to check for interferences.

MEASUREMENT:

16. Set spectrophotometer according to manufacturer's instructions and to conditions on page 7013-1.
17. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 10% HNO_3 and an appropriate amount of the 50 mg/mL Cs solution, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of aluminum in the sample, C_s, and average media blank, C_b, from the calibration graph.
19. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of aluminum in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Estimated LOD was 2 μg Al per sample [2]. Only the analytical procedure was evaluated for this method.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] User check, UBTL, NIOSH Seq. #3990-0 (unpublished, November 29, 1983).
[3] Winefordner, J. D., Ed., Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
[4] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS.

TABLE 1 - ALUMINUM EXPOSURE LIMITS

	OSHA mg/m^3	NIOSH mg/m^3	ACGIH mg/m^3
Total Dust	no PEL	10	10
Respirable Fraction	no PEL	5	--
Pyro powders	no PEL	5	5
Welding fumes	no PEL	5	5
Soluble salts	no PEL	2	2
Alkyls	no PEL	2	2

AMINES, ALIPHATIC 2010

(1) Diethylamine: $(C_2H_5)_2NH$	MW: 73.14	CAS: 109-89-7	RTECS: HZ8750000
(2) Dimethylamine: $(CH_3)_2NH$	45.08	124-40-3	IP8750000

METHOD: 2010, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : See Table 1
NIOSH: See Table 1
ACGIH: See Table 1

PROPERTIES: See Table 1

SYNONYMS: (1) DEA; N,N-diethamine; N-ethylethanamine;
(2) N-methylmethanamine; DMA

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg / 75 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 3 L @ OSHA standards (Table 1)
-MAX: 30 L

SHIPMENT: refrigerated

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: (1) −5.0%; (2) 0.8%

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: (1) ±16.0%; (2) ±12.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: amines listed above

DESORPTION: 1 mL dilute H_2SO_4 in 10% (v/v) aqueous methanol, 3 h ultrasonic

INJECTION VOLUME: 1 µL

COLUMN: 1.8 m x 4-mm ID glass, 4% Carbowax 20M + 0.8% KOH on Carbosieve B (60/80 mesh)

CARRIER GAS: nitrogen, 30 mL/min

CALIBRATION: standard solutions of analyte in dilute sulfuric acid

RANGE: (1) 0.5 to 11 mg per sample [1]
(2) 0.15 to 2.6 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: The working ranges for 20-L air samples are 8 to 183 ppm (25 to 550 mg/m^3) for diethylamine and 4 to 71 ppm (7.5 to 130 mg/m^3) for dimethylamine. A nitrogen-specific detector instead of an FID will greatly increase sensitivity. This alternative detector has been used for amines with a 30 m x 0.25-mm x 0.25-µm film DB-5 fused-silica capillary column, with column temperature 60 °C for 1 min, programmed to 300 °C at 10°/min; detector, 300 °C and injector, 250 °C.

INTERFERENCES: This method has been evaluated only in dry air [1]. Silica gel may have a reduced capacity at high humidity. The methanol peak could interfere in low-level analyses.

OTHER METHODS: This revises and combines Methods S139 and S142 [2]. The methods for other aliphatic amines are similar [3,4,5,6]. To avoid possible sample instability on silica gel, OSHA developed a method (OSHA 34) which employs XAD-7 coated with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole for sampling followed by HPLC of the derivative [7].

REAGENTS:

1. Sulfuric acid, 0.1 M, in 10% (v/v) aqueous methanol (90% H_2O + 10% methanol).*
2. Potassium hydroxide (KOH) solution, 0.3 M.*
3. Amines, highest purity available.*
   NOTE: Dimethylamine is commercially available as a 40% aqueous solution (Aldrich Co. or equivalent).
4. Calibration stock solution.* Dilute 1 mL of amine to 10 mL with deionized water. Check concentration by titrating with standard sulfuric acid.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, compressed and filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube flame-sealed ends, with plastic caps, 7 cm x 6-mm OD x 4-mm ID, containing two sections of 20/40 mesh silica gel (front = 150 mg; back = 75 mg). Silanized glass wool plug precedes front. Urethane foam plugs, separate and retain the back section. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Refrigerated, bagged ("Blue-Ice," or equivalent).
4. Gas chromatograph, FID, integrator, and column (page 2010-1).
5. Vials, glass, 2-mL, with PTFE-lined caps.
6. Ultrasonic bath.
7. Syringes, 20-μL, 10-μL, 1-μL.
8. Pipets, 0.5-, 1-, 2-, and 10-mL.
9. Volumetric flasks, 10-mL.
10. File.
11. Tweezers.

SPECIAL PRECAUTIONS: The amines are highly flammable and have strong ammoniacal odors. They can cause severe eye damage and can easily be absorbed through the skin [8]. Sulfuric acid is highly corrosive, and potassium hydroxide is caustic. All work with these compounds should be performed in a hood. Use proper protective clothing including gloves, safety glasses, and laboratory coat.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the samplers immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1.0 L/min for a total sample size of 3 to 30 L.
4. Cap the samplers and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 0.1 M H_2SO_4 in aqueous methanol. Tightly cap the vial.
7. Agitate the vials in ultrasonic water bath for 3 h.
   NOTE: The water in the ultrasonic bath can get hot (ca. 50-60 °C) during the desorption period. Therefore, all vials must be tightly capped to minimize evaporation losses.
8. Neutralize the sample solution as follows: let silica gel particles settle for a few minutes. Transfer a 500-μL aliquot of the supernatant liquid to a clean vial. Add 500 μL 0.3 M KOH. (The pH of the solution should be greater than 10). Analyze the solutions immediately (steps 12 through 14).
   NOTE: Ensure that no silica gel is present when adding KOH to prevent loss of analyte [1].

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of interest.
   a. Add aliquots of the calibration stock solutions to 10-mL volumetric flasks and dilute to the mark with 0.1 M sulfuric acid in aqueous methanol.
   b. Neutralize the standards as in step 8.
   c. Analyze with samples and blanks (steps 12 through 14).
   d. Prepare a calibration graph (peak area or peak height vs. mg of amine per sample).
10. Determine desorption (DE) at least once for each lot of silica gel used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus media blanks.
   a. Measure the amount of silica gel used in the front sorbent section into a vial.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a dilution there of directly onto the silica gel.
   c. Cap vial. Allow to stand overnight.
   d. Desorb and neutralize as in steps 6 through 8.
   e. Analyze together with working standards and blanks (steps 12 through 14).
   f. Prepare a graph of DE vs. mg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2010-1. Use the following conditions as a guide.

	Temperature (°C)		
Compound	Injection	Column	Detector
Diethylamine	160	70	200
Dimethylamine	155	60	200

NOTE: Use a removable glass liner at the inlet to the GC column. Remove the glass liner from the gas chromatograph and clean it with water and acetone rinses at the end of each day. In order to prevent salt buildup, the glass GC liner was soaked in a saturated KOH solution and packed with KOH-coated glass wool [9].

13. Inject sample aliquot manually using solvent flush technique or with autosampler.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, mg (corrected for DE), of analytes found in sample front (W_f) and back (Wb) sorbent sections and in the media blank front (B_f) and blank back (B_b) sorbent sections from the calibration graph.
16. Calculate concentration of analyte, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions, biases, and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard [1,2,3]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere. Sample stability was not determined.

Substance	SAMPLING			MEASUREMENT			OVERALL		
	BT[a] Vol. (L)	Conc. (mg/m^3)	Range (mg/m^3)	Range (mg/sample)	Precision ($\hat{S}_r$)	DE	Bias (%)	Precision ($\hat{S}_{rT}$)	Accuracy (±%)
Diethylamine	>46	160	36-165	1.8-7.1	0.02	0.82	5	0.07	18.7
Dimethylamine	>45.6	42.5	7.02-29.5	0.4-1.7	0.03	0.92	1.1	0.062	13.2

[a]Breakthrough (BT) experiments performed at flow rate of 0.2 L/min.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd. ed., Vol. 3, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[3] Ibid., Vol. 1, P&CAM 221, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[4] Ibid., S144, S146, and S150.

[5] Campbell, Evan E., G.O. Wood, and R.G. Anderson. "Development of Air Sampling Techniques," Los Alamos Scientific Laboratory, Progress Reports (unpublished) LA-5634-PR (June 1974), LA-5973-PR (July 1975), and LA-6057-PR (September 1975).

[6] Wood, G.O. and R.G. Anderson. "Development of Air Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory, Progress Reports (unpublished) LA-6216-PR (February 1976) and LA-6513-PR (September 1976).

[7] OSHA Manual of Analytical Methods, USDOL OSHA Salt Lake City Technical Center, Salt Lake City, UT. Available from ACGIH, Cincinnati, OH (1991).

[8] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981).

[9] Andre, C.E. and A.R. Mosier. "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," Anal. Chem., 45. 1971 (1973).

METHOD REVISED BY:

Paula Fey O'Connor, NIOSH/DPSE.

Table 1. Exposure Limits and Properties.

Compound	Exposure Limits, ppm			mg/m^3/ppm @ NTP	Properties
	OSHA	NIOSH	ACGIH		
Diethylamine	25	10; STEL 25	5 (skin) STEL 15	2.99	Liquid; d 0.708 g/mL @ 20 °C; MP −50 °C; BP 55.5 °C; vapor density (air = 1) 2.5; VP 25.9 kPa (195 mm Hg) @ 20 °C; explosive limits in air 1.8 to 10.1% (v/v)
Dimethylamine	10	10	5; STEL 5	1.84	Gas; MP −92.2 °C; BP 6.88 °C; vapor density (air = 1) 1.6; VP 173.9 kPa (1307.2 mm Hg) @ 20 °C; explosive limits in air 2.8 to 14% (v/v)

AMINES, AROMATIC 2002

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 2002, Issue 2 **EVALUATION: FULL (1-3); PARTIAL (4,5)** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

SYNONYMS: (1) aniline: benzenamine; aminobenzene; phenylamine
(2) o-toluidine: 2-aminotoluene
(3) 2,4-xylidine: 2,4-dimethylaniline; dimethylaminobenzene
(4) N,N-dimethyl-p-toluidine: p-dimethylaminotoluene
(5) N,N-dimethylaniline: N,N-dimethylbenzeneamine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: Table 2

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: (1), (2), and (3) stable for ≥ 7 days [1]; stability data not available for (4) and (5)

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: amines listed above

DESORPTION: 1 mL 95% ethanol; 1 h in ultrasonic bath

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: stainless steel, 0.6 m x 3-mm OD, packed with 80/100 mesh Chromosorb 103

CALIBRATION: standard solutions of analytes in 95% ethanol

RANGE: 0.1 to 3 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]; not determined for (3)

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: See Table 2 for working ranges. A modification of this method has been used for aniline and o-toluidine at a vulcanized rubber manufacturing plant [2]. Applicability of this method for simultaneous determination of the analytes has not been investigated. A nitrogen-specific GC detector instead of an FID will greatly increase sensitivity.

INTERFERENCES: None known. Silica gel has reduced capacity for organic compounds at high humidity.

OTHER METHODS: This combines Methods S162 (xylidine) [3], S164 (dimethylaniline) [3], S168 (o-toluidine) [3], S310 (aniline) [3], P&CAM 280 (N,N-dimethyl-p-toluidine) [4], and P&CAM 168 (aromatic amines) [5,6].

REAGENTS:

1. Ethanol, 95%, non-denatured, chromatographic quality.
2. n-Hexane.
3. Benzene.*
4. Analytes, reagent grade.*
5. Aniline calibration stock solution, 102.2 mg/mL.* Dissolve 1 mL anlline in 2 mL benzene; dilute to 10 mL with hexane.
   NOTE: Benzene possibly could be replaced with toluene, alcohol, or acetone to minimize the analyst's exposure to suspect carcinogens. Effects of this substitution are not known and should be tested.
6. o-Toluidine calibration stock solution, 100.6 mg/mL.* Dilute 1 mL o-toluidine to 10 mL with n-hexane.
7. 2,4-Xylidine calibration stock solution, 97.8 mg/mL.* Dilute 1 mL 2,4-xylidine to 10 mL with n-hexane.
8. N,N-Dimethyl-p-toluidine calibration stock solution, 93.5 mg/mL.* Dilute 1 mL N,N-dimethyl-p-toluidine to 10 mL with n-hexane.
9. N,N-Dimethylaniline calibration stock solution, 95.6 mg/mL.* Dilute 1 mL N,N-dimethylaniline to 10 mL with hexane.
10. Hydrogen, prepurified.
11. Helium, purified.
12. Nitrogen, purified.
13. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; with plastic caps; containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg; back = 75 mg). For N,N-dimethyl-p-toluidine, a front section of 100 mg and back section of 50 mg may be used. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2002-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-, 25-, 50- and 100-μL.
6. Pipets, 1- and 2-mL.
7. Ultrasonic bath.
8. File.
9. Tweezers.
10. Flasks, volumetric, 10-mL.

SPECIAL PRECAUTIONS: n-Hexane and ethanol are flammable. Aniline, o-toluidine, 2,4-xylidine, and benzene are suspect carcinogens [7,8]. Absorption through skin is a potential hazard. All work with these chemicals should be performed in a hood. Use proper protective clothing including gloves. Analytes (1), (2), (3), and (5) are severe poisons.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate for a total sample size according to Table 3.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 95% ethanol to each vial. Attach crimp cap to each vial.
7. Agitate 1 h in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 3 mg analyte per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, in n-hexane to 95% ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a dilution thereof, in hexane directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2002-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Use the following conditions as a guide (these were used in development of the methods [1]):

	TEMPERATURES, °C		
COMPOUND	Injection	Column	Detector
Aniline	230	165	245
o-Toluidine	240	180	265
2,4-Xylidine	230	170	235
N,N-Dimethyl-p-toluidine	250	180	250
N,N-Dimethylaniline	150	100 for 4 min, then 8°C/min to 225	250

NOTE: If peak response is above the linear range of the working standards, dilute with 95% ethanol, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area or height.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_B - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions, biases and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one and two times the OSHA standard [1]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere. The first three analytes were stable on silica gel for at least one week. Method S164 using collection on activated charcoal was also developed for N,N-dimethylaniline [3].

Substance	Sampling: Breakthrough volume in dry air at concentration (L)	Sampling: Breakthrough volume in dry air at concentration (mg/m^3)	Range mg/m^3 (volume)	Bias (%)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)	Measurement: Range (mg)	Measurement: Precision ($\hat{S}_r$)	Desorption efficiency
Aniline	>44.4	38	9.5-38.2 (20 L)	-4.9	0.60	±15.1	0.20-0.82	0.013	0.980-1.00
o-Toluidine	>221.3	47	11.7-46.9 (50 L)	-1.5	0.060	±12.0	0.55-2.2	0.032	0.970-0.983
2,4-Xylidine	>44.4	50	12.5-50.0 (20 L)	-1.2	0.057	±11.2	0.25-1.01	0.021	0.959-1.015
N,N-Dimethyl-p-toluidine	*	*	9.4-30.0 (100 L)	*	*	*	0.47	0.035	0.88
N,N-Dimethyl-aniline	*	*	*	-7.9	0.090	±16.0	0.05-3.0	*	0.997 (1.9-mg samples)

*Not determined

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] UBTL, Inc., Sequence #2300-S, Aniline (May 15, 1980), and Sequence #2551-M, o-Toluidine (August 28, 1980) (NIOSH, unpublished).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Ibid., Vol. 4, P&CAM 280, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[5] Ibid., Vol. 1, P&CAM 168, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] Campbell, E. E., G. O. Wood and R. G. Anderson. Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR and LA-5634-PR, Los Alamos, NM (November, 1972; January, 1973; June, 1973; August, 1973; December, 1973; and June, 1974).

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METHOD WRITTEN BY:

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TABLE 1. PHYSICAL PROPERTIES AND PERSONAL EXPOSURE LIMITS

Substance Formula	MW	BP (°C)	MP (°C)	d, g/mL @ 20 °C	VP @ 20 °C kPa (mm Hg)	Conversion factor (ppm to mg/m^3 @ NTP)
Aniline; C_6H_7N	93.13	184	-6	1.022	0.089 (0.3)	3.81
o-Toluidine; C_7H_9N	107.16	200	-15	1.006	0.043 (0.32)	4.38
2,4-Xylidine; $C_8H_{11}N$	121.18	214	-14	0.9723	<0.1 (<1)	4.95
N,N-Dimethyl-p-toluidine; $C_9H_{13}N$	135.21	211	NA	0.935	NA	5.53
N,N-Dimethylaniline; $C_8H_{11}N$	121.18	192	2	0.956	<0.1 (0.5)	4.95

NA = not available.

TABLE 2. GENERAL INFORMATION.

Substance	CAS	RTECS	Exposure Limits (ppm) OSHA	NIOSH	ACGIH
Aniline	62-53-3	BW6650000	5 (skin)	lowest feasible (carcinogen)	2 (skin)
o-Toluidine	95-53-4	XU2975000	5 (skin)	lowest feasible (carcinogen; skin)	2 (skin) (carcinogen)
2,4-Xylidine	1300-73-8	ZE8575000	5 (skin)	2 (skin)	0.5 (skin)
N,N-Dimethyl-p-toluidine	99-97-8	XU5803000	-----	-----	-----
N,N-Dimethylaniline	121-69-7	BX4275000	5 (skin)	5 TWA; 10 STEL (skin)	5 TWA; 10 STEL (skin)

TABLE 3. SAMPLING FLOW RATES AND VOLUMES.

Substance	SAMPLING Flow Rate (L/min)	Volume (L) MIN	MAX	Working Range (mg/m^3)
Aniline	0.02 - 0.2	5	30	5 - 60 (20-L samples)
o-Toluidine	0.02 - 1.0	10	150	5 - 60 (55-L samples)
2,4-Xylidine	0.02 - 0.2	3	20	3 - 75 (20-L samples)
N,N-Dimethyl-p-toluidine	0.02 - 1.0	*	*	9 - 30 (100-L samples)
N,N-Dimethylaniline	0.02 - 1.0	3	30	1.3 - 79 (38-L samples)

*Not determined.

AMINOETHANOL COMPOUNDS I 2007

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 2007, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS and SYNONYMS: 2-aminoethanol: ethanolamine; 2-hydroxyethylamine
2-dibutylaminoethanol: 2-n-dibutylaminoethanol; DBAE
2-diethylaminoethanol: 2-hydroxytriethylamine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 300 mg/150 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 4 L
-MAX: 24 L

FIELD TREATMENT: add 20 μL conc. HCl to silica gel immediately after sampling

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1,2]

BIAS: − 2.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056 [2]

ACCURACY: ± 12.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 2 mL 4:1 (v/v) methanol:water; stand 2 h with occasional shaking

INJECTION VOLUME: 3 μL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C, 3 min; 90 to 225 °C @ 16°/min, hold 6 min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 1.8 m x 2-mm ID silanized glass, 10% Carbowax 20 M + 2% KOH on 80/100 mesh Chromosorb WAW

CALIBRATION: solutions of analyte in 4:1 methanol:water containing 0.12 N HCl

RANGE: 0.1 to 6 mg per sample [2]

ESTIMATED LOD: 0.005 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.026 @ 0.6 to 2.7 mg per sample [2]

APPLICABILITY: The working range is 5 to 300 mg/m^3 for each compound in a 20-L air sample. Water vapor does not significantly affect collection efficiency [3]. Sensitivity may be improved at least ten-fold by using a photoionization or nitrogen-selective detector.

INTERFERENCES: None identified [3]. The chromatographic column or separation conditions may be changed to circumvent interference problems. A DB-5 fused silica capillary column may be used.

OTHER METHODS: This revises P&CAM 270 [3], S140 [4], and Method 2007 (dated 5/15/85).

REAGENTS:

1. Eluent: Four parts methanol to one part distilled water (v/v).
   NOTE: Do not use deionized water which may contain formaldehyde.
2. Analyte, reagent grade.*
3. Alkalinizing solution: 0.20 N NaOH (8.0 g NaOH/L) in eluent.
4. HCl, conc. (38%, 12 N) (needed for field use).*
5. HCl, 0.12 N, in eluent. Dilute 10.0 mL conc. HCl with eluent to make 1 L solution.
6. Benzaldehyde.
7. Calibration stock solutions, 10 mg/mL, in 0.12 N HCl in eluent for each analyte.
8. Nitrogen or helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.
11. pH paper.
12. KOH, saturated solution.
13. Glass wool.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 45/60 mesh chromatographic grade silica gel (front = 300 mg; back = 150 mg) separated by a plug of silylated glass wool. A silylated plug of glass wool is at each end of the tube. Pressure drop across the tube at 0.2 L/min airflow must be less than 3.2 kPa. Tubes are commercially available. Do not use sampling tubes constructed with metal parts or urethane foam plugs. Conc. HCl will react with these materials.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Syringe for dispensing HCl, 50-μL with glass barrel, PTFE-tipped plunger and inert (platinum or PTFE) needle (for field use).
4. Gas chromatograph, FID, integrator and column (page 2007-1).
5. Coated capillary injection port liner: Soak liner and small quantity of glass wool in saturated KOH. Air-dry liner and glass wool. Loosely pack glass wool in liner.
6. Vials, 2-mL, glass, PTFE-lined crimp caps.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-μL, readable to 0.1 μL.
9. Micropipets, 10- to 100-μL.
10. Pipets, 0.5- and 2-mL, with pipet bulb.

SPECIAL PRECAUTIONS: The analytes are eye irritants [5]. Avoid skin contact or inhalation of conc. HCl.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 4 to 24 L.
   NOTE: If samples are to be eluted immediately or will be stored in a freezer for less than 14 days, the following step may be eliminated.
4. Immediately after sampling, stabilize the samples by adding exactly 20 μL conc. HCl to each section of silica gel in each sampler using a syringe.
   NOTE 1: The amount of HCl added must be measured carefully because the sample will be neutralized and made alkaline (step 9) for proper chromatography.
   NOTE 2: Iron impurities in silica gel will turn yellow upon addition of acid.
5. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

6. Place the first glass wool plug and the front section of the sampler in a vial. Place the second plug and backup section in a separate vial.
7. Add 2.0 mL eluent to each vial. Attach cap to each vial.
   NOTE: If conc. HCl was not added to the silica gel after sampling, desorb the samples in 2.0 mL 0.12 N HCl in eluent. The acid increases desorption efficiency.
8. Allow to stand 2 h with occasional agitation.
9. Transfer a 0.5-mL aliquot of each sample to another vial. Add 0.5 mL alkalinizing solution and attach cap. Mix thoroughly. Check the solution pH with pH paper. If the solution pH is <9 add alkalinizing solution until solution pH is >9.
10. If 2-aminoethanol is present, repeat step 9 with another 0.5-mL aliquot. Add 10 μL benzaldehyde to the basic solution, mix thoroughly and let stand 20 min.
    NOTE: Benzaldehyde derivatizes 2-aminoethanol to 2-benzylideneaminoethanol which has a higher molecular weight, thereby decreasing the GC detection limit. Underivatized 2-aminoethanol can be determined by this method if the sample size is large.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 0.005 to 6 mg of each analyte.
    a. Add known amounts of analyte or calibration stock solution to 0.12 N HCl in eluent in 10-mL volumetric flasks and dilute to the mark.
    b. Treat the working standards with base and benzaldehyde as needed (steps 9 and 10).
    c. Analyze together with samples and blanks (steps 14 and 15).
    d. Prepare calibration graph (peak area vs. mg analyte).
12. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
    c. Add 20.0 μL conc. HCl.
    d. Cap the tube. Allow to stand overnight.
    e. Desorb (steps 6 through 10) and analyze with working standards (steps 14 and 15).
    f. Prepare a graph of DE vs. mg analyte recovered.
13. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

14. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2007-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The temperature program separates all three compounds. Isothermal column conditions are 225, 150, and 90 °C for 2-aminoethanol, 2-dibutylaminoethanol and 2-diethylaminoethanol, respectively. The column packing degrades rapidly at 225 °C; keep operating time at a minimum near this temperature.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
    NOTE 3: When using a capillary column system, use the split injection port liner coated with KOH to improve amine peak shape.
15. Measure peak area.

CALCULATIONS:

16. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

All three compounds were evaluated under Method P&CAM 270 using a smaller bed of silica gel (front = 150 mg; back = 150 mg) than given above [3]. Desorption efficiencies for 0.1 mg analyte were found to be 0.97 for 2-aminoethanol, 0.85 for 2-diethylaminoethanol, and 0.93 for 2-dibutylaminoethanol [3]. Only 2-diethylaminoethanol was evaluated under Method S140 using the suggested sorbent tube. In all cases, laboratory testing was performed with spiked samples and generated atmosphere [1,2,6]. All analytes were stable on silica gel up to four weeks when stabilized with acid. Results were:

Compound	Method	Range Studied (mg/m^3)	Sample size (L)	Precision	
				Measurement ($\bar{S}_r$)	Overall ($\hat{S}_{rT}$)
2-aminoethanol	P&CAM 270 [3]	30.4 to 63.6	30	<0.070	0.057
2-dibutylaminoethanol	P&CAM 270 [3]	unknown	unknown	unknown	unknown
2-diethylaminoethanol	S140 [4]	25 to 113	24	0.026	0.056

Method S140 [4] was issued on January 19, 1979, and validated over the range 25 to 113 mg/m^3 at 23 °C and 762 mm Hg using 24-L samples [2,7]. Coast Engineering Laboratory 40/60 mesh silica gel was the collecting medium. Average recovery was 97.1%, representing a non-significant bias. The concentration of 2-diethylaminoethanol was independently verified using midget bubblers containing 15 mL 2% HCl. Desorption efficiency was 0.964 in the range 0.6 to 2.3 mg per sample. Breakthrough (5% on back section) was not achieved after 5.3 h when sampling an atmosphere containing 88 mg/m^3 2-diethylaminoethanol at 0.2 L/min at 82% relative humidity.

REFERENCES:

[1] Wood, G. O. and J. W. Nickols. Development of Air-Monitoring Techniques Using Solid Sorbents, October 1, 1976 - December 31, 1977, Progress Report LA-7295-PR, Los Alamos Scientific Laboratory, Los Alamos, NM, NIOSH IA-77-12 (1978).

[2] Backup Data Report No. S140, prepared under NIOSH Contract 210-76-0123 (NIOSH, unpublished, 1979); Report on NIOSH Sequence #5162 (unpublished, April 2, 1986).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 270, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

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METHOD REVISED BY:

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TABLE 1. STRUCTURAL FORMULAS, MOLECULAR WEIGHTS, PERMISSIBLE EXPOSURE LIMITS AND PROPERTIES.

Compound	CAS RTECS	Formula	MW	mg/m^3 = 1 ppm @ NTP	OSHA NIOSH ACGIH (ppm)	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
2-aminoethanol	141-43-5 KJ5775000	$HOCH_2CH_2NH_2$	61.08	2.50	3 TWA 3 TWA; 6 STEL 3 TWA; 6 STEL	171	48 kPa (470 ppm)	1.0180
2-dibutylamino-ethanol	102-81-8 KK3850000	$(C_4H_9)_2N(CH_2)_2OH$	173.30	7.09	no standard 2 TWA (skin) 2 TWA (skin)	228	not available	0.859
2-diethylamino-ethanol	100-37-8 KK5075000	$(C_2H_5)_2N(CH_2)_2OH$	117.19	4.79	10 TWA (skin) 10 TWA (skin) 10 TWA (skin)	163	130 kPa (1300 ppm)	0.8921

(1) $HOCH_2CH_2NH_2$	MW: 61.10	CAS: 141-43-5	RTECS: KJ5775000
(2) $(HOCH_2CH_2)_2NH$	105.14	111-42-2	KL2975000
(3) $(HOCH_2CH_2)_3N$	149.19	102-71-6	KL9275000

METHOD: 3509, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) 2-aminoethanol; monoethanolamine; MEA
(2) 2,2'-iminodiethanol; diethanolamine; DEA
(3) 2,2',2"- nitrilotriethanol; triethanolamine; TEA

SAMPLING

SAMPLER: IMPINGER
(15 mL 2 mM hexanesulfonic acid)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 5 L
-MAX: 300 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 3 weeks @ 20 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1] and Table 2

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, ion pairing [2,3]

ANALYTE: MEA, DEA, TEA

INJECTION LOOP VOLUME: 50 µL

ELUENT: 2 mM hexanesulfonic acid (HSA), 1 mL/min (2 mM HSA/0.5% v/v acetonitrile may also be used to reduce run time)

COLUMNS: Ion-pairing guard and cation separator, Dionex MPIC-NG1,MPIC-NS1, and cation suppressor

CONDUCTIVITY SETTING: 3 µS full scale

RANGE: see EVALUATION OF METHOD [1] and Table 2

ESTIMATED LOD: 7 to 20 µg per sample (Table 2)

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD [1] and Table 2

APPLICABILITY: The working ranges for MEA, DEA, and TEA are 0.08 to 12 ppm (0.2 to 30 mg/m^3), 0.09 to 7 ppm (0.4 to 30 mg/m^3) and 0.1 to 5 ppm (0.6 to 30 mg/m^3), respectively, for a 100-L air sample. The method is better suited to area sampling than personal sampling because it uses an impinger for sample collection.

INTERFERENCES: Larger amines such as cocmorpholine, triethylenediamine, 4-ethylmorpholine, 2-oxybis(N,N-dimethyl)ethylamine, n-cetyl-N,N-dimethylamine do not elute under these analytical conditions and do not interfere. Other low molecular weight amines may interfere. Sodium and ammonium ions can interfere with MEA.

OTHER METHODS: This is adapted from the method of Bouyoucos and Melcher [2,3]. There are no other NIOSH methods for DEA or TEA. MEA can be determined by method 2007, using silica gel collection and gas chromatographic analysis.

REAGENTS:

1. Hexanesulfonic acid (HSA), 2 mM (diluted from 0.1M solution obtained from Dionex Corp.).
2. Acetonitrile, reagent grade.
3. Ethanolamine*, high purity.
4. Diethanolamine*, high purity.
5. Triethanolamine*, high purity.
6. Water, distilled.
7. Regenerant for IC suppressor. For fiber suppressor use 40 mM tetramethylammonium hydroxide (TMAOH) at 2 mL/min. For cation micromembrane suppressor use 2 mM TMAOH at 4 mL/min. Prepare fresh weekly and protect from atmospheric CO_2 (which can lead to high background).
8. Calibration stock solution, 1 μg/μL. Weigh 0.10 g of each amine into 100-mL volumetric flask and dilute to mark with 2 mM hexanesulfonic acid. Store in a polyethylene bottle.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget impinger containing 15 mL of 2 mM HSA.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing and glass wool trap.
3. Ion chromatograph, with ion-pairing guard and separator columns, cation suppressor (fiber suppressor or micromembrane suppressor), integrator and strip chart recorder (page 3509-1).
4. Marker, China.
5. Vials, scintillation, plastic, 20-mL, for shipping and storage of samples.
6. Syringes, 10-mL, polypropylene, with luer tip.
7. Filters, luer tip, with membrane filter, 13- or 25-mm, 0.45-μm pore size.
8. Micropipets (or microliter syringes), 1- to 500-μL.
9. Flasks, volumetric, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipet, 15-mL.

SPECIAL PRECAUTIONS: Ethanolamines can cause skin and eye irritation [4]. Usual laboratory safety procedures should be exercised.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the impinger with 15 mL of 2 mM HSA. Mark the initial liquid level.
3. Attach impinger to sampling pump with flexible tubing. Insert a glass wool trap between the impinger and sampling pump to prevent splashover.
4. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 5 to 300 L.
5. Fill the sample solution in the impinger to the 15-mL mark with distilled water.
6. Transfer each impinger solution to a vial for shipment. Pack securely to avoid spillage during transit.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range of interest.
   a. Add known aliquots of calibration stock solution to 50-mL volumetric flasks and dilute to the mark with eluent.
   b. Store working standards in tightly-capped polyethylene bottles (glass may introduce sodium ions, a chromatographic interference). Prepare fresh weekly.
   c. Analyze working standards together with samples and blanks (steps 8 through 11).
   d. Prepare a calibration graph for each analyte (peak height vs. μg analyte).

MEASUREMENT:

8. Set the ion chromatograph to manufacturer's recommendations and to conditions given on page 3509-1. When using fiber or micromembrane suppression, if the background level is high, make several injections of acetonitrile through the sample loop to lower the background level.
   NOTE: Filter all samples, eluents, and water flowing through the ion chromatograph to avoid plugging system valves or columns.
9. Transfer a portion of sample solution to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.
10. Inject 50-μL sample aliquot. For manual operation, inject 2 to 3 mL of sample from syringe (through inline filter) to ensure complete rinse of the sample loop.
11. Measure peak height. If sample peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, μg, of analyte in the impinger (W) and in the average media blank (B) from the calibration graph.
13. Calculate the concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated for DEA with generated air samples and for all three specified amines with liquid spiked samples [5]. Samples for DEA were generated from methanol solution delivered by a syringe pump to an ultrasonic nebulizer producing a mist which was mixed with dry, heated air in the initial mixing chamber to evaporate the methanol. The flow passed into a sampling manifold where it was mixed with humidified air to maintain a relative humidity of 73-78%. The system was monitored by measuring the level of methanol in the sampling manifold with a Miran 1A infrared analyzer. The recovery of DEA calculated from the methanol concentration varied from 70-95% in different generation runs. After studies were complete, the initial mixing chamber was rinsed with 2 mM HSA and was found to contain 52 mg DEA, and a rinse of the sampling chamber contained 23 mg DEA, indicating that DEA was lost in the generator during sample generation, and explaining the variation in recovery vs. that calculated from the methanol concentration. In the first run, four samples were generated to test the generation system. These samples were expected to contain 1305 μg DEA based on monitoring of the methanol concentration. They were found to have 1237 $\pm$ 56 μg DEA, giving a recovery of 94.8%. Next, twelve samples at each of two levels were generated for storage studies. All samples were collected at 0.75 L/min and stored at room temperature (20 °C). Finally, six samples including backup impingers were generated for breakthrough studies. The results of the storage and breakthrough studies are given below:

Storage studies:	2-Day Storage			21-Day Storage			Recovery
	N	Found, μg	RSD	N	Found, μg	RSD	after 21 days
Low level	5	226	4.9	5	215	13.4	95.1%
High level	6	885	3.3	4	865	3.0	97.7%

Breakthrough studies (stored 39 days at 20 °C):	N	Found, μg	RSD	Breakthrough (average)
Front section	6	4433	7.2	
Back section	6	137	N/A	2.68% (range 1.0-5.4%)
Total	6	4570	8.2	

The method was further evaluated by spiking 2 mM hexanesulfonic acid impinger solutions with all three ethanolamines, at 2, 10, and 20 times the estimated LOQ, six spikes per analyte at each level, and analyzing them after storage at room temperature (20 °C) either for 2 days or for 21 days. Recovery of all analytes and at all levels tested (42 to 409 μg MEA, 79 to 712 μg DEA, and 117 to 1161 μg TEA) was between 94 and 106% after 3 weeks storage.

REFERENCES:

[1] Bolyard, Michele and George Williamson, Method Development Efforts for Ethanolamine Compounds, NIOSH/MRSB, Unpubl. (NIOSH) 1988.

[2] Determination of Ethanolamines in Refinery Water, Application Note #39, Dionex Corporation, Sunnyvale, CA, (February, 1982).

[3] Bouyoucos, Spiros A. and Richard G. Melcher., Collection of ethanolamines in air and determination by mobile phase ion chromatography, Am. Ind. Hyg. Assoc. J. 47(3), 185-188 (1986).

[4] NIOSH Pocket Guide to Chemical Hazards, U.S. Dept. of Health and Human Services, Publ. (NIOSH) 90-117, National Institute for Occupational Safety and Health, Cincinnati, OH 45226 (1990).

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METHOD REVISED BY:

George Williamson, NIOSH/DPSE.

TABLE 1. EXPOSURE LIMITS AND PROPERTIES.

Compounds	Exposure limits, ppm OSHA	NIOSH	ACGIH	Properties
Monoethanolamine (MEA)	3	3;* STEL 6	3; STEL 6	liquid; d 1.02 g/mL @ 20 °C; BP 170 5 °C; VP <0.13 kPa (<1 mm Hg); flash point 152 °C
Diethanolamine (DEA)	No PEL	3	3	crystals or liquid; d 1.088 g/mL @ 30 °C; MP 28 °C; BP 269 °C; VP <0.001 kPa (0.01 mm Hg); flash point 152 °C
Triethanolamine (TEA)	No PEL	No REL	5 mg/m^3	liquid; d 1.124 g/mL @ 20 °C; MP 21.2 °C; BP 335 °C (decomp.); VP 0.001 kPa (<0.01 mm Hg); flash point 191 °C

* Group III Pesticide

TABLE 2. RANGE, LOD, AND LOQ.

	Range Studied (mg/sample)	mg/m^3=1ppm @ NTP	LOD (µg/sample)	LOQ (µg/sample)	Measurement precision ($\bar{S}_r$)
Monoethanolamine (MEA)	0.04 to 0.4	2.50	7	20	0.028
Diethanolamine (DEA)	0.07 to 4.5	4.30	13	40	0.064
Triethanolamine (TEA)	0.12 to 1.16	6.10	20	60	0.079

AMMONIA

NH_3 MW: 17.03 CAS: 7664-41-7 RTECS: BO0875000

METHOD: 6015, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 50 ppm
NIOSH: 25 ppm; STEL 35 ppm; Group III pesticide
ACGIH: 25 ppm; STEL 35 ppm
(1 ppm = 0.697 mg/m^3 @ NTP)

PROPERTIES: gas; MP -77.7 °C; BP -33.4 °C; explosive range 16 to 25% v/v in air; vapor density 0.6 (air = 1)

SYNONYMS: none

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(sulfuric acid-treated silica gel)
A 0.8-micron MCE prefilter may be used to remove particulate interferences.

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 0.1 L @ 50 ppm
-MAX: 96 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
ACCURACY:	not determined
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: indophenol blue

EXTRACTION: 20 mL deionized water

COLOR DEVELOPMENT: EDTA antiprecipitant, phenolate coupling agent, nitroprusside intensifier, hypochlorite.

WAVELENGTH: 630 or 660 nm

CALIBRATION: standard solutions of ammonium chloride in deionized water

RANGE: 1.5 to 20 μg per sample [1]

ESTIMATED LOD: 0.5 μg per sample [1]

PRECISION ($\bar{S}_r$): not determined

APPLICABILITY: The working range is 0.2 to 400 ppm (0.15 to 300 mg/m^3) for a 10-L air sample. This method is applicable to STEL measurements.

INTERFERENCES: None identified.

OTHER METHODS: This method is based on the sampling procedure of Method S347 [2], the automated analytical procedure of EPA Method 350.1 [3], and Standard Methods 417G [4]. NIOSH Method 6701 [5] was less sensitive, employing a passive liquid sorbent badge for collection followed by ion chromatography. NIOSH Method P&CAM 205 [6] used impinger collection and Nessler's reagent for manual colorimetric analysis. OSHA has both impinger collection with ion specific electrode analysis (ID-164) [7] and sulfuric acid-impregnated beaded carbon collection followed by ion chromatography analysis (ID-188) [8].

REAGENTS:

1. Water, distilled and deionized. Special precaution must be taken to ensure that distilled water is free of ammonia, by passing it through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Regenerate the ion exchange column according to the instructions of the manufacturer.
   NOTE: All solutions must be made using ammonia-free water.
2. Sulfuric acid, conc., reagent grade.
3. Phenol.
4. Sodium hydroxide, reagent grade.
5. Brij-35.
6. Ammonium chloride.
7. Chloroform.
8. Sulfuric acid 5N. Air scrubber solution (AAII). Carefully add 140 mL of concentrated sulfuric acid to approximately 500 mL of ammonia-free distilled water. Cool to room temperature and dilute to 1 L with ammonia-free water.
9. Sodium phenolate. In a 1-liter flask, dissolve 83 g phenol (or 80 mL 90% liquid phenol) in 500 mL distilled water. In small increments, cautiously add with agitation, 32 g NaOH (96 g 50% NaOH for TRAACS). Periodically cool flask under water faucet. When cool, dilute to 1 L with distilled water. Filter if necessary. Store in amber glass bottle. For AAII add 0.5 mL Brij-35.
10. Sodium hypochlorite solution: Dilute one volume of a bleach solution containing 5.25% NaOCl (such as "Clorox") with an equal volume of deionized water. Available chlorine level should approximate 2 to 3%.
11. Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g EDTA (disodium salt) and six pellets NaOH in 1 L of deionized water. (For TRAACS, dissolve 41 g EDTA, 1 g 50% NaOH, and 3-6 mL Brij-35.)
12. Sodium nitroprusside (0.05% $Na_2Fe(CN)_5NO \cdot 2H_2O$): Dissolve 0.5 g sodium nitroprusside in 1 L deionized water (or 1.1 g for TRAACS).
    NOTE: Sodium nitroprusside solution is light-sensitive. Store in and use from a brown bottle.
13. Calibration stock solution (100 mg NH_3/L): Dissolve 0.3144 g anhydrous ammonium chloride, NH_4Cl, dried at 105 °C, in deionized water, and dilute to 1 L. Add 1 mL chloroform as a preservative.

EQUIPMENT:

1. Sampler:
   a. Prefilter (to remove particulate interferences): 37-mm cellulose ester membrane filter (0.8-μm pore size) supported by stainless steel screen in two piece cassette filter holder.
   b. Sulfuric acid-treated silica gel sampling tubes. Glass tube with both ends unsealed and fire-polished, 6.0 cm long with a 6-mm O.D. and a 4-mm I.D. containing two sections of 20/40 mesh sulfuric acid-treated silica gel (200 mg front/100 mg back) separated by a 2-mm portion of glass wool. Plugs of silylated glass wool are placed at the ends of the tube. The pressure drop across the tube must be <13 inches of water at a flow rate of 0.2 L/min (see APPENDIX). The glass tubes should be rinsed and dried with acetone before packing. The tubes are capped with plastic caps. Tubes are commercially available.
2. Personal sampling pump calibrated, 0.1 to 0.2 L/min, with flexible tubing.
3. Technicon AutoAnalyzer Unit (AAII) (or TRAACS 800 equivalent) consisting of an autosampler, and analytical cartridge (AAII), proportioning pump, colorimeter equipped with 15-mm, 30-mm, or 50-mm tubular flow cell and 630- to 660-nm filters, a data collection system, and recorder.
4. pH Meter and pH electrode.
5. Plastic vials, 80-mL or 50-mL.
6. Polyethylene centrifuge tubes.
7. Magnetic stirrer and stirring bars.
8. Pipets: delivery type of convenient sizes.
9. Volumetric flasks: 1-L and 50-mL and other convenient sizes for preparing standard solutions.
10. Stopwatch.
11. Manometer.

SPECIAL PRECAUTIONS: Phenol is both corrosive and poisonous from ingestion, inhalation, or absorption through the skin [10]. Avoid skin contact and inhalation of vapors. Sodium hydroxide, sulfuric acid, and sodium hypochlorite (bleach) are all corrosive. Avoid contact with skin or inhalation of vapors. Chloroform is believed to be carcinogenic [10], with reports of mutagenic and teratogenic effects in animals. Handle in a hood and avoid skin contact. Sodium nitroprusside (sodium nitroferricyanide) is highly toxic. Use extreme caution to avoid ingestion or inhalation of dust.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.1 and 0.2 liter/minute for a total sample size of 0.1 to 96 L.
3. Cap the sampling tubes with plastic (not rubber) caps immediately after sampling.
4. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove the plastic caps. Transfer the front and back sections of sulfuric acid-treated silica gel to separate 80-mL vials. Discard glass wool plugs. Analyze the two sections separately.
   NOTE: Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.
6. Add 20 mL of ammonia-free deionized water to each vial. Cap and shake vigorously. Desorption is complete in 45 minutes. Adjust the pH of each sample to 5.0 to 6.5 with sodium hydroxide.
   NOTE: Analyses should be completed within one day after the ammonia is desorbed.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.05 to 1 μg/mL. Using the stock solution, prepare standards such as the following in 100-mL volumetric flasks (prepare fresh daily):
   a. Add known amounts of calibration stock solution to deionized water in 100-mL volumetric flasks and dilute to the mark. Prepare fresh daily.

NH_3, μg/mL	mL Stock Solution/100 mL
0.05	0.05
0.10	0.10
0.20	0.20
0.40	0.40
0.80	0.80
1.00	1.00

   b. Analyze working standards together with samples and blanks (steps 9 through 12).
   c. The instrument automatically generates calibration graph (peak height versus concentration). Sample concentrations will be printed out directly from this graph.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibrating graph is in control.

MEASUREMENT:

9. For a working range of 0.05 to 1.0 μg NH_3/mL, set up the manifold as shown in Figure 1 for AAII and as shown in Figure 2 for TRAACS. Higher concentrations may be accommodated by sample dilution.
10. Allow both the colorimeter and the recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding deionized water through the sample line.
11. For normal conditions use a 30 or 40/hour 2:1 cam with a common wash for the AAII. For the TRAACS use a sampling rate between 90 and 120/hour with a 3:1, 4:1, or 5:1 sample/wash ratio.
12. Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples. Begin analysis.

CALCULATIONS:

13. Read NH_3 concentration (μg/mL) found in sample front (W_f) and back (W_b) sorbent sections directly from the instrument printout.
14. Calculate the concentration (C) of NH_3 in the volume, V (L), of air sampled from the sample solution concentrations, W_f and W_b (μg/mL), multiplied by the appropriate solution volumes, V_f and V_b (mL):

$$C = \frac{W_f V_f + W_b V_b}{V}, \text{ mg/m}^3.$$

REFERENCES:

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[3] Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 Revised March 1983, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.
[4] Standard Methods for the Examination of Water and Wastewater, 16th ed., 1985, APHA, AWWA, WPCF.
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[7] "Ammonia in Workplace Atmosphere" Method ID-164, Inorganic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah.
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[9] The Merck Index, 11th Edition, 7206 Phenol, 2141 Chloroform, Merck & Co., Inc., Rahway, NJ (1989).
[10] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD WRITTEN BY:

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APPENDIX: PREPARATION OF SULFURIC ACID-TREATED SILICA GEL

1. Place 6 g of 20/40 mesh silica gel in 250-mL beaker.

2. Add 15 mL 0.4 N sulfuric acid to the beaker. Stir the mixture, and cover the beaker with a watch glass.

3. Heat the silica gel-acid mixture in a fume hood with a Bunsen burner to a very gentle boil. Evaporate approximately one-half of the liquid.

4. Place the covered beaker in a drying oven at 120 °C until the remainder of the water has been evaporated.

5. The prepared acid-treated silica gel should flow freely and not adhere to the beaker. Store in silica gel in a desiccator until ready for use.

FIGURE 1 (AAII)
Ammonia Manifold

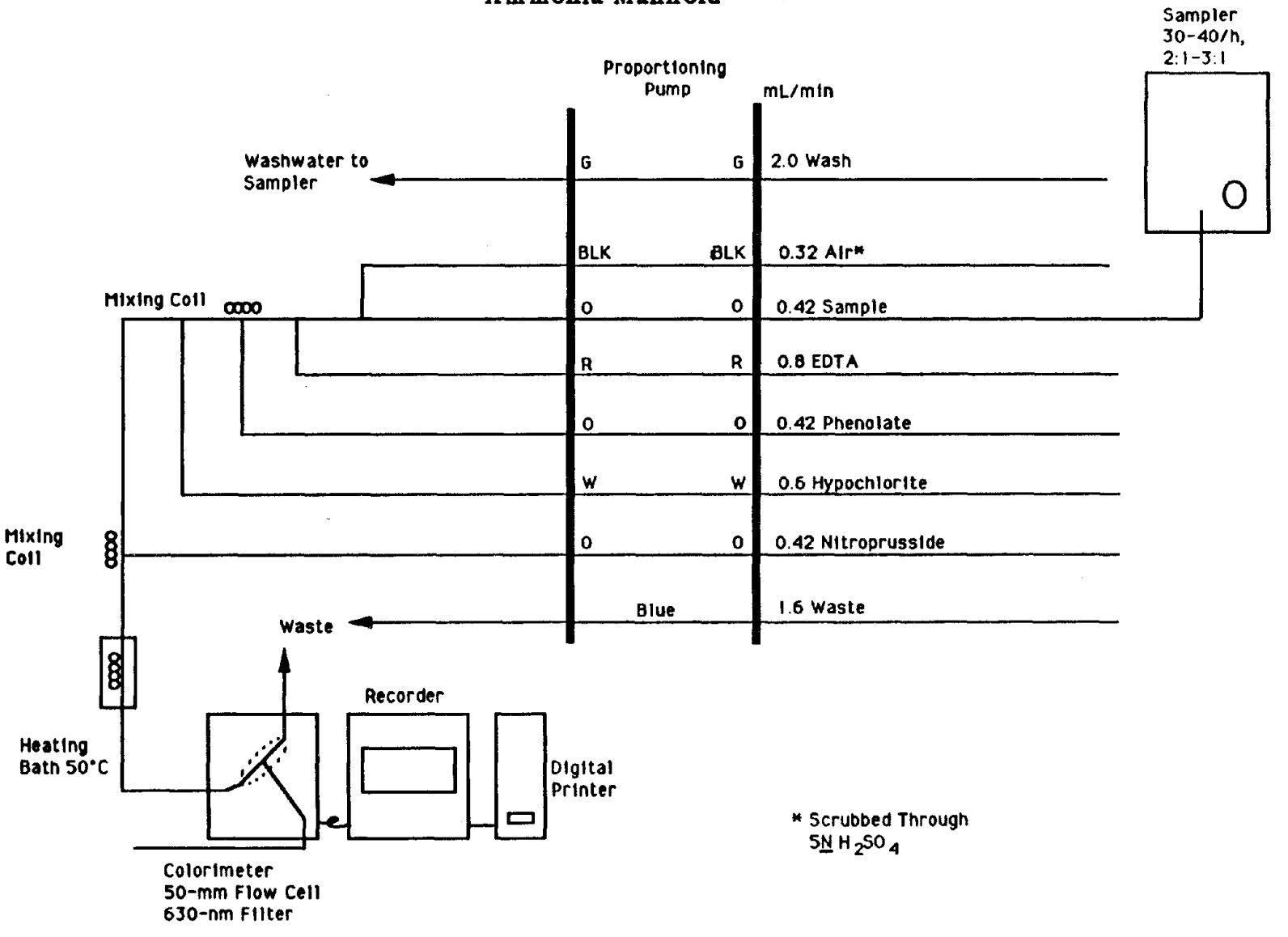
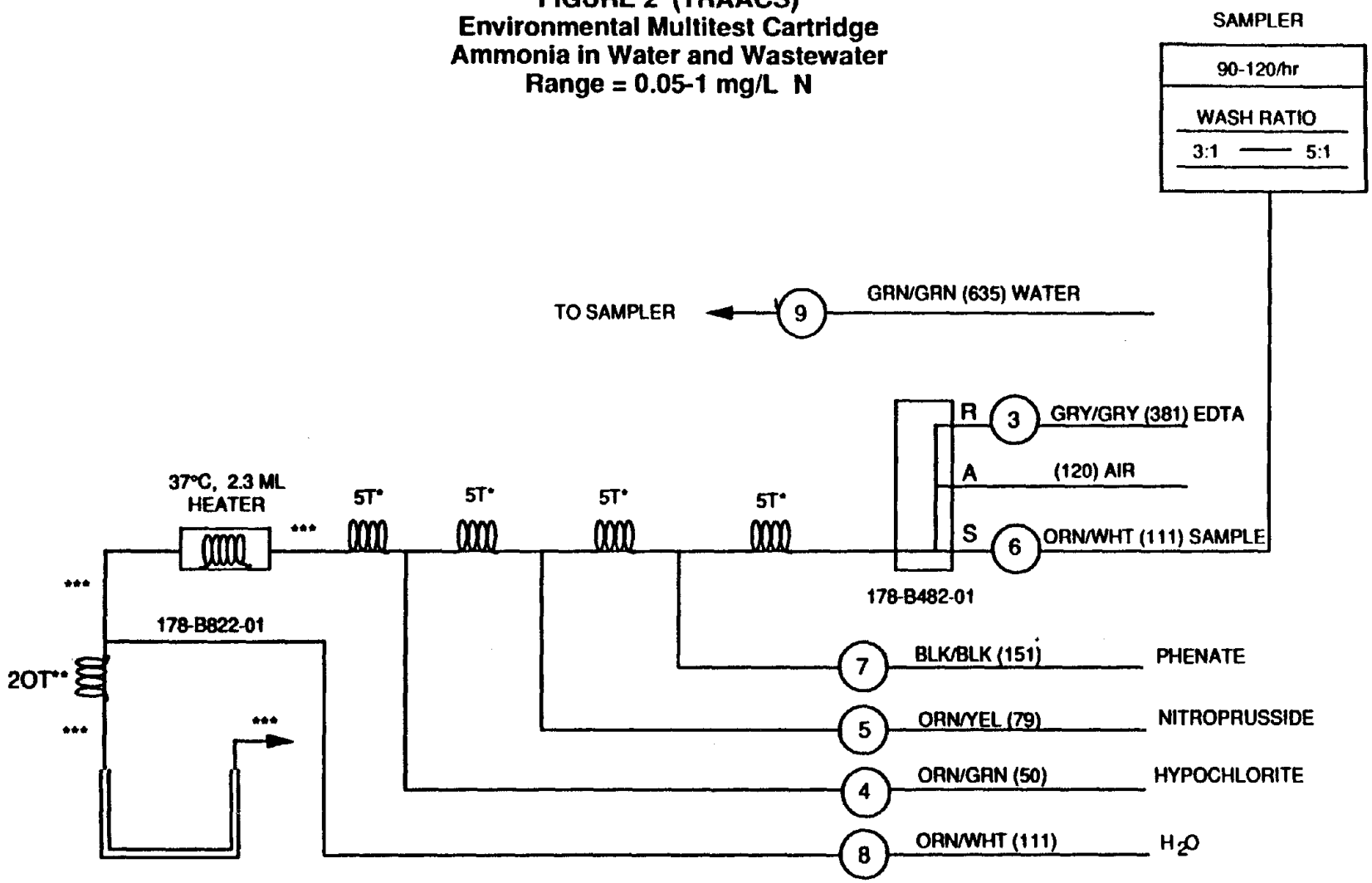


FIGURE 2 (TRAACS)
Environmental Multitest Cartridge
Ammonia in Water and Wastewater
Range = 0.05-1 mg/L N



NOTES: Numbers in Parentheses Denote Flowrates in µL/minute.
Circled Numbers are pump tube positions.
*165-G005-01
**165-G005-03
***Denotes 0.030" x 0.062" I.A. Polyethylene Tubing.

n-AMYL ACETATE

See ESTERS I (Method 1450) for procedure

sec-AMYL ACETATE

See ESTERS I (Method 1450) for procedure

ANILINE

See AMINES, AROMATIC (Method 2002) for procedure

ANISIDINE

$CH_3OC_6H_4NH_2$ MW: 123.16 CAS: (o-) 90-04-0 (p-) 104-94-9 RTECS: (o-) BZ5410000 (p-) BZ5450000

METHOD: 2514, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985** **Issue 2: 15 August 1994**

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); o-isomer suspect carcinogen
ACGIH: 0.1 ppm (skin) (0.5 mg/m^3)
(1 ppm = 5.03 mg/m^3 @ NTP)

PROPERTIES: o-isomer: liquid; d 1.092 g/mL @ 15 °C; BP 225 °C; MP 5 °C; VP 0.1 mm Hg @ 27 °C
p-isomer: solid; MP 57 °C; BP 246 °C

SYNONYMS: o-isomer: 2-aminoanisole; 2-methoxybenzenamine; o-methoxyaniline
p-isomer: 4-aminoanisole; 4-methoxybenzenamine; p-methoxyaniline

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2, 150 mg/75 mg)

FLOW RATE: 0.5 to 1.0 L/min

VOL-MIN: 24 L
-MAX: 320 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.13 to 0.58 mg/m^3 [1] (225-L samples)

BIAS: 0.12%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.068 [1]

ACCURACY: ± 13.3%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: o-anisidine and p-anisidine

DESORPTION: 5 mL methanol; stand 15 min

INJECTION VOLUME: 10 µL

MOBILE PHASE: 35% acetonitrile/65% water @ 1.2 mL/min; ambient temperature

COLUMN: 50 cm x 2-mm ID stainless steel packed with µ-Bondapak C_{18} or equivalent

DETECTOR: UV absorption @ 254 nm

CALIBRATION: analytes dissolved in methanol

RANGE: 12 to 360 µg per sample (each isomer) [2]

ESTIMATED LOD: 0.35 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.029 @ 30 to 240 µg per sample [1]

APPLICABILITY: The working range is 0.06 to 0.8 mg/m^3 (0.012 to 0.16 ppm) for a 200-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S163 [2]. This method replaces P&CAM 168 [3] because XAD-2 has a much greater capacity than silica gel for o-anisidine at high humidity [1].

REAGENTS:

1. p-Anisidine, reagent grade.*
2. o-Anisidine, reagent grade.*
3. Methanol, HPLC grade.*
4. Acetonitrile, HPLC grade.*
5. Water, distilled, deionized.
6. Methylene chloride.
7. Calibration stock solution, 15.0 mg/mL p-anisidine and 15.3 mg/mL o-anisidine. Dissolve 750 mg p-anisidine and 700 μL o-anisidine in methanol to make 50 mL solution.
8. HPLC mobile phase: 35% acetonitrile/65% water. Filter (5-μm PTFE) and degas prior to use.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 (front = 150 mg; back = 75 mg) separated and held in place by plugs of silylated glass wool. Pressure drop across the tube must be <3.4 kPa (2.5 cm Hg) at 1 L/min airflow. Tubes are commercially available, (SKC Cat. No. 226-30-05, or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. HPLC with UV absorption detector at 254 nm, integrator and column (page 2514-1).
4. Vials, 20-mL, scintillation.
5. Pipet, 5-mL.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 5- and 50-mL.

SPECIAL PRECAUTIONS: Anisidine can irritate the skin. Methanol and anisidine can be absorbed through the skin. Avoid inhalation of vapors of these compounds and of acetonitrile [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.0 L/min for a total sample size of 24 to 320 L. Do not sample at less than 0.5 L/min.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sections of the sampler in separate vials. Discard the glass wool plugs.
6. Add 5.0 mL methanol to each vial. Cap each vial and swirl vigorously.
7. Allow to stand for 15 min. Analyze within one day.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.4 to 360 μg anisidine per sample for each isomer.
   a. Add a known volume of calibration stock solution, or a dilution thereof in methanol, to a 5-mL volumetric flask and dilute to the mark with methanol.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg analyte) for each isomer.
9. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the concentration range of interest. Prepare four tubes at each of five levels.
   a. Remove and discard the back sorbent section of a media blank sampler.

b. Inject a known amount (e.g., 1 to 20 μL) of calibration stock solution, or a dilution thereof in methanol, directly onto the front section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare graphs of DE vs. μg isomer recovered.

10. Analyze three quality control blind spikes and three analyst spikes with each subsequent set from the same lot to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set HPLC to conditions given on page 2514-1. Inject sample aliquot.
NOTE: Sensitivity is ca. 0.083 absorbance unit/mg of either isomer in a 10-mL injection volume with a 1-cm flow cell. Approximate retention times are 7.5 min for p-anisidine and 12 min for o-anisidine.
12. Measure peak area.

CALCULATIONS:

13. Determine the quantities (sum of quantities of the o- and the p-isomers corrected for DE), mg of analytes found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate the sum of the concentrations, C, of the isomers in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S163 was issued on February 16, 1979 [2], and was validated over the range 0.13 to 0.58 mg/m^3 for the o-isomer and 0.12 to 0.58 mg/m^3 for the p-isomer using 225-L air samples [1,5]. The generation system was constructed so that samples were generated for both isomers at the same time. Concentrations were verified by an independent method using bubblers containing methanol and HPLC analysis [1]. The overall precision, $\hat{S}_{rT}$, for the combined sampling and measurement of both isomers was 0.068 with an average recovery of 100.7% for the o-isomer and 99.7% for the p-isomer [1], which represent non-significant biases for the isomers. A separate breakthrough test was conducted for each isomer with XAD-2. Samples were taken at ca. 1.0 L/min. o-Anisidine was generated at 1.03 mg/m^3 with a relative humidity of 81% at 21 °C. Breakthrough (3%) from 150 mg XAD-2 occurred after 236 min, but did not increase above this amount up to 479 min. p-Anisidine was generated at 1.04 mg/m^3 with a relative humidity of 82% at 20 °C. Breakthrough did not occur during the 361-min test. Samples containing both isomers were stored for one week at room temperature and found to be stable. Desorption efficiencies averaged 0.95 and 0.91 for o- and p-anisidine, respectively, in the range 30 to 240 μg per sample.

REFERENCES:

[1] NIOSH Backup Data Report S163 (unpublished, February, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S163, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Ibid., Vol. 1, P&CAM 168, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[5] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Edward Slick, NIOSH/DPSE; S163 originally validated under NIOSH Contract 210-76-0123.

ARSENIC and compounds, as As (except AsH_3 and As_2O_3)

7900

As MW: 74.92 CAS: 7440-38-2 RTECS: CG525000

METHOD: 7900, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.01 mg/m³
NIOSH: C 0.002 mg/m³/15 min; carcinogen
ACGIH: 0.01 mg/m³; carcinogen

PROPERTIES: soft, reactive metalloid; MP 848 °C; valence ± 3, 5 in salts

SYNONYMS: vary depending upon the compound

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.002 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable if refrigerated

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: see APPLICABILITY

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME ARSINE GENERATION

ANALYTE: arsenic

ASHING: conc. HNO_3, 3 mL; conc. H_2SO_4, 1 mL; conc. $HClO_4$, 1 mL; 140 °C

FINAL SOLUTION: 4% H_2SO_4, 25 mL

FLAME: hydrogen-argon

WAVELENGTH: 193.7 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

CALIBRATION: As in 4% H_2SO_4

RANGE: 0.05 to 2.0 μg per sample [1]

ESTIMATED LOD: 0.02 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.11 [1]

APPLICABILITY: The working range is 0.00025 to 0.01 mg/m³ for a 200-L air sample and 0.002 to 0.07 mg/m³ for a 30-L air sample. **This method collects particulate arsenic only; if arsenic trioxide vapor is present, use the sampler in Method 7901.** This is an elemental analysis, not compound specific. Volatile organic arsenic compounds, As_2O_3 vapor, and arsine are not collected efficiently by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of D_2 or H_2 continuum.

OTHER METHODS: This revises P&CAM 139 [1]); a similar method appears in the criteria document [2]. Method 7901 uses a sampler designed to collect As_2O_3 vapor and an alternate measurement technique (graphite furnace-AAS). Method 7300 (ICP-AES) also gives an alternate measurement technique.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Sulfuric acid, conc.
4. Perchloric acid, conc.*
5. Calibration stock solution, 1000 mg/mL.* Commercially available or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Add 10 mL conc. HNO_3 and dilute to 1 L with distilled or deionized water.
6. Ashing acid, 3 volumes HNO_3, 1 volume H_2SO_4, and 1 volume $HClO_4$.
7. Hydrogen.
8. Argon.
9. Distilled or deionized water.
10. Sodium borohydride, pellets.
11. Air, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with appropriate hydrogen burner head or quartz tube furnace, and arsenic hollow cathode lamp or EDL and arsine generation system.
4. Regulators, two-stage, for air, hydrogen and argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Pipets, volumetric, as needed.*
8. Hotplate, surface temperature 140 °C.

* Clean all glassware with conc. nitric acid before use and rinse thoroughly with distilled or deionized water.

SPECIAL PRECAUTIONS: Arsenic is a recognized carcinogen. Handle appropriately [2]. Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed ca. 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
   NOTE: Analyze the backup pad separately if qualitative indication of As_2O_3 vapor is desired. Use Method 7901 if quantitative collection of As_2O_3 vapor is desired.
4. Add 5 mL ashing acid and cover with a watchglass.
5. Heat on hotplate (140 °C) until the solution is colorless.
6. Add 1 mL conc. HNO_3 and/or 70% $HClO_4$ drop by drop as needed to complete the ashing.
7. Remove the watchglass.
8. Heat on 140 °C hotplate until dense SO_3 fumes appear.
9. Allow the mixture to cool.
10. Transfer the solution quantitatively to a 25-mL volumetric flask.
11. Dilute to volume with distilled or deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Prepare working standards. Add known amounts, covering the range 0.2 to 8 μg As/100 mL (0.05 to 2 μg As per sample), of 1000 μg/mL As calibration stock solution to 100-mL volumetric flasks containing 4 mL conc. H_2SO_4 and dilute to volume with distilled or deionized water.

13. Analyze working standards together with the blanks and samples (steps 18 through 25).
14. Prepare calibration graph (absorbance vs. solution concentration, μg/mL).
15. Analyze a standard for every 10 samples.
16. Check analytical recoveries with at least one spiked media blank per 10 samples.
17. Use method of standard additions occasionally to check for interferences.

ANALYTICAL PROCEDURE:

18. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7900-1.
19. Set up arsine generator per manufacturer's instructions.
20. Pipet 5 mL aliquot of the 25-mL sample into the arsine generation flask.
21. Add 25 mL distilled or deionized water, 3 mL conc. HCl, and mix well.
22. Connect the flask to the generation system.
23. Introduce a single sodium borohydride pellet or sodium borohydride solution to the sample solution.
24. Allow the gases to flush into the flame of the atomic absorption instrument.
25. Record the absorbance readings.
    NOTE: If the absorbance values of the samples are above the linear range of the standards, dilute the solutions, or use a smaller aliquot, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

26. Using the measured absorbances, calculate the corresponding solution concentrations (μg/mL) of As in the sample, C_s, and average media blank, C_b, from the calibration graph.
27. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of As in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method was evaluated in July, 1976, over the range 0.02 to 3 mg per sample by laboratory testing with spiked filters. Precision and accuracy data are given on page 7900-1 [1].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 139, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (1975).

METHOD WRITTEN BY:

Mark Millson, NIOSH/DPSE.

ARSENIC, organo- 5022

(1) $CH_3AsO_3H_2$	MW: (1) 139.96	CAS: (1) 124-58-3	RTECS: (1) PA1575000
(2) $(CH_3)_2AsO_2H$	(2) 137.99	(2) 75-60-5	(2) CH7525000
(3) $H_2NC_6H_4AsO_3H$	(3) 217.07	(3) 98-50-0	(3) CF7875000

METHOD: 5022, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.5 mg/m^3 (as As)
NIOSH: no REL
ACGIH: 0.2 mg/m^3 (as As)

PROPERTIES: solids; MP (1) 161 °C, (2) 195 °C; (3) 232 °C

SYNONYMS: (1) Methylarsonic acid: methanearsonic acid. (2) Dimethylarsinic acid: cacodylic acid; hydroxydimethyl arsine oxide. (3) p-Aminophenyl arsonic acid: p-arsanilic acid; atoxylic acid.

SAMPLING

SAMPLER: FILTER (1-μm PTFE)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L @ 0.01 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.005 to 0.2 mg/m^3 [1,2]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): 0.047 @ 0.02 mg/m^3 [1]; 0.14 @ 0.005 mg/m^3 [1]

ACCURACY: ± 20% @ 0.02 mg/m^3

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY/ HYDRIDE ATOMIC ABSORPTION

ANALYTE: anions (IC); AsH_3 (AAS)

EXTRACTION: borate-carbonate buffer, 25 mL

ION CHROMATOGRAPHY:
INJECTION LOOP VOLUME: 0.8 mL
COLUMNS: two, 3 x 150-mm anion
ELUENT: borate-carbonate buffer; 2.5 mL/min; 3450 kPa (500 psi); ambient temperature

AAS:
QUARTZ FURNACE: 800 °C
WAVELENGTH: 193.7 nm (no D_2)

CALIBRATION: organoarsenicals in water

RANGE: 0.5 to 2 μg As per sample

ESTIMATED LOD: 0.2 μg As per sample [1]

PRECISION ($\bar{S}_r$): Table 1

APPLICABILITY: The working range is 0.005 to 10 mg/m^3 (as As) for a 100-L air sample. The method is designed to quantitate particulate organo-arsenic compounds.

INTERFERENCES: Inorganic arsenic (III) co-elutes with dimethylarsenic acid using Eluent A but the two may be separated with Eluent B. Other ions at high concentrations in the sample can interfere with the chromatographic separation of the arsenicals. As_2O_3 is not efficiently sampled by this sampler; for quantitation of that compound see Method 7901.

OTHER METHODS: This is P&CAM 320 in revised format [2]. Method 7200 measures total As by hydride/AAS. Method 7901 measures As_2O_3, which can exist as a vapor and aerosol.

REAGENTS:

1. Deionized water.
2. Hydrochloric acid, conc.
3. Eluent A (2.4 mM HCO_3^-/1.9 mM CO_3^{2-}/1.0 mM $B_4O_7^{2-}$). Dissolve 0.8067 g $NaHCO_3$, 0.8055 g Na_2CO_3, and 1.5257 g $Na_2B_4O_7 \cdot 10H_2O$ in 4 L deionized water.
4. Eluent B (5 mM $B_4O_7^{2-}$). Dissolve 7.6284 g $Na_2B_4O_7 \cdot 10H_2O$ in 4 L deionized water.
5. Potassium persulfate solution,* $K_2S_2O_8$, saturated in 15% (v/v) HCl.
6. Sodium borohydride, 1% $NaBH_4$ (w/v) in 0.2% KOH (w/v). Add 5 g $NaBH_4$ and 1 g KOH to deionized water; dilute to 500 mL. Prepare fresh weekly.
7. Stock standards, 1000 µg As/mL:
   a. Methylarsonic acid.* Dissolve 0.9341 g $CH_3AsO_3H_2$ (Ansul Co., Weslaco, TX), in deionized water; dilute to 500 mL.
   b. Dimethylarsenic acid.* Dissolve 0.9210 g $(CH_3)_2AsO_2H$ (Ansul Co.) in deionized water; dilute to 500 mL.
   c. p-Aminophenylarsonic acid.* Dissolve 1.4485 g p-$H_2NC_6H_4AsO_3H_2$ in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water. Protect from light.
   d. Arsenic trioxide.* Dissolve 0.6602 g As_2O_3 in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water.
   e. Arsenic pentoxide.* Dissolve 0.7669 g As_2O_5 in 5 mL 1 N NaOH. Dilute to 500 mL with deionized water.
8. Calibration stock solution, 1 µg/mL mixed analyte. Dilute 0.1 mL of each stock standard (REAGENTS, 7.) with Eluent A in a 100-mL volumetric flask. Prepare fresh daily.
9. Argon.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: PTFE polyethylene-backed membrane filter, 1-µm pore size (MilliporeType FA or equivalent), 37-mm diameter with backup pad; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Ion chromatograph with suppressor and detector bypassed. Route column effluent via Microbore PTFE tubing (0.3-mm ID x 0.6-mm OD, Dionex) directly into arsine generator (Figure 1).
4. Syringes, plastic, 10-mL, with male luer fittings.
5. Arsine generator: proportioning pump with flow-rated pump tubes and 1.5-mm ID x 3-mm OD manifold mixing coils, 5-turn and 20-turn (Technicon or equivalent), 1.5-mm ID x 3.5-mm OD glass "T" connectors; gas-liquid separator and expansion chamber (Figure 2); ~1 m of 1/4" OD PTFE tubing; three PTFE 1/4" ID Swagelok fittings; and rotometer (100 to 900 mL/min).
6. Atomic absorption spectrophotometer (reciprocal linear UV dispersion ~0.65 nm/mm); As electrodeless discharge lamp and power supply; and atomization cell (16-cm x 13-mm ID windowless quartz tube with 18-cm x 4-mm ID inlet tube fused in the center), wound with Nichrome wire (14 Ω/m, spaced 2 to 3 mm between turns and wrapped with heat resistant tape) (Figure 3). Temperature in the cell is measured by a thermocouple (800 °C). Mount the cell on top of a single-slot AAS burner head and align with burner alignment controls.
7. Beakers, 50-mL.*
8. Ultrasonic waterbath.
9. Volumetric flasks, 10-, 100- and 500-mL.
10. Pipets, 25-µL and 0.1- to 1-mL.

* Soak all glassware in mild detergent, rinse with deionized water, 10% HNO_3, and deionized water.

SPECIAL PRECAUTIONS: Potassium persulfate is a powerful oxidizing agent. Arsine gas is extremely toxic and can be fatal. The arsenic compounds used in the stock standards are poisonous [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample volume of 50 to 1000 L.
3. Cap the cassettes and pack securely for shipment.

SAMPLE PREPARATION:

4. For each sample, pipet 25 mL Eluent A into a clean 50-mL beaker.
5. Open the cassette, remove the PTFE filter with clean forceps, and transfer it to the beaker. Place the exposed side of the filter in contact with the solution. Cover beaker.
6. Agitate contents of the beaker for 30 min in an ultrasonic water bath. If the extracts will not be analyzed immediately, store at ca. 4 °C until measurement.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.2 to 2 μg As per sample (0.008 to 0.08 μg As/mL).
   a. Add known amounts of calibration stock solution to Eluent A in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 8 through 12).
   c. Prepare calibration graph for each arsenic species (peak area or height vs. μg As).

MEASUREMENT:

8. Set the ion chromatograph to the conditions given on page 5022-1. Allow the columns to equilibrate with eluent $\geq$1 h before connecting effluent to the arsine generator.
   NOTE: Eluent A allows the separation of methylarsonic acid (t_r = 2 min), p-aminophenylarsonic acid (t_r = 4 min), and As(V) (t_r = 7.5 min); As(III) and dimethylarsenic acid (t_r = 1 min) are not resolved. If a signal is obtained at the approximate retention time of the latter two compounds, or if both compounds are known to be present in the sample, perform a second analysis using Eluent B (lower ionic strength). If either of the two compounds is known not to be present, Eluent A will effectively determine the remaining compounds. With Eluent B the other species have very long retention times and will accumulate on the column, tying up active resin sites. Therefore, flush the column with Eluent A after each 10 to 15 samples and reequilibrate with Eluent B before further analysis.
9. Connect the IC effluent to the arsine generator into which the following flow:

Saturated $K_2S_2O_8$ solution:	0.8 mL/min
$NaBH_4$ solution:	2.0 mL/min
Ar carrier gas:	300 mL/min

   NOTE: The gaseous arsines formed in the arsine generator are first separated from liquid solution using the gas-liquid separator (Figure 2) and then transferred by argon carrier gas through PTFE tubing to the heated quartz furnace.
10. Set the AAS according to manufacturer's recommendations and to the conditions given on page 5022-1. Align the quartz cell in the optical path. Heat the quartz cell gradually to 800 °C using a variable transformer and thermocouple.
11. Using a syringe, inject a sample aliquot (ca. 2 to 3 mL) into the chromatograph, flushing the injection loop to avoid contamination from the previous injection. Rinse the syringe with deionized water and dry it between samples, or use disposable syringes.

12. Identify the component peaks. Measure peak height or area.

CALCULATIONS:

13. From the calibration graphs, calculate the amount (μg) of arsenic for each species in the sample (W) and in the average media blank (B).
14. Calculate the arsenic concentrations, C, (mg/m^3) in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The measurement precision obtained under the conditions recommended in this procedure is presented in Table 1 [1]. The overall precision of the method was tested using filters loaded in a dynamic aerosol generation/sampling system with particulates of the three organoarsenical compounds. The concentration levels tested for each species were 5, 10, and 20 μg As/m^3 of air. Depending on the concentration and species, the relative standard deviation ranged from 14.4% at the lowest level to 4.7% at the highest level.

The collection efficiency of the method for organoarsenicals in the range of 5 to 20 μg/m^3 using a 300-L sample was found to be >99%. The collection efficiency of the method for inorganic arsenic was not determined.

The accuracy of the overall method was determined by analyzing additional aerosol samples from each set using Neutron Activation (NAA) and X-ray Fluorescence (XRF) analyses. Since NAA and XRF techniques provide only the total elemental arsenic, the total arsenic obtained from the IC-AAS analysis was used for comparison. The accuracy ranged from 90 to 120% of the values obtained by NAA and XRF.

REFERENCES:

[1] Colovos, G., N. Hester, G. Ricci, and L. Shepard: "Development of a Method for the Determination of Organoarsenicals in Air," NIOSH Contract #210-77-0134, available through National Technical Information Service, Springfield, VA 22161 as Order No. PB83-180794.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 320, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] The Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE; P&CAM 320 originally developed under NIOSH Contract 210-77-0134.

TABLE 1. SENSITIVITY, DETECTION LIMIT AND WORKING RANGE DATA FOR ANALYSIS OF PARTICULATE ARSENICALS [1].

		Detection Limit (as As)		Range[1]		
Arsenical	Sensitivity (ng/mL/1% Abs)	300 L Sample Volume ($\mu g/m^3$)	Solution ng/mL	300 L Sample Volume ($\mu g/m^3$)	Solution ng/mL	Measurement Precision (% $\bar{S}_r$)
Dimethylarsenic acid	1.3	0.62	7	1.7 - 6.7	20 - 80	11.2 - 1.6
Arsenic (III)	2.1	0.71	8	1.7 - 6.7	20 - 80	11.2 - 1.3
Methylarsonic acid	2.1	0.72	9	1.7 - 6.7	20 - 80	8.1 - 4.4
p-Aminophenyl-arsonic acid	6.3	0.64	8	1.7 - 6.7	20 - 80	6.0 - 3.0
Arsenic (V)	13.0	0.46	6	1.7 - 6.7	20 - 80	10.8 - 1.0

[1]The upper limit of the range can be increased by using higher concentration standards which are injected via loops of smaller volume. Although not tested with air samples, the useful range can be extended from 5 $\mu g/m^3$ down to 1.7 $\mu g/m^3$ based upon the measurement range.

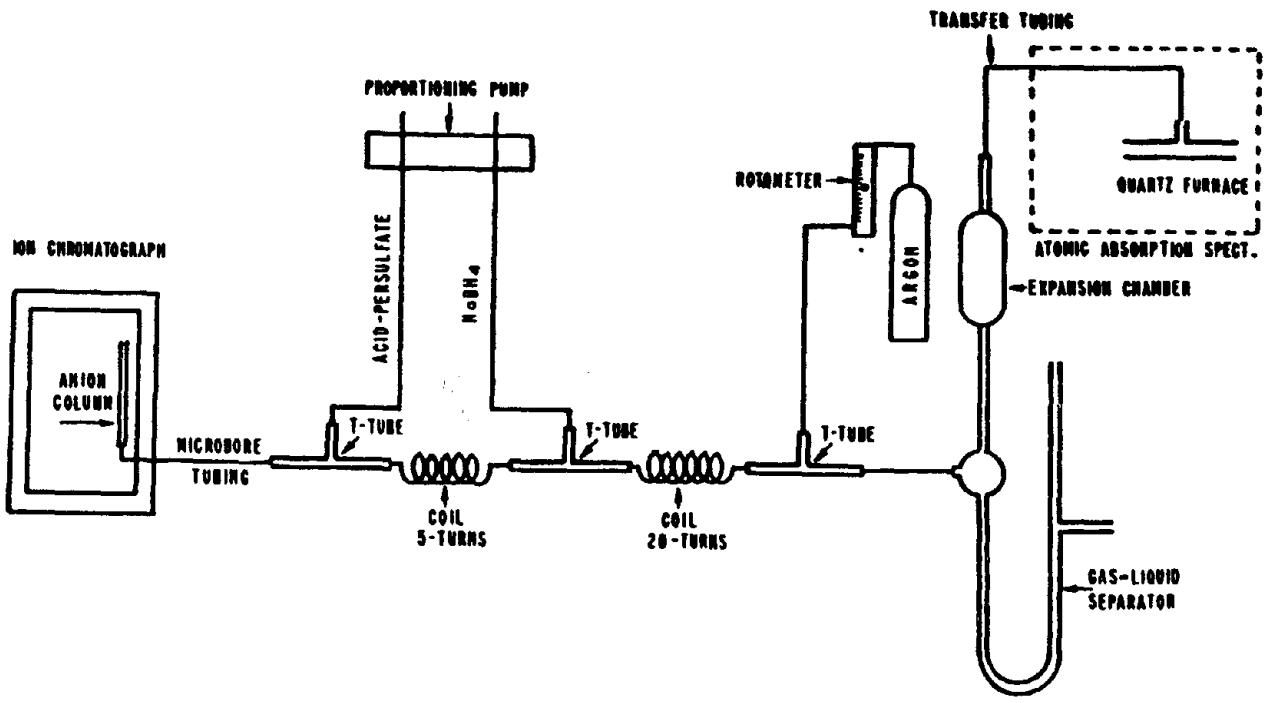


FIGURE 1. IC/AAS Analytical System.

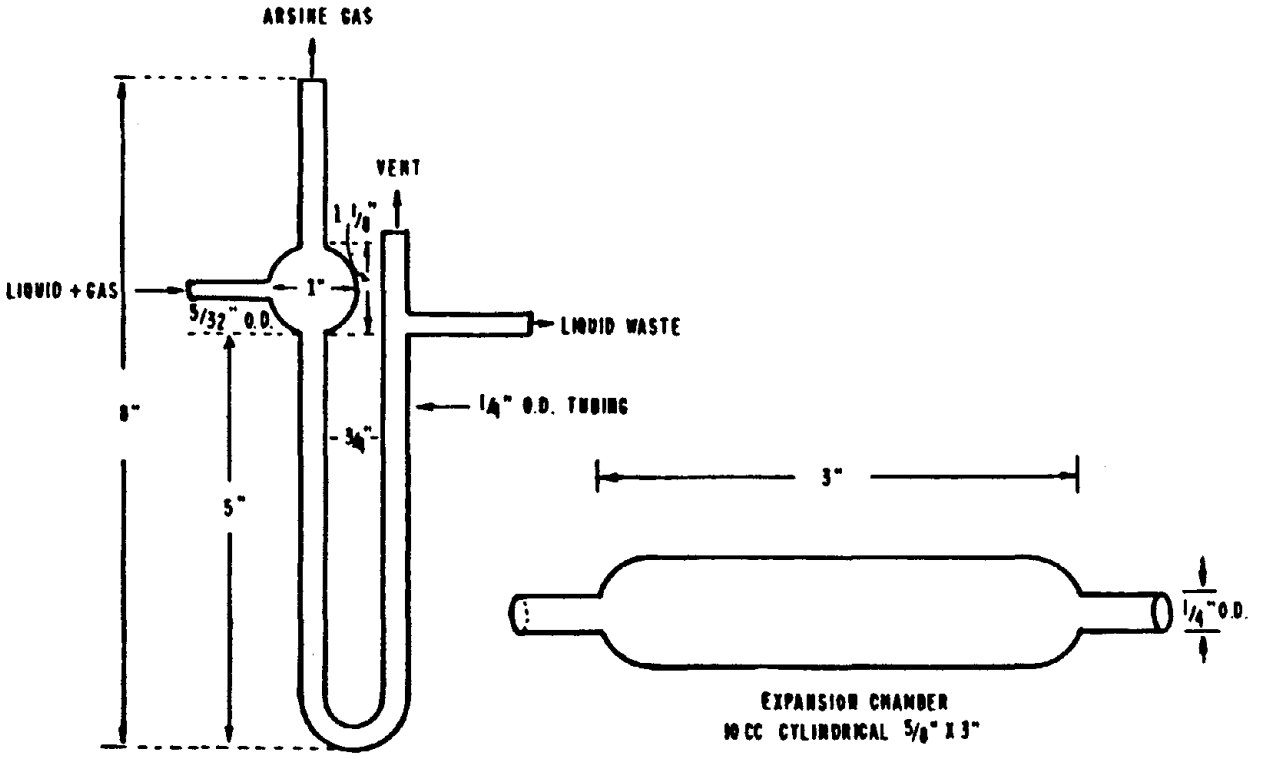


FIGURE 2. Gas-Liquid Separator and Expansion Chamber.

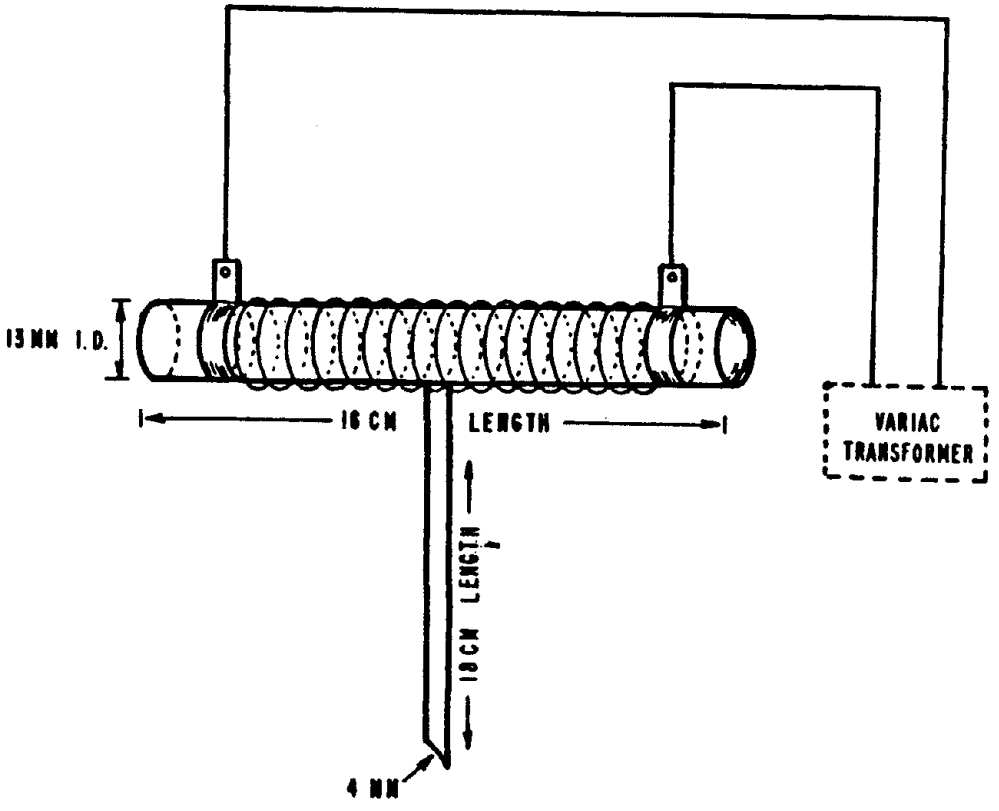


FIGURE 3. Quartz Furnace Atomization Cell.

ARSENIC TRIOXIDE, as As 7901

As_2O_3 MW: 197.84 CAS: 1327-53-3 RTECS: CG3325000

METHOD: 7901, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.01 mg/m^3 (As)
NIOSH: C 0.002 mg/m^3 (As)/15 min; carcinogen
ACGIH: 0.01 mg/m^3; carcinogen

PROPERTIES: solid; MP 275 °C or 313 °C (sublimes); VP 0.0075 Pa (5.6 x 10^{-5} mm Hg; 0.45 µg As/m^3) @ 25 °C

SYNONYMS: arsenous acid anhydride; arsenous sesquioxide; arsenolite; claudetite

SAMPLING

SAMPLER: FILTER (Na_2CO_3-impregnated, 0.8-µm cellulose ester membrane + backup pad)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.01 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.67 to 32 µg/m^3 [1,2] (400-L samples)
BIAS:	− 0.55%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.075 [1,2]
ACCURACY:	± 11.9%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: arsenic

ASHING: 15 mL HNO_3 + 6 mL H_2O_2; 150 °C

FINAL SOLUTION: 10 mL 1% HNO_3, 0.1% Ni^{2+}

WAVELENGTH: 193.7 nm; D_2 or H_2 correction

GRAPHITE TUBE: pyrolytic

GRAPHITE FURNACE: DRY: 100 °C, 70 sec; CHAR: 1300 °C, 30 sec; ATOMIZE: 2700 °C, 10 sec

INJECTION: 25 µL

CALIBRATION: As in 1% HNO_3, 0.1% Ni^{2+}

RANGE: 0.3 to 13 µg per sample

ESTIMATED LOD: 0.06 µg per sample

PRECISION ($\bar{S}_r$): 0.029 [3,4]

APPLICABILITY: The working range is 0.001 to 0.06 mg/m^3 for a 200-L air sample. This method collects particulate arsenic compounds as well as arsenic trioxide vapor. **If only total particulate arsenic is of interest, the use of the treated filter and analysis of the backup pad is not required.** Arsine is not collected by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of a deuterium background corrector. Matrix modification with Ni^{2+} solution allows the use of a higher char temperature in the graphite furnace. Other particulate arsenic compounds will interfere.

OTHER METHODS: This method combines and replaces P&CAM 346 [3], S309 [4], and P&CAM 286 [5]. Method 7300 (ICP-AES) and arsine generation (Method 7900 and the criteria document method [1]) are for particulate arsenic compounds. Other methods (P&CAM 173 [7], P&CAM 180 [8], and P&CAM 188 [9]) have not been revised because of interferences or poor sensitivity.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Dilute 10 mL conc. HNO_3 to 1 L with distilled or deionized water.
3. Hydrogen peroxide, 30% (w/w).
4. Ni^{2+} in 1% HNO_3, 1000 μg/mL. Dilute 4.95 g $Ni(NO_3)_2$ to 1 L with 1% HNO_3.
5. Calibration stock solution*, 1000 μg As/mL, commercially available, or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Dilute to 1 L with 1% HNO_3.
6. 1 M Na_2CO_3:glycerol solution, 20:1. Dissolve 9.5 g sodium carbonate in 100 mL distilled or deionized water. Add 5 mL pure glycerol.
7. Distilled or deionized water.
8. Argon.

* See Special Precautions

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, and cellulose backup pad in cassette filter holder treated as follows:
   a. Remove inlet plug from the loaded cassette.
   b. Add 250 mL 20:1 Na_2CO_3:glycerol solution with a micropipet directly onto filter (wet entire surface).
   c. Attach to vacuum source and draw 30 to 60 L clean air through the filter.
   d. Let dry overnight or dry 8 h @ 120 °C. Replace the inlet plug.
   e. Use within one week.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
   NOTE: The treated filter has a high pressure drop; a personal sampling pump with flow rate control is required.
3. Atomic absorption spectrophotometer with graphite furnace atomizer, arsenic electrodeless discharge lamp, and background correction.
4. Regulator, two-stage for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.*
6. Volumetric flasks, 10-mL.*
7. Assorted volumetric pipets as needed.*
8. Hotplate, surface temperature to 150 °C.
9. Steambath.

* Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a carcinogen [6]. Handle appropriately. Perform all digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer both the treated filter and backup pad to a clean beaker.
4. Add 15 mL conc. HNO_3 and cover with a watchglass.
   NOTE: Start reagent blanks at this step.
5. Heat on a 150 °C hotplate until the liquid volume is reduced to about 1 mL.

6. Carefully rinse the material on the bottom of the watchglass, and the sides of the beaker into the sample solution with distilled water. Add 6 mL 30% H_2O_2.
7. Evaporate just to dryness on the steambath.
8. Cool beakers. Add 10.0 mL 1000 μg/mL Ni^{2+} solution, cover, and mix for 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

9. Dilute the calibration stock solution 1:100 with 1000 μg/mL Ni^{++} solution. This standard is 10.0 μg/mL As. Prepare fresh daily.
10. Prepare six working standards covering the range 0 to 1.25 μg/mL As.
    a. Add aliquots of the 10.0 μg/mL As solution to 10-mL volumetric flasks and dilute to volume with 1000 μg/mL Ni^{2+} solution.
    b. Analyze the working standards together with the samplers and blanks (steps 13 and 14).
    c. Prepare calibration graph (absorbance vs. solution concentration, μg/mL). Inject a standard for every other sample to check instrument drift.
11. Check recoveries with at least two spiked media blanks per ten samples.
12. Use method of additions occasionally to check for interferences.

MEASUREMENT:

13. Set spectrophotometer according to manufacturer's recommendations to conditions on page 7901-1.
14. Inject standards and samples. Record absorbance (peak height) readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 1000 μg/mL Ni^{2+} solution, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

15. Record the actual solution volumes to which the sample, V_s (mL), and media blanks, V_b (mL) were diluted in step 8.
16. Calculate the solution concentration of arsenic in the sample, C_s (μg/mL), and average media blank, C_b (μg/mL), from the calibration graph.
17. Calculate the concentration of arsenic, C (mg/m^3), in the air volume sampled, V(L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S309 [4] was issued on September 26, 1975, and validated with aerosols generated from As_2O_3 solutions in dilute NaOH [2]. Method P&CAM 346 was developed in August, 1981, over the range 0.67 to 32.2 $\mu g/m^3$ for a 400-L air sample, corresponding to 0.268 to 12.8 μg As per sample [1]. Atmospheres were generated by passing air over heated As_2O_3. Collection efficiencies (CE) for As_2O_3 under these conditions were determined to be 0.42 and 0.67 for untreated 0.8-mm cellulose ester membrane filters, and cellulose backup pads, respectively. Under the same conditions, the Na_2CO_3-treated filter had CE = 0.93 [5]. This method was used in a lead-acid battery manufacturing plant in which vapor was found to be significant [10].

REFERENCES:

[1] Carlin, L. M., G. Colovos, D. Garland, M. E. Jamin, M. Klenck, T. J. Long, and C. L. Nealy. Analytical Methods Evaluation and Validation - As, Ni, W, V, Talc, and Wood Dust, Rockwell International, Final Report on NIOSH Contract No. 210-79-0060; available as Order No. PB 83-155325 from NTIS, Springfield, VA 22161.

[2] Documentation of the NIOSH Validation Tests, S309, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[3] Ibid, NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 346, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

[4] Ibid, V. 3, S309, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[5] Ibid, P&CAM 286.

[6] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (1975).

[7] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141-C (1979).

[8] Ibid, V. 1, P&CAM 180, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[9] Ibid, P&CAM 188.

[10] Costello, R. J., P. M. Eller, and R. D. Hull. Measurement of Multiple Inorganic Arsenic Species, Am. Ind. Hyg. Assoc. J., 44, 21-28 (1983).

METHOD REVISED BY:

M. Millson and P. M. Eller, Ph.D., NIOSH/DPSE; P&CAM 346 originally developed under NIOSH Contract 210-79-0060.

ARSINE

AsH_3 MW: 77.95 CAS: 7784-42-1 RTECS: CG6475000

METHOD: 6001, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.05 ppm
NIOSH: C 0.002 mg/m^3/15 min; carcinogen
ACGIH: 0.05 ppm; carcinogen
(1 ppm = 3.19 mg/m^3 @ NTP)

PROPERTIES: gas; d 3.484 g/L @ 20 °C;
BP −62.5 °C; MP −116.3 °C

SYNONYMS: hydrogen arsenide; arsenic trihydride.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.1 L @ 0.05 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.09 to 0.4 mg/m^3 [1] (10-L samples);
0.001 to 0.01 mg/m^3 [2]

BIAS: −6.13% at 0.01 to 0.2 L/min rates [1];
−11% @ 0.876 L/min [2]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 [2]

ACCURACY: ± 23.2%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: arsenic

DESORPTION: 1 mL 0.01 M HNO_3; 30 min in ultrasonic bath

MATRIX MODIFIER: Ni^{2+}, 1000 µg/mL

WAVELENGTH: 193.7 nm; D_2 or H_2 correction

GRAPHITE FURNACE: DRY: 40 sec @ 110 °C; CHAR: 15 sec @ 1200 °C; ATOMIZE 7 sec @ 2540 °C

INJECTION: 50 µL

CALIBRATION: As(III) in 0.01 M HNO_3 with 100 mg charcoal present

RANGE: 0.01 to 0.3 µg per sample [2]

ESTIMATED LOD: 0.004 µg per sample

PRECISION ($\bar{S}_r$): 0.060 @ 0.012 to 0.11 µg per sample [2]

APPLICABILITY: The working range is 0.0003 to 0.06 ppm (0.001 to 0.2 mg/m^3) for a 10-L air sample. This is an elemental analysis and is not compound-specific.

INTERFERENCES: Use background correction to control molecular absorption. Other arsenic compounds (gases or aerosols) may be collected on the sampler and would be erroneously reported as arsine. A cellulose ester filter in front of the charcoal tube may be used to remove aerosols [3,4]. The effect of relative humidity on the capacity of charcoal for arsine has not been studied.

OTHER METHODS: This method combines and replaces P&CAM 265 [5] and S229 [6] for arsine.

REAGENTS:

1. Water, distilled or deionized.
2. Nitric acid, conc.*
3. Nitric acid, 0.01 M. Dilute 0.4 mL conc. HNO_3 to 1 L with water.
4. Nitric acid, 0.1 M. Dilute 4 mL conc. HNO_3 to 1 L with water.
5. Arsenic stock solution, 1000 μg As(III)/mL.* Commercial standard or dissolve 1.322 g dried, certified reagent As_2O_3 in 100 mL 0.1 M HNO_3; dilute to 1 L with 0.1 M HNO_3.
6. Calibration stock solution, 1.0 μg As(III)/mL.* Dilute 0.1 mL arsenic stock solution (1000 μg As/mL) to 100 mL with 0.01 M HNO_3. Prepare fresh daily.
7. Nickel nitrate solution, 1000 μg Ni/mL. Commercial nickel atomic absorption standard or dissolve 3.112 g dried reagent $Ni(NO_3)_2$ in 100 mL 0.1 M HNO_3; dilute to 1 L with water.
8. Argon, compressed.
9. Arsine, *99%, or certified mixture in nitrogen.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
   NOTE: Use a cellulose ester membrane filter in front of the sampler if particulate arsenic is present [3,4].
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace, non-pyrolytic tubes, background correction and electrodeless discharge (and power supply) or hollow cathode lamp for arsenic.
4. Volumetric flasks, 1-L and 100-mL.*
5. Micropipets, 5- to 500-μL.*
6. Centrifuge tubes, 10- or 15-mL.*
7. Ultrasonic bath.
8. Centrifuge.
9. Syringe, gas, 0.1-mL, readable to 1 μL.

*Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a human carcinogen [7]. Perform all concentrated acid handling in a fume hood. Arsine is extremely poisonous by inhalation. Handle in well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: Use a cellulose ester membrane prefilter if particulate arsenic compounds may be present [3,4].
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 10 L.
4. Cap the sampler with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate centrifuge tubes. Discard the glass wool and foam plugs.
6. Add 1.0 mL 0.01 M HNO_3 to each tube. Cap each tube.

7. Agitate for 30 min in an ultrasonic bath.
8. Centrifuge each tube.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.004 to 0.3 μg arsenic per sample.
   a. Add known amounts of calibration stock solution and 0.01 M HNO_3 for a 1.0-mL final solution volume to centrifuge tubes containing 100 mg activated charcoal from a media blank sampler.
   b. Analyze standards together with samples and blanks (steps 12 and 13). Analyze a working standard for every five samples to check for instrument drift.
   c. Prepare a calibration graph (absorbance vs. μg arsenic).
10. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the range 0.004 to 2 μg arsenic per sample. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of pure arsine gas (or a certified gas mixture containing arsine) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 8) and analyze together with working standards (steps 12 and 13).
   e. Prepare a graph of DE vs. μg arsenic recovered.
11. Analyze three quality control spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set the spectrophotometer and furnace to manufacturer's recommendations and to conditions given on page 6001-1.
13. Inject a 50-μL aliquot of sample or standard followed by a 50-μL aliquot of nickel nitrate solution prior to initiating the analysis program. Measure peak area.
   NOTE 1: If sample absorbance is above the linear range of the standards, dilute with 0.01 M HNO_3, reanalyze and apply the appropriate dilution factor in calculations.
   NOTE 2: Monitor the reproducibility of peak area for a working standard throughout the measurements. If erratic results occur, reoptimize instrumental parameters and replace the graphite tube.

CALCULATIONS:

14. Determine the mass, μg, of arsine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections by multiplying the mass of arsenic found for each of these sections by 1.040 (M.W. of arsine/M.W. of arsenic).
   NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of arsine in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S229 [6] was evaluated over the range 0.094 to 0.404 mg/m^3 using 10-L air samples collected on SKC Lot 105 activated coconut charcoal [1]. Breakthrough (onto the backup section) did not occur after 240 min of sampling at 0.227 L/min from an arsine concentration of 0.405 mg/m^3 (0.022 mg loading). The recovery was found to be 93.7%. Desorption efficiency was 0.90 at 1 μg arsine per sample and 1.00 at 2 and 4 μg arsine per sample.

Method P&CAM 265 [5] was evaluated over the range 0.001 to 0.01 mg/m^3 using 15-L air samples [2]. These samples were collected on SKC Lot 106 activated coconut charcoal at a sampling flow rate of 0.875 L/min for 15 min. At this flow rate, a collection efficiency of 89.1% was found [3]. The effect of high humidity on the sampler capacity was not studied. Desorption efficiency was 0.90 in the range 0.015 to 0.2 μg arsine per sample.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S229, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), also available as Order No. PB 263959 from NTIS, Springfield, VA 22161 (1975).
[2] Evaluation and Refinement of Personal Sampling Method for Arsine, NIOSH Research Report, prepared under NIOSH Contract No. 210-76-0142 (NIOSH, unpublished, 1977).
[3] Costello, R. J., P. M. Eller and R. D. Hull. Measurement of Multiple Inorganic Arsenic Species, Am. Ind. Hyg. Assoc. J., 44(1), 21-28 (1983).
[4] Methods 7900 (Arsenic) and 7901 (Arsenic Trioxide), this Manual.
[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 265, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S229, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[7] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-149 (1977).

METHOD REVISED BY:

R. D. Hull, Ph.D., NIOSH/DBBS.

ASBESTOS (bulk) by PLM 9002

various MW: various CAS: 1332-21-4 RTECS: CI6475000

METHOD: 9002, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

EPA Standard (Bulk): 1% **PROPERTIES:** solid, fibrous, crystalline, anisotropic

SYNONYMS [CAS #]: actinolite [77536-66-4], or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4].

SAMPLING

BULK SAMPLE: 1 to 10 grams

SHIPMENT: seal securely to prevent escape of asbestos

SAMPLE STABILITY: stable

BLANKS: none required

ACCURACY

RANGE STUDIED: <1% to 100% asbestos

BIAS: not determined

PRECISION: not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, STEREO AND POLARIZED LIGHT, WITH DISPERSION STAINING

ANALYTE: actinolite asbestos, amosite, anthophyllite asbestos, chrysotile, crocidolite, tremolite asbestos

EQUIPMENT: microscope, polarized light; 100-400X dispersion staining objective, stereo microscope: 10-45X

RANGE: 1% to 100% asbestos

ESTIMATED LOD: <1% asbestos [1]

PRECISION: not determined

APPLICABILITY: this method is useful for the qualitative identification of asbestos and the semi-quantitative determination of asbestos content of bulk samples. The method measures percent asbestos as perceived by the analyst in comparison to standard area projections, photos, and drawings, or trained experience. The method is not applicable to samples containing large amounts of fine fibers below the resolution of the light microscope.

INTERFERENCES: Other fibers with optical properties similar to the asbestos minerals may give positive interferences. Optical properties of asbestos may be obscured by coating on the fibers. Fibers finer than the resolving power of the microscope (ca. 0.3 μm) will not be detected. Heat and acid treatment may alter the index of refraction of asbestos and change its color.

OTHER METHODS: This method (originally designated as method 7403) is designed for use with NIOSH Methods 7400 (phase contrast microscopy) and 7402 (electron microscopy/EDS). The method is similar to the EPA bulk asbestos method [1].

REAGENTS:

1. Refractive index (RI) liquids for Dispersion Staining: high-dispersion (HD) series, 1.550, 1.605, 1.620.
2. Refractive index liquids: 1.670, 1.680, and 1.700.
3. Asbestos reference samples such as SRM #1866, available from the National Institute of Standards and Technology.*
4. Distilled Water (optional).
5. Concentrated HCl: ACS reagent grade.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sample containers: screw-top plastic vials of 10- to 50-mL capacity.
2. Microscope, polarized light, with polarizer, analyzer, port for retardation plate, 360° graduated rotating stage, substage condenser with iris, lamp, lamp iris, and:
   a. Objective lenses: 10X, 20X, and 40X or near equivalent.
   b. Ocular lense: 10X minimum.
   c. Eyepiece reticle: crosshair.
   d. Dispersion staining objective lens or equivalent.
   e. Compensator plate: ca. 550 nm ± 20 nm, retardation: "first order red" compensator.
3. Microscope slides: 75 mm x 25 mm.
4. Cover slips.
5. Ventilated hood or negative-pressure glove box.
6. Mortar and pestle: agate or porcelain.
7. Stereomicroscope, ca. 10 to 45X.
8. Light source: incandescent or fluorescent.
9. Tweezers, dissecting needles, spatulas, probes, and scalpels.
10. Glassine paper or clean glass plate.
11. Low-speed hand drill with coarse burr bit (optional).

SPECIAL PRECAUTIONS: Asbestos, a human carcinogen, should be handled only in an exhaust hood (equipped with a HEPA filter) [2]. Precautions should be taken when collecting unknown samples, which may be asbestos, to preclude exposure to the person collecting the sample and minimize the disruption to the parent material [3]. Disposal of asbestos-containing materials should follow EPA Guidelines [4].

SAMPLING:

1. Place 1 to 10 g of the material to be analyzed in a sample container.
   NOTE: For large samples (i.e., whole ceiling tiles) that are fairly homogenous, a representative small portion should be submitted for analysis. Sample size should be adjusted to ensure that it is representative of the parent material.
2. Make sure that sample containers are taped so they will not open in transit.
3. Ship the samples in a rigid container with sufficient packing material to prevent damage or sample loss.

SAMPLE PREPARATION:

4. Visually examine samples in the container and with a low-magnification stereomicroscope in a hood. (If necessary, a sample may be carefully removed from the container and placed on glassine transfer paper or clean glass plate for examination). Break off a portion of the sample and examine the edges for emergent fibers. Note the homogeneity of the sample. Some hard tiles can be broken, and the edges examined for emergent fibers. If fibers are found, make an estimate of the amount and type of fibers present, confirm fiber type (step 14) and quantify (step 15).

5. In a hood, open sample container and with tweezers remove small, representative portions of the sample.
   a. If there are obvious separable layers, sample and analyze each layer separately.
   b. If the sample appears to be slightly inhomogeneous, mix it in the sample container with tweezers or a spatula before taking the portion of analysis. Alternatively, take small representative portions of each type of material and place on a glass slide.
   c. On hard tiles that may have thin, inseparable layers, use a scalpel to cut through all the layers for a representative sample. Then cut it into smaller pieces after placing RI liquid on it before trying to reduce the thickness. Alternatively, use a low-speed hand drill equipped with a burr bit to remove material from hard tiles. Avoid excessive heating of the sample which may alter the optical properties of the material.
      NOTE: This type of sample often requires ashing or other specialized preparation, and may require transmission electron microscopy for detection of the short asbestos fibers which are characteristic of floor tiles.
   d. If the sample has large, hard particles, grind it in a mortar. Do not grind so fine that fiber characteristics are destroyed.
   e. If necessary, treat a portion of the sample in a hood with an appropriate solvent to remove binders, tars, and other interfering materials which may be present in the sample. Make corrections for the non-asbestos material removed by this process.
      NOTE: Other methods of sample preparation such as acid washing and sodium metaphosphate treatment and ashing may be necessary, especially to detect low concentrations of asbestos. If needed, use as described in Reference [1].
6. After placing a few drops of RI liquid on the slide, put a small portion of sample in the liquid. Tease apart with a needle or smash small clumps with the flat end of a spatula or probe, producing a uniform thickness or particles so that better estimates of projected area percentages can be made. Mix the fibers and particles on the slide so that they are as homogeneous as possible.
   NOTE: An even dispersion of sample should cover the entire area under the cover slip. some practice will be necessary to judge the right amount of material to place on the slide. Too little sample may not give sufficient information and too much sample cannot be easily analyzed.

CALIBRATION AND QUALITY CONTROL:

7. Check for contamination each day of operation. Wipe microscope slides and cover slips with lens paper before using. Check refractive index liquids. Record results in a separate logbook.
8. Verify the refractive indices of the refractive index liquids used once per week of operation. Record these checks in a separate logbook.
9. Follow the manufacturer's instructions for illumination, condenser alignment and other microscope adjustments. Perform these adjustments prior to each sample set.
10. Determine percent of each identified asbestos species by comparison to standard projections (Figure 1) [1]. If no fibers are detected in a homogeneous sample, examine at least two additional preparations before concluding that no asbestos is present.
11. If it appears that the preparation technique might not be able to produce a homogeneous or representative sample on the slide, prepare a duplicate slide and average the results. Occasionally, when the duplicate results vary greatly, it will be necessary to prepare additional replicate slides and average all the replicate results. Prepare duplicate slides of at least 10% of the samples analyzed. Average the results for reporting.
12. Analyze about 5% blind samples of known asbestos content.
13. Laboratories performing this analytical method should participate in the National Voluntary Laboratory Accreditation Program [5] or a similar interlaboratory quality control program. Each analyst should have complete formal training in polarized light microscopy and its application to crystalline materials. In lieu of formal training, laboratory training in asbestos bulk analysis under the direction of a trained asbestos bulk analyst may be substituted. Owing to the subjective nature of the method, frequent practice is essential in order to remain proficient in estimating projected area percentages.

QUALITATIVE ASSESSMENT:

14. Scan the slide to identify any asbestos minerals using the optical properties of morphology, refractive indices, color, pleochroism, birefringence, extinction characteristics, sign of elongation, and dispersion staining characteristics.

    NOTE: Identification of asbestos using polarized light microscopy is unlike most other analytical methods. The quality of the results is dependent on the skill and judgment of the analyst. This method does not lend itself easily to a step-wise approach. Various procedures devised by different analysts may yield equivalent results. The following step-wise procedure repeatedly utilizes the sample preparation procedure previously outlined.

    a. Prepare a slide using 1.550 HD RI liquid. Adjust the polarizing filter such that the polars are partially crossed, with ca. 15° offset. Scan the preparation, examining the morphology for the presence of fibers. If no fibers are found, scan the additional preparations. If no fibers are found in any of the preparations, report that the sample does not contain asbestos, and stop the analysis at this point.

    b. If fibers are found, adjust the polarizing filter such that the polars are fully crossed. If all of the fibers are isotropic (disappear at all angles of rotation) then those fibers are not asbestos. Fibrous glass and mineral wool, which are common components of suspect samples, are isotropic. If only isotropic fibers are found in the additional preparations, report no asbestos fibers detected, and stop the analysis.

    c. If anisotropic fibers are found, rotate the stage to determine the angle of extinction. Except for tremolite-actinolite asbestos which has oblique extinction at 10-20°, the other forms of asbestos exhibit parallel extinction (Table 1). Tremolite may show both parallel and oblique extinction.

    d. Insert the first order red compensator plate in the microscope and determine the sign of elongation. All forms of asbestos have a positive sign of elongation except for crocidolite. If the sign of elongation observed is negative, go to step "g."

       NOTE: To determine the direction of the sign of elongation on a particular microscope configuration, examine a known chrysotile sample and note the direction (NE-SW or NW-SE) of the blue coloration. Chrysotile has a positive sign of elongation.

    e. Remove the first-order red compensator and uncross the polarizer. Examine under plane polarized light for blue and gold-brown Becke colors at the fiber-oil interface (i.e., index of refraction match). Becke colors are not always evident. Examine fiber morphology for twisted, wavy bundles of fibers which are characteristic of chrysotile. Twisted, ribbon-like morphology with cellular internal features may indicate cellulose fibers. It may be necessary to cross the polars partially in order to see the fibers if the index of refraction is an exact match at 1.550. If the fibers appear to have higher index of refraction, go to step "h," otherwise continue.

    f. Identification of chrysotile. Insert the dispersion staining objective. Observation of dispersion staining colors of blue and blue-magenta confirms chrysotile. Cellulose, which is a common interfering fiber at the 1.550 index of refraction, will not exhibit these dispersion staining colors. If chrysotile is found, go to step 15 for quantitative estimation.

    g. Identification of crocidolite. Prepare a slide in 1.700 RI liquid. Examine under plane-polarized light (uncrossed polars); check for morphology of crocidolite. Fibers will be straight, with rigid appearance, and may appear blue or purple-blue. Crocidolite is pleochroic, i.e., it will appear to change its color (blue or gray) as it is rotated through plane polarized light. Insert the dispersion staining objective. The central stop dispersion staining color are red magenta and blue magenta, however, these colors are sometimes difficult to impossible to see because of the opacity of the dark blue fibers. If observations above indicate crocidolite, go to step 15 for quantitative estimation.

    h. Identification of amosite. Prepare a slide in 1.680 RI liquid. Observed the fiber morphology for amosite characteristics: straight fibers and fiber bundles with broom-like or splayed ends. If the morphology matches amosite, examine the fibers using the dispersion staining objective. Blue and pale blue colors indicate the cummingtonite form of amosite, and gold and blue colors indicate the grunerite form of amosite. If amosite is confirmed by this test,

go to step 15 for quantitative estimation, otherwise continue.

i. Identification of anthophyllite-tremolite-actinolite. Prepare a slide in 1.605 HD RI liquid. Examine morphology for comparison to anthophyllite-tremolite-actinolite asbestos. The refractive indices for these forms of asbestos vary naturally within the species. Anthophyllite can be distinguished from actinolite and tremolite by its nearly parallel extinction. Actinolite has a light to dark green color under plane-polarized light and exhibits some pleochroism. For all three, fibers will be straight, single fibers possibly with some larger composite fibers. Cleavage fragments may also be present. Examine using the central stop dispersion staining objective. Anthophyllite will exhibit central stop colors of blue and gold/gold-magenta; tremolite will exhibit pale blue and yellow; and actinolite will exhibit magenta and golden-yellow colors.

NOTE: In this refractive index range, wollastonite is a common interfering mineral with similar morphology including the presence of cleavage fragments. It has both positive and negative sign of elongation, parallel extinction, and central stop dispersion staining colors of pale yellow and pale yellow to magenta. If further confirmation of wollastonite versus anthophyllite is needed, go to step "j". If any of the above forms of asbestos were confirmed above, go to step 15 for quantitative estimation. If none of the tests above confirmed asbestos fibers, examine the additional preparations and if the same result occurs, report the absence of asbestos in this sample.

j. Wash a small portion of the sample in a drop of concentrated hydrochloric acid on a slide. Place the slide, with cover slip in place, on a warm hot plate until dry. By capillary action, place 1.620 RI liquid under the cover clip and examine the slide. Wollastonite fibers will have a "cross-hatched" appearance across the length of the fibers and will not show central stop dispersion colors. Anthophyllite and tremolite will still show their original dispersion colors.

NOTE: There are alternative analysis procedures to the step-wise approach outlined above which will yield equivalent results. Some of these alternatives are:

i. Perform the initial scan for the presence of asbestos using crossed polars as well as the first-order red compensator. This allows for simultaneous viewing of birefringent and amorphous materials as well as determine their sign of elongation. Some fibers which are covered with mortar may best be observed using this configuration.

ii. Some analysts prefer to mount their first preparation in a RI liquid different than any asbestos materials and conduct their initial examination under plane-polarized light.

iii. If alternative RI liquids are used from those specified, dispersion staining colors observed will also change. Refer to an appropriate reference for the specific colors associated with asbestos in the RI liquids actually used.

QUANTITATIVE ASSESSMENT:

15. Estimate the content of the asbestos type present in the sample using the 1.550 RI preparation. Express the estimate as an area percent of all material present, taking into account the loading and distribution of all sample material on the slide. Use Figure 1 as an aid in arriving at your estimate. If additional unidentified fibers are present in the sample, continue with the qualitative measurement (step 14).

NOTE: Point-counting techniques to determine percentages of the asbestos minerals are not generally recommended. The point-counting method only produces accurate quantitative data when the material on the slide is homogeneous and has a uniform thickness, which is difficult to obtain [6]. The point-counting technique is, recommended by the EPA to determine the amount of asbestos in bulk [1]; however, in the more recent Asbestos Hazard Emergency Response Act (AHERA) regulations, asbestos quantification may be performed by a point-counting or equivalent estimation method [7].

16. Make a quantitative estimate of the asbestos content of the sample from the appropriate combination of the estimates from both the gross and microscopic examinations. If asbestos fibers are identified, report the material as "asbestos-containing". Asbestos content should be reported as a range of percent content. The range reported should be indicative of the analyst's precision in estimating asbestos content. For greater quantities use Figure 1 in arriving at your estimate.

EVALUATION OF METHOD:

The method is compiled from standard techniques used in mineralogy [8-13], and from standard laboratory procedures for bulk asbestos analysis which have been utilized for several years. These techniques have been successfully applied to the analysis of EPA Bulk Sample Analysis Quality Assurance Program samples since 1982 [1,5]. However, no formal evaluation of this method, as written, has been performed.

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METHOD WRITTEN BY:

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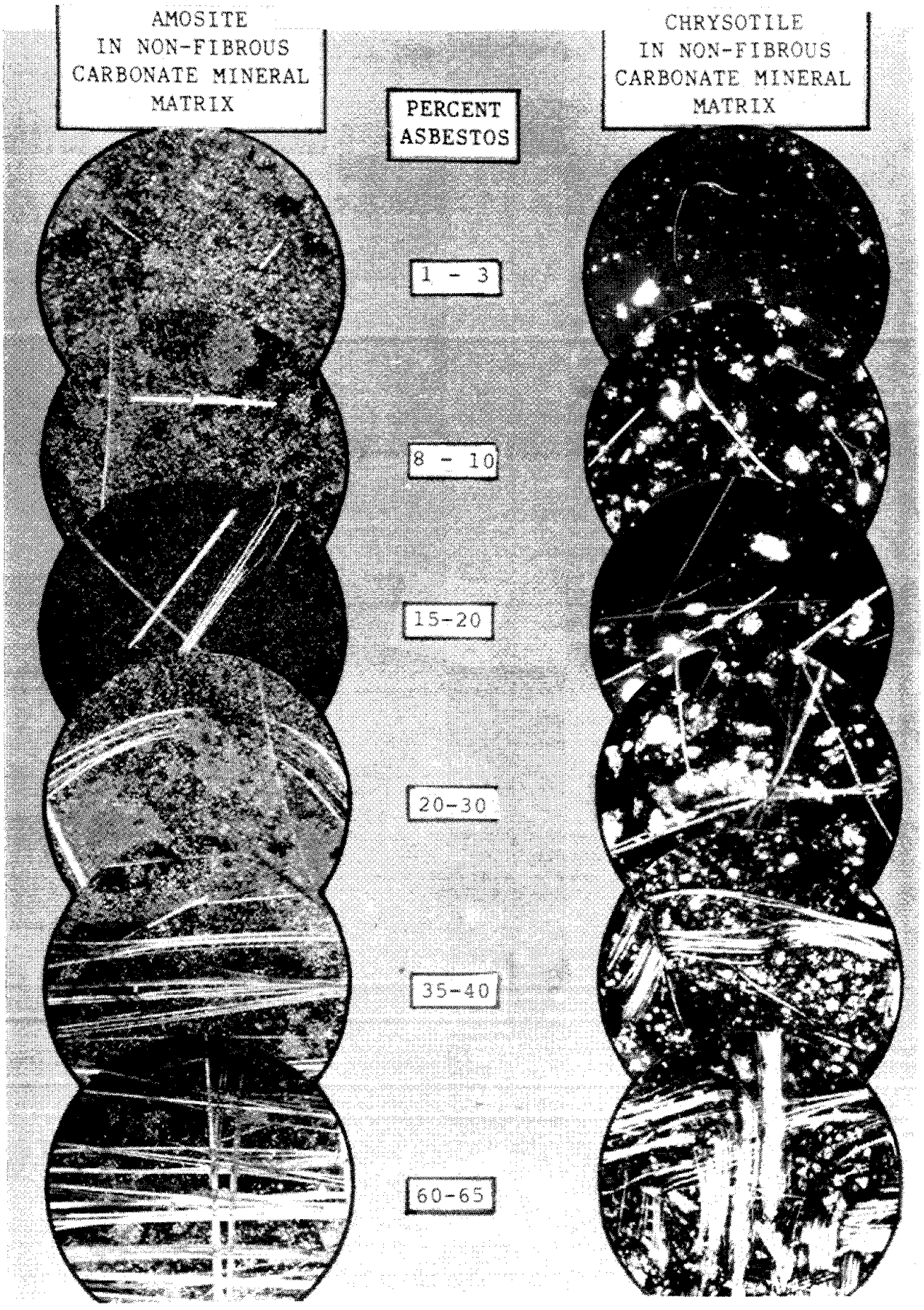
AMOSITE
IN NON-FIBROUS
CARBONATE MINERAL
MATRIX
PERCENT
ASBESTOS
CHRYSOTILE
IN NON-FIBROUS
CARBONATE MINERAL
MATRIX
1 - 3
8 - 10
15-20
20-30
35-40
60-65

Table 1. Optical Properties of Asbestos Fibers

		Refractive Index (Approximate Values)		
Mineral	Morphology and Color	⊥ to Elongation	∥ to Elongation	Birefringence
Chrysotile	Wavy fibers with kinks. Splayed ends on larger bundles. Colorless to light brown upon being heated. Nonpleochroic. Aspect ratio typically >10:1.	1.54	1.55	0.002 - 0.014
Cummingtonite-Grunerite (Amosite)	Straight fibers and fiber bundles. Bundle ends appear broom-like or splayed. Colorless to brown upon heating. May be weakly pleochroic. Aspect ratio typically >10:1.	1.67	1.70	0.02 - 0.03
Crocidolite (Riebeckite)	Straight fibers and fiber bundles. Longer fibers show curvature. Splayed ends on bundles. Characteristic blue color. Pleochroic. Aspect ratio typically >10:1.	1.71	1.70	0.014 - 0.016 Interference colors may be masked by blue color.
Anthophyllite	Straight fibers and fiber bundles. Cleavage fragments may be present. Colorless to light brown. Nonpleochroic to weakly pleochroic. Aspect ratio generally <10:1.	1.61	1.63	0.019 - 0.024
Tremolite-Actinolite	Straight and curved fibers. Cleavage fragments common. Large fiber bundles show splayed ends. Tremolite is colorless. Actinolite is green and weakly to moderately pleochroic. Aspect ratio generally <10:1.	1.60 - 1.62 (tremolite) 1.62 - 1.67 (actinolite)	1.62 - 1.64 (tremolite) 1.64 - 1.68 (actinolite)	0.02 - 0.03

Table 1. Optical Properties of Asbestos Fibers (Continued)

			Central Stop Dispersion Staining Colors		
Mineral	Extinction	Sign of Elongation	RI Liquid	⊥ to Vibration	∥ to Vibration
Chrysotile	Parallel to fiber length	+ (length slow)	1.550 HD	Blue	Blue-magenta
Cummingtonite-Grunerite (Amosite)	Parallel to fiber length	+ (length slow)	1.670 Fibers subjected to high temperatures will not dispersion-stain.	Red magenta to blue	Yellow
Cummingtonite			1.680	pale blue	blue
Grunerite			1.680	blue	gold
Crocidolite (Riebeckite)	Parallel to fiber length	- (length fast)	1.700	Red magenta	Blue-magenta
			1.680	yellow	pale yellow
Anthophyllite	Parallel to fiber length	+ (length slow)	1.605 HD	Blue	Gold to gold-magenta
			1.620 HD	Blue-green	Golden-yellow
Tremolite-Actinolite	Oblique - 10 to 20° for fragments. Some composite fibers show ∥ extinction.	+ (length slow)	1.605 HD	Pale blue (tremolite)	Yellow (tremolite)
				Yellow (actinolite)	Pale yellow (actinolite)

HD = high-dispersion RI liquid series.

ASBESTOS, CHRYSOTILE by XRD 9000

$Mg_3Si_2O_5(OH)_4$ MW: ca. 283 CAS: 12001-29-5 RTECS: CI6478500

METHOD: 9000, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

EPA Standard (Bulk): 1% by weight

PROPERTIES: solid, fibrous mineral; conversion to Forsterite at 580 °C; attacked by acids; loses water above 300 °C

SYNONYMS: Chrysotile

SAMPLING

BULK SAMPLE: 1 to 10 grams

SHIPMENT: seal securely to prevent escape of asbestos

SAMPLE STABILITY: indefinitely

BLANKS: none required

ACCURACY

RANGE STUDIED: 1 to 100% in talc [1]

BIAS: negligible if standards and samples are matched in particle size [1]

OVERALL PRECISION ($\hat{S}_{rT}$): unknown; depends on matrix and concentration

ACCURACY: ± 14% to ± 25%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: chrysotile

PREPARATION: grind under liquid N_2; wet-sieve through 10-μm sieve

DEPOSIT: 5 mg dust on 0.45-μm Ag membrane filter

XRD: Cu target X-ray tube; Optimize for intensity; 1° slit; Integrated intensity with background subtraction

CALIBRATION: suspensions of asbestos in 2-propanol

RANGE: 1 to 100% (w/w) asbestos

ESTIMATED LOD: 0.2% asbestos in talc and calcite; 0.4% in heavy X-ray absorbers such as Fe_2O_3

PRECISION ($\bar{S}_r$): 0.07 (5 to 100%); 0.10 (@ 3%); 0.125 (@ 1%)

APPLICABILITY: Analysis of percent chrysotile asbestos in bulk samples.

INTERFERENCES: Antigorite (massive serpentine), Chlorite, Kaolinite, Bementite, and Brushite interfere. X-ray fluorescence and absorption is a problem with some elements; fluorescence can be circumvented with a diffracted beam monochromator, and absorption is corrected for in this method.

OTHER METHODS: This is P&CAM 309 [2] applied to bulk samples only, since the sensitivity is not adequate for personal air samples. The EPA Test Method for the determination of asbestos in bulk insulation samples is similar to this one [3]. Method 7400 is an optical counting procedure for airborne fibers in personal samples. Methods 7402 (Asbestos by Transmission Electron Microscopy) and 9002 (Asbestos by Polarized Light Microscopy) are also useful for positive identification of asbestos.

REAGENTS:

1. Chrysotile*, available from: Analytical Reference Minerals, Measurements Research Branch, DPSE, NIOSH, 4676 Columbia Parkway, Cincinnati, OH 45226; or UICC Asbestos Reference Sample Set, UICC MRC Pneumoconiosis Unit Llandough Hospital, Penarth, Glamorgan, CF6 1XW, UK.2.
2. 2-Propanol.*
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Vials, plastic (for bulk sample).
2. Freezer mill, liquid N_2-cooled, (Spex Model 6700 or equivalent), grinding vials (Spex 6701), extractor (Spex 6704).
3. Ultrasonic bath.
4. Sieve, 10-μm, for wet-sieving.
5. Filters, polycarbonate, 1.0-μm, 37-mm (Nuclepore or equivalent).
6. Filtration apparatus and side-arm vacuum flask with 25- and 37-mm filter holders.
7. Oven, drying, 110 °C.
8. Analytical balance, readable to 0.01 mg.
9. Beaker, Griffin, 50-mL, with watchglass cover.
10. Filters, silver membrane, 25-mm diameter, 0.45-μm pore size (Millipore Corp., Poretics Corp., or equivalent).
11. Desiccator.
12. Bottles, glass, 1-L, with ground glass stoppers.
13. Wash bottle, polyethylene.
14. Magnetic stirrer.
15. X-ray powder diffractometer with copper target x-ray tube and scintillation detector.
16. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
17. Volumetric pipettes and flasks.

SPECIAL PRECAUTIONS: Asbestos, a human carcinogen, should be handled in a hood [4].

2-Propanol is flammable.

SAMPLING:

1. Place several grams of the dust to be analyzed in a plastic vial, seal the vial securely and ship in a padded carton.

SAMPLE PREPARATION:

2. Place ca. 0.5 g of sample dust in a grinding vial and grind in a liquid nitrogen-cooled mill for 2 to 10 min.
3. Wet sieve the ground dust using a 10-μm sieve and 2-propanol. Place the dust on the sieve and place the sieve directly in an ultrasonic bath or in a wide dish in the bath. Use enough 2-propanol to cover the dust (put water in the bath if a dish is used to contain the 2-propanol). Apply ultrasonic power to sieve the dust.
   NOTE: It may take some time to obtain several mg of dust. Heating of the 2-propanol is likely and cooling periods may be required.
4. Recover the sieved sample dust from the 2-propanol by filtering the suspension through a non-fibrous filter (polycarbonate) or by driving off the 2-propanol on a hot plate. Dry the sieved sample in 110 °C oven for 4 h or more.

9 5. Weigh out ca. 5 mg of the sieved material onto a small square of tared weighing paper. Record the actual weight, W, to the nearest 0.01 mg. Transfer the dust to a 50-mL beaker, washing the weighing paper with several mL of 2-propanol. Add 10 to 15 mL 2-propanol to the beaker.

6. Cover the beaker with a watchglass. Agitate in an ultrasonic bath at least 3 min until all agglomerated particles are dispersed. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.

7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.

   NOTE: Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration for sufficient time to produce a dry filter.

8. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze working standard filters:

   a. Prepare two suspensions of chrysotile asbestos in 2-propanol by weighing 10 and 100 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.

      NOTE: Depending on the particle size of the standard, it may need to be ground and wet sieved (step 3). Dry the standards in a 110 °C oven for 4 h or more. Store in a desiccator.

   b. Suspend the powder in the 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.

   c. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the 10 or 100 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the delivered suspension.

   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times. Prepare working standard filters, in triplicate, by this technique, at e.g., 0, 20, 30, 50 100, 200 and 500 μg.

   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the sample holder.

   f. Analyze by XRD (step 12). The XRD intensities (12.d.) are designated I_x° and are then normalized (12.e.) to obtain $\hat{I}_x^\circ$. The intensities for standards greater than 200 mg should be corrected for matrix absorption (12.f. and 13).

   g. Prepare a calibration graph by plotting $\hat{I}_x^\circ$, as a function of μg of each standard.

      NOTE: Poor repeatability (greater than 10% above 0.04 mg chrysotile) indicates that new standards should be made. The data should lie along a straight line. It is preferable to use a weighted least squares with $1/\sigma^2$ weighing, where σ^2 is the variance of the data at a given loading.

   h. Determine the slope, m, of the calibration curve in counts/μg. The intercept on the abscissa should be within ± 5 μg of zero.

NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline has been calculated or interference by another phase.

10. Select six silver membrane filters as media blanks (for determination of sample self-absorption, step 13) randomly from the same box of filters to be used for depositing the samples. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on sample holders. Determine the net normalized count for the silver peak, $\hat{I}^{\circ}_{Ag}$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 degrees 2-theta) of the sample to determine the presence of chrysotile and interferences. The expected diffraction peaks are as follows:

	Peak (2-Theta Degrees)	
Mineral	Primary	Secondary
Chrysotile	12.08	24.38
Silver	38.12	44.28

12. Mount the filter (sample, standard or blank) in the XRD instrument and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses.
    b. Measure the diffraction peak area of a chrysotile peak that is free of interference. Scan times should be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for the sample peak on each sample and standard:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N.$$

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently; net intensities should be normalized to the most recently measured reference intensity.

    f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-theta range used for the analyte and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

13. Calculate the percentage of chrysotile in the bulk dust sample:

$$C = \frac{(\hat{I}_x \cdot f(T) - b) \cdot 100}{m \cdot W}, \%$$

where: $\hat{I}_x$ = normalized intensity for sample peak

b = intercept of calibration graph ($\hat{I}_x^\circ$ vs. W)

m = slope of calibration graph (counts/μg)

$f(T) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

$R = \sin(\theta_{Ag})/\sin(\theta_x)$

$T = \hat{I}_{Ag}/(\text{average } \hat{I}_{Ag}^\circ)$ = transmittance of sample

$\hat{I}_{Ag}$ = normalized silver peak intensity from sample

average $\hat{I}_{Ag}^\circ$ = normalized silver peak intensity from media blanks (average of six values)

W = mass of deposited sample in μg.

NOTE: For a more detailed discussion of the absorption correction procedure, see references [5] to [8].

EVALUATION OF METHOD:

This method is based on the work of B.A. Lange in developing P&CAM 309 [1,2]. Samples in the range of 1 to 100% chrysotile in talc were studied to establish the feasibility of an XRD method for airborne asbestos. Analytical precision was as follows:

% Chrysotile in Talc	$\bar{S}_r$ (%)
100	6.9
10	4.7
7	9.8
5	8.2
3	10.1
1	12.5

This work also showed that bias of results after absorption corrections are made is negligible.

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METHOD REVISED BY:

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TABLE 1. ABSORPTION CORRECTION FACTOR AS A FUNCTION OF TRANSMITTANCE FOR SOME CHRYSOTILE-SILVER PEAK COMBINATIONS.

Transmittance	Chrysotile	f(T)		Transmittance	f(T)	
T	Silver	12.08 / 38.12	24.38 / 38.12	*T*	12.08 / 38.12	24.38 / 38.12
1.00		1.0000	1.0000	0.69	1.6839	1.3142
0.99		1.0157	1.0078	0.68	1.7151	1.3277
0.98		1.0317	1.0157	0.67	1.7470	1.3414
0.97		1.0480	1.0237	0.66	1.7797	1.3555
0.96		1.0647	1.0319	0.65	1.8132	1.3698
0.95		1.0817	1.0402	0.64	1.8475	1.3845
0.94		1.0991	1.0486	0.63	1.8827	1.3995
0.93		1.1168	1.0572	0.62	1.9188	1.4148
0.92		1.1350	1.0659	0.61	1.9558	1.4305
0.91		1.1535	1.0747	0.60	1.9938	1.4465
0.90		1.1724	1.0837	0.59	2.0328	1.4629
0.89		1.1917	1.0928	0.58	2.0728	1.4797
0.88		1.2114	1.1021	0.57	2.1139	1.4969
0.87		1.2316	1.1115	0.56	2.1560	1.5145
0.86		1.2522	1.1212	0.55	2.1993	1.5325
0.85		1.2733	1.1309	0.54	2.2438	1.5510
0.84		1.2948	1.1409	0.53	2.2895	1.5700
0.83		1.3168	1.1510	0.52	2.3365	1.5895
0.82		1.3394	1.1613	0.51	2.3848	1.6095
0.81		1.3624	1.1718	0.50	2.4344	1.6300
0.80		1.3859	1.1825	0.49	2.4855	1.6510
0.79		1.4100	1.1933	0.48	2.5380	1.6727
0.78		1.4346	1.2044	0.47	2.5921	1.6950
0.77		1.4598	1.2157	0.46	2.6478	1.7179
0.76		1.4856	1.2272	0.45	2.7051	1.7414
0.75		1.5120	1.2389	0.44	2.7642	1.7657
0.74		1.5390	1.2508	0.43	2.8251	1.7907
0.73		1.5666	1.2630	0.42	2.8879	1.8165
0.72		1.5949	1.2754	0.41	2.9526	1.8431
0.71		1.6239	1.2881	0.40	3.0195	1.8705
0.70		1.6536	1.3010			

ASBESTOS and OTHER FIBERS by PCM 7400

Various MW: Various CAS: Various RTECS: Various

METHOD: 7400, Issue 2 **EVALUATION: FULL** **Issue 1: Rev. 3 on 15 May 1989**
Issue 2: 15 August 1994

OSHA : 2 asbestos fiber (≥ 5 μm long)/cc; C 10 f/cc; carcinogen
MSHA: 5 asbestos fibers (> 5 μm long)/cc
NIOSH: 0.1 f/cc (fibers > 5 μm long)/400 L; carcinogen
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc; carcinogen

PROPERTIES: solid, fibrous, crystalline, anisotropic

SYNONYMS [CAS #]: actinolite **[77536-66-4]** or ferroactinolite **[15669-07-5]**; amosite **[12172-73-5]**; anthophyllite **[77536-67-5]**; chrysotile **[12001-29-5]**; serpentine **[18786-24-8]**; crocidolite **[12001-28-4]**; tremolite **[77536-68-6]**; amphibole asbestos **[1332-21-4]**; fibrous glass.

SAMPLING

SAMPLER: FILTER (0.45- to 1.2-μm cellulose ester membrane, 25-mm; conductive cowl on cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust to give 100 to 1300 fiber/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.115 to 0.13 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone - collapse/triacetin - immersion method [2]

COUNTING RULES: described in previous version of this method as "A" rules [1,3]

EQUIPMENT:
1. positive phase-contrast microscope
2. Walton-Beckett graticule (100-μm field of view) Type G-22
3. phase-shift test slide (HSE/NPL)

CALIBRATION: HSE/NPL test slide

RANGE: 100 to 1300 fibers/mm^2 filter area

ESTIMATED LOD: 7 fibers/mm^2 filter area

PRECISION ($\bar{S}_r$): 0.10 to 0.12 [1]; see EVALUATION OF METHOD

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. The method gives an index of airborne fibers. It is primarily used for estimating asbestos concentrations, though PCM does not differentiate between asbestos and other fibers. Use this method in conjunction with electron microscopy (e.g., Method 7402) for assistance in identification of fibers. Fibers < ca. 0.25 μm diameter will not be detected by this method [4]. This method may be used for other materials such as fibrous glass by using alternate counting rules (see Appendix C).

INTERFERENCES: If the method is used to detect a specific type of fiber, any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This revision replaces Method 7400, Revision #3 (dated 8/15/89).

REAGENTS:

1. Acetone,* reagent grade.
2. Triacetin (glycerol triacetate), reagent grade.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically conductive extension cowl and cellulose ester filter, 0.45- to 1.2-μm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use to check for clarity and background. Discard the filter lot if mean is >5 fibers per 100 graticule fields. These are defined as laboratory blanks. Manufacturer-provided quality assurance checks on filter blanks are normally adequate as long as field blanks are analyzed as described below.
   NOTE 2: The electrically conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling.
   NOTE 3: Use 0.8-μm pore size filters for personal sampling. The 0.45-μm filters are recommended for sampling when performing TEM analysis on the same samples. However, their higher pressure drop precludes their use with personal sampling pumps.
   NOTE 4: Other cassettes have been proposed that exhibit improved uniformity of fiber deposit on the filter surface, e.g., bellmouthed sampler (Envirometrics, Charleston, SC). These may be used if shown to give measured concentrations equivalent to sampler indicated above for the application.
2. Personal sampling pump, battery or line-powered vacuum, of sufficient capacity to meet flow-rate requirements (see step 4 for flow rate), with flexible connecting tubing.
3. Wire, multi-stranded, 22-gauge; 1", hose clamp to attach wire to cassette.
4. Tape, shrink- or adhesive-.
5. Slides, glass, frosted-end, pre-cleaned, 25 x 75-mm.
6. Cover slips, 22- x 22-mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
7. Lacquer or nail polish.
8. Knife, #10 surgical steel, curved blade.
9. Tweezers.

EQUIPMENT:

10. Acetone flash vaporization system for clearing filters on glass slides (see ref. [5] for specifications or see manufacturer's instructions for equivalent devices).
11. Micropipets or syringes, 5-μL and 100- to 500-μL.
12. Microscope, positive phase (dark) contrast, with green or blue filter, adjustable field iris, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
13. Graticule, Walton-Beckett type with 100-μm diameter circular field (area = 0.00785 mm^2) at the specimen plane (Type G-22). Available from Optometrics USA, P.O. Box 699, Ayer, MA 01432 [phone (508)-772-1700], and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. (see APPENDIX A for the custom-ordering procedure).
14. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd. (address above).
15. Telescope, ocular phase-ring centering.
16. Stage micrometer (0.01-mm divisions).

SPECIAL PRECAUTIONS: Acetone is extremely flammable. Take precautions not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. To reduce contamination and to hold the cassette tightly together, seal the crease between the cassette base and the cowl with a shrink band or light colored adhesive tape. For personal sampling, fasten the (uncapped) open-face cassette to the worker's lapel. The open face should be oriented downward.
    NOTE: The cowl should be electrically grounded during area sampling, especially under conditions of low relative humidity. Use a hose clamp to secure one end of the wire (Equipment, Item 3) to the monitor's cowl. Connect the other end to an earth ground (i.e., cold water pipe).
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Handle field blanks in a manner representative of actual handling of associated samples in the set. Open field blank cassettes at the same time as other cassettes just prior to sampling. Store top covers and cassettes in a clean area (e.g., a closed bag or box) with the top covers from the sampling cassettes during the sampling period.
4. Sample at 0.5 L/min or greater [6]. Adjust sampling flow rate, Q (L/min), and time, t (min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 ($3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area A_c = 385 mm^2) for optimum accuracy. These variables are related

to the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

NOTE 1: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. The collection efficiency does not appear to be a function of flow rate in the range of 0.5 to 16 L/min for asbestos fibers [7]. Relatively large diameter fibers (>3 μm) may exhibit significant aspiration loss and inlet deposition. A sampling rate of 1 to 4 L/min for 8 h is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If $\geq$ 50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.

NOTE 2: OSHA regulations specify a minimum sampling volume of 48 L for an excursion measurement, and a maximum sampling rate of 2.5 L/min [3].

5. At the end of sampling, replace top cover and end plugs.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE 1: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index $\leq$1.46. This method collapses the filter for easier focusing and produces permanent (1 - 10 years) mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" or similar flash vaporization techniques may be used outside the laboratory [2]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [3,7,8,9]). Unless the effective filtration area is known, determine the area and record the information referenced against the sample ID number [1,9,10,11].

NOTE 2: Excessive water in the acetone may slow the clearing of the filter, causing material to be washed off the surface of the filter. Also, filters that have been exposed to high humidities prior to clearing may have a grainy background.

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [2].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade surgical steel knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.

b. Insert slide with wedge into the receiving slot at base of "hot block". Immediately place tip of a micropipet containing ca. 250 µL acetone (use the minimum volume needed to consistently clear the filter sections) into the inlet port of the PTFE cap on top of the "hot block" and inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 sec for the filter to clear, remove pipet and slide from their ports.
   CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous use of this device in an unventilated space may produce explosive acetone vapor concentrations.
c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation. Avoid excess pressure and movement of the cover glass.
   NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.
d. Mark the outline of the filter segment with a glass marking pen to aid in microscopic evaluation.
e. Glue the edges of the cover slip to the slide using lacquer or nail polish [12]. Counting may proceed immediately after clearing and mounting are completed.
   NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturers instructions. At least once daily use the telescope ocular (or Bertrand lens, for some microscopes) supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of microscope cleanings and major servicing.
    a. Each time a sample is examined, do the following:
       (1) Adjust the light source for even illumination across the field of view at the condenser iris. Use Kohler illumination, if available. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contract optics.
       (2) Focus on the particulate material to be examined.
       (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
    b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
       (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
       (2) Bring the blocks of grooved lines into focus in the graticule area.
          NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible when centered in the graticule area. Blocks 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.
       (3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.
11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis [13]. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field

and reference samples (e.g., PAT, AAR, commercial samples). The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.

b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter precision. Obtain separate values of relative standard deviation (S_r) for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, >20 to 50 fibers in 100 graticule fields, and >50 to 100 fibers in 100 graticule fields. Maintain control charts for each of these data files.

NOTE: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [9]

12. Prepare and count field blanks along with the field samples. Report counts on each field blank.

NOTE 1: The identity of blank filters should be unknown to the counter until all counts have been completed.

NOTE 2: If a field blank yields greater than 7 fibers per 100 graticule fields, report possible contamination of the samples.

13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the absolute value of the difference between the square roots of the two counts (in fiber/mm^2) exceeds 2.77 $(X)S_r'$, where X = average of the square roots of the two fiber counts (in fiber/mm^2) and $S_r' = \frac{S_r}{2}$, where S_r is the intracounter relative standard deviation for the appropriate count range (in fibers) determined in step 11. For more complete discussions see reference [11].

NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data [13].

NOTE 2: If a pair of counts is rejected by this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.

14. The analyst is a critical part of this analytical procedure. Care must be taken to provide a non-stressful and comfortable environment for fiber counting. An ergonomically designed chair should be used, with the microscope eyepiece situated at a comfortable height for viewing. External lighting should be set at a level similar to the illumination level in the microscope to reduce eye fatigue. In addition, counters should take 10-to-20 minute breaks from the microscope every one or two hours to limit fatigue [14]. During these breaks, both eye and upper back/neck exercises should be performed to relieve strain.

15. All laboratories engaged in asbestos counting should participate in a proficiency testing program such as the AIHA-NIOSH Proficiency Analytical Testing (PAT) Program for asbestos and routinely exchange field samples with other laboratories to compare performance of counters.

NOTE: OSHA requires that each analyst performing this method take the NIOSH direct training course #582 or equivalent [3]. Instructors of equivalent courses should have attended the NIOSH #582 course at NIOSH within three years of presenting an equivalent course.

MEASUREMENT:

16. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.

17. Adjust the microscope (Step 10).

NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 μm) [4].

18. Counting rules: (same as P&CAM 239 rules [1,10,11]: see examples in APPENDIX B).

a. Count any fiber longer than 5 μm which lies entirely within the graticule area.

(1) Count only fibers longer than 5 μm. Measure length of curved fibers along the curve.
(2) Count only fibers with a length-to-width ratio equal to or greater than 3:1.

b. For fibers which cross the boundary of the graticule field:
(1) Count as 1/2 fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rules a and b above.
(2) Do not count any fiber which crosses the graticule boundary more than once.
(3) Reject and do not count all other fibers.

c. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.

d. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.

19. Start counting from the tip of the filter wedge and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate or bubble covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

NOTE 1: When counting a graticule field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 seconds per field is appropriate for accurate counting.

NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report <u>total</u> fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters >1 μm), polarized light microscopy (as in NIOSH Method 7403) may be used to identify and eliminate interfering non-crystalline fibers [15].

NOTE 3: Do not count at edges where filter was cut. Move in at least 1 mm from the edge.

NOTE 4: Under certain conditions, electrostatic charge may affect the sampling of fibers. These electrostatic effects are most likely to occur when the relative humidity is low (below 20%), and when sampling is performed near the source of aerosol. The result is that deposition of fibers on the filter is reduced, especially near the edge of the filter. If such a pattern is noted during fiber counting, choose fields as close to the center of the filter as possible [5].

NOTE 5: Counts are to be recorded on a data sheet that provides, as a minimum, spaces on which to record the counts for each field, filter identification number, analyst's name, date, total fibers counted, total fields counted, average count, fiber density, and commentary. Average count is calculated by dividing the total fiber count by the number of fields observed. Fiber density (fibers/mm^2) is defined as the average count (fibers/field) divided by the field (graticule) area (mm^2/field).

CALCULATIONS AND REPORTING OF RESULTS

20. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the average fiber count per graticule field, F/n_f, minus the mean field blank count per graticule field, B/n_b, by the graticule field area, A_f (approx. 0.00785 mm^2):

$$E = \frac{(\frac{F}{n_f} - \frac{B}{n_b})}{A_f}, \text{ fibers/mm}^2.$$

NOTE: Fiber counts above 1300 fibers/mm^2 and fiber counts from samples with >50% of filter area covered with particulate should be reported as "uncountable" or "probably biased." Other fiber counts outside the 100-1300 fiber/mm^2 range should be reported as having "greater than optimal variability" and as being "probably biased."

21. Calculate and report the concentration, C (fibers/mL), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (approx. 385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

22. Report intralaboratory and interlaboratory relative standard deviations (from Step 11) with each set of results.

NOTE: Precision depends on the total number of fibers counted [1,16]. Relative standard deviation is documented in references [1,15-17] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Fig. 1).

EVALUATION OF METHOD:

A. This method is a revision of P&CAM 239 [10]. A summary of the revisions is as follows:
   1. Sampling:
      The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [10].
   2. Sample Preparation Technique:
      The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [2,4,10]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
   3. Measurement:
      a. The Walton-Beckett graticule standardizes the area observed [14,18,19].
      b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [4,14].
      c. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (a total of 78.5 fibers counted in 100 fields, each with field area = .00785 mm^2.) Lower levels generally result in an overestimate of the fiber count when compared to results in the recommended analytical range [20]. The recommended loadings should yield intracounter S_r in the range of 0.10 to 0.17 [21,22,23].

B. Interlaboratory comparability:
At international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [9]. The relative standard deviations (S_r) varied with sample type and laboratory. The ranges were:

	Intralaboratory S_r	Interlaboratory S_r	Overall S_r
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)**	0.11 to 0.29	0.20 to 0.35	0.25

* Under AIA rules, only fibers having a diameter less than 3 μm are counted and fibers attached to particles larger than 3 μm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.
** See Appendix C.

A NIOSH study conducted using field samples of asbestos gave intralaboratory S_r in the range 0.17 to 0.25 and an interlaboratory S_r of 0.45 [21]. This agrees well with other recent studies [9,14,16].

At this time, there is no independent means for assessing the overall accuracy of this method. One measure of reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the interlaboratory variability, as well as showing how the results of this method relate to the theoretically attainable counting precision and to measured intra- and interlaboratory S_r. (NOTE: The following discussion does not include bias estimates and should not be taken to indicated that lightly loaded samples are as accurate as properly loaded ones).

Theoretically, the process of counting randomly (Poisson) distributed fibers on a filter surface will give an S_r that depends on the number, N, of fibers counted:

$$S_r = 1/(N)^{1/2} \quad (1)$$

Thus S_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual S_r found in a number of studies is greater than these theoretical numbers [17,19,20,21].

An additional component of variability comes primarily from subjective interlaboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [15] found this subjective component of intralaboratory S_r to be approximately 0.2 and estimated the overall S_r by the term:

$$\frac{[N + (0.2 \cdot N)^2]^{1/2}}{N} \quad (2)$$

Ogden found that the 90% confidence interval of the individual intralaboratory counts in relation to the means were +2 S_r and - 1.5 S_r. In this program, one sample out of ten was a quality control sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of field sample results in 46 laboratories, the Asbestos Information Association also found that the variability had both a constant component and one that depended on the fiber count [14]. These results gave a subjective interlaboratory component of S_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [21]. This value falls slightly above the range of S_r (0.25 to 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH PAT program for laboratory-generated samples [17].

A number of factors influence S_r for a given laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an interlaboratory quality assurance program using field samples, the value for the subjective component of variability is chosen as 0.45. It is hoped that the laboratories will carry out the recommended interlaboratory quality assurance programs to improve their performance and thus reduce the S_r.

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [16].

For example, if a sample yields a count of 24 fibers, Figure 1 indicates that the mean interlaboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500-L volume, then the measured concentration is 0.02 fibers/mL (assuming 100 fields counted, 25-mm filter, 0.00785 mm^2 counting field area). If this same sample were counted by a group of laboratories, there is a 90% probability that the mean would fall between 0.01 and 0.08 fiber/mL. These limits should be reported in any comparison of results between laboratories.

Note that the S_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory S_r is smaller, then it is more correct to use that smaller S_r. However, the estimated S_r of 0.45 is to be used in the absence of such information. Note also that it has been found that S_r can be higher for certain types of samples, such as asbestos cement [9].

Quite often the estimated airborne concentration from an asbestos analysis is used to compare to a regulatory standard. For instance, if one is trying to show compliance with an 0.5 fiber/mL standard using a single sample on which 100 fibers have been counted, then Figure 1 indicates that the 0.5 fiber/mL standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fiber/mL (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/mL; i.e., 0.16 + 2.13 x 0.16 = 0.5.

It can be seen from Figure 1 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use +213% and −49% as the upper and lower confidence values of the mean for a 100-fiber count.

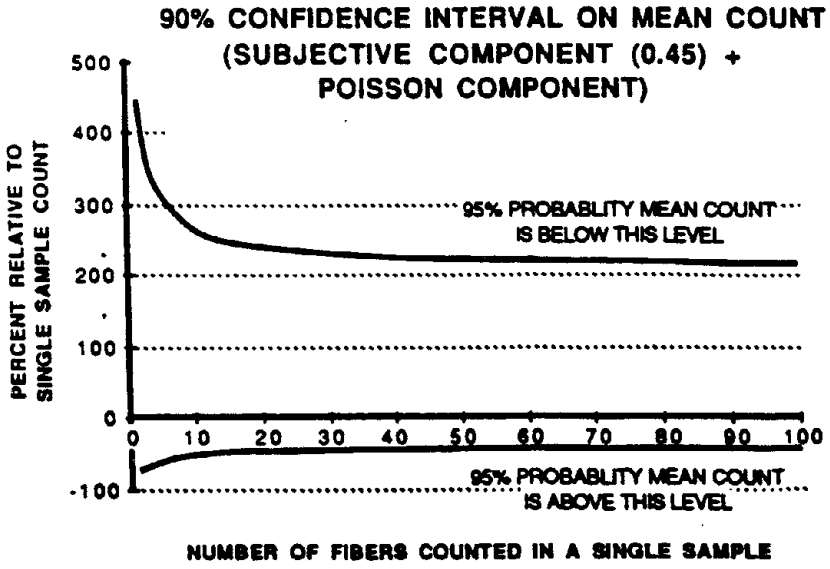

Figure 1. Interlaboratory Precision of Fiber Counts

The curves in Figures 1 are defined by the following equations:

$$UCL = \frac{2X + 2.25 + [(2.25 + 2X)^2 - 4(1 - 2.25 S_r^2) X^2]^{1/2}}{2(1 - 2.23 S_r^2)} \quad (3)$$

$$LCL = \frac{2X + 4 - [(4 + 2X)^2 - 4(1 - 4 S_r^2) X^2]^{1/2}}{2(1 - 4 S_r^2)} \quad (4)$$

where S_r = subjective interlaboratory relative standard deviation, which is close to the total interlaboratory S_r when approximately 100 fibers are counted.
X = total fibers counted on sample
LCL = lower 95% confidence limit.
UCL = upper 95% confidence limit.
Note that the range between these two limits represents 90% of the total range.

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METHOD WRITTEN BY:

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APPENDIX A: CALIBRATION OF THE WALTON-BECKETT GRATICULE:

Before ordering the Walton-Beckett graticule, the following calibration must be done to obtain a counting area (D) 100 μm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
3. Install the 40 to 45X phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (μm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D. \quad (5)$$

Example: If L_o = 112 μm, L_a = 4.5 mm and D = 100 μm, then d_c = 4.02 mm.

8. Check the field diameter, D (acceptable range 100 μm ± 2 μm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (acceptable range 0.00754 mm^2 to 0.00817 mm^2).

APPENDIX B: COMPARISON OF COUNTING RULES:

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. The rules will be discussed as they apply to the labeled objects in the figure.

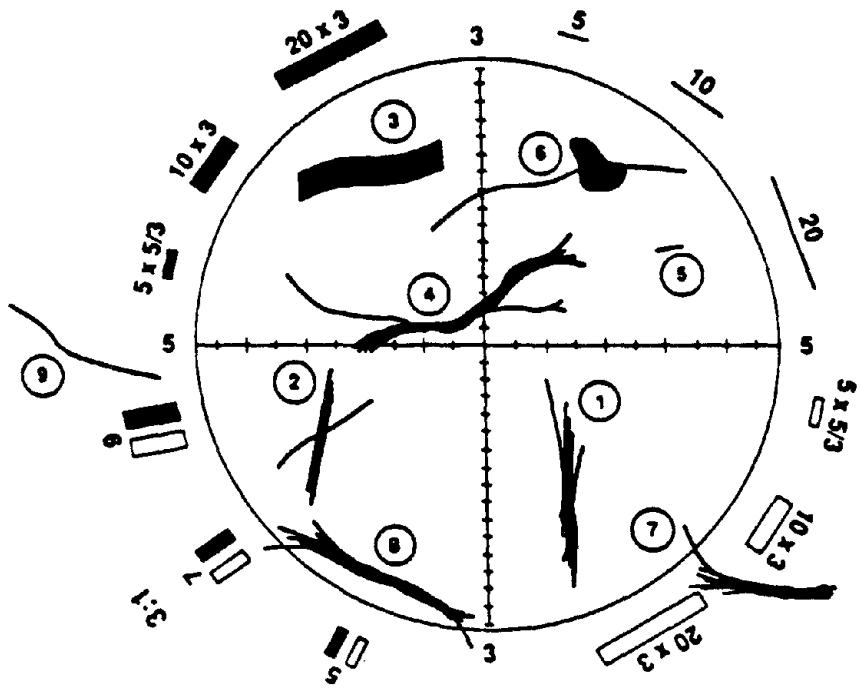

Figure 2. Walton-Beckett graticule with fibers.

These rules are sometimes referred to as the "A" rules.

FIBER COUNT

Object	Count	DISCUSSION
1	1 fiber	Optically observable asbestos fibers are actually bundles of fine fibrils. If the fibrils seem to be from the same bundle the object is counted as a single fiber. Note, however, that all objects meeting length and aspect ratio criteria are counted whether or not they appear to be asbestos.
2	2 fiber	If fibers meeting the length and aspect ratio criteria (length >5 μm and length-to-width ratio >3 to 1) overlap, but do not seem to be part of the same bundle, they are counted as separate fibers.
3	1 fiber	Although the object has a relatively large diameter (>3 μm), it is counted as fiber under the rules. There is no upper limit on the fiber diameter in the counting rules. Note that fiber width is measured at the widest compact section of the object.
4	1 fiber	Although long fine fibrils may extend from the body of a fiber, these fibrils are considered part of the fiber if they seem to have originally been part of the bundle.
5	Do not count	If the object is $\leq$5 μm long, it is not counted.
6	1 fiber	A fiber partially obscured by a particle is counted as one fiber. If the fiber ends emanating from a particle do not seem to be from the same fiber and each end meets the length and aspect ratio criteria, they are counted as separate fibers.
7	1/2 fiber	A fiber which crosses into the graticule area one time is counted as 1/2 fiber.
8	Do not count	Ignore fibers that cross the graticulate boundary more than once. count
9	Do not count	Ignore fibers that lie outside the graticule boundary.

APPENDIX C. ALTERNATE COUNTING RULES FOR NON-ASBESTOS FIBERS

Other counting rules may be more appropriate for measurement of specific non-asbestos fiber types, such as fibrous glass. These include the "B" rules given below (from NIOSH Method 7400, Revision #2, dated 8/15/87), the World Health Organization reference method for man-made mineral fiber [24], and the NIOSH fibrous glass criteria document method [25]. The upper diameter limit in these methods prevents measurements of non-thoracic fibers. It is important to note that the aspect ratio limits included in these methods vary. NIOSH recommends the use of the 3:1 aspect ratio in counting fibers.

It is emphasized that hybridization of different sets of counting rules is not permitted. Report specifically which set of counting rules are used with the analytical results.

"B" COUNTING RULES:

1. Count only ends of fibers. Each fiber must be longer than 5 μm and less than 3 μm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules 1 and 2 above. Add split ends to the count as appropriate if the split fiber segment also meets the criteria of rules 1 and 2 above.
4. Count visibly free ends which meet rules 1 and 2 above when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 μm in diameter.
5. Count free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules 1 and 2 above.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 graticule fields. Stop at 100 graticule fields, regardless of count.
7. Divide total end count by 2 to yield fiber count.

APPENDIX D. EQUIVALENT LIMITS OF DETECTION AND QUANTITATION

fiber density on filter*		fiber concentration in air, f/cc	
fibers per 100 fields	fibers/mm^2	400-L air sample	1000-L air sample
200	255	0.25	0.10
100	127	0.125	0.05
LOQ.....80	102	.....0.10	.....0.04
50	64	0.0625	0.025
25	32	0.03	0.0125
20	25	0.025	0.010
10	12.7	0.0125	0.005
8	10.2	0.010	0.004
LOD.....5.5	7	.....0.00675	.....0.0027

* Assumes 385 mm^2 effective filter collection area, and field area = 0.00785 mm^2, for relatively "clean" (little particulate aside from fibers) filters.

ASBESTOS by TEM 7402

FORMULA: Various MW: Various CAS: Various RTECS: Various

METHOD: 7402 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 2 asbestos fibers (>5 μm long)/cc; C 10 f/cc; carcinogen
MSHA: 2 asbestos fibers (>5 μm long)/cc
NIOSH: 0.1 f/cc (fibers > 5 μm long)/400 L; carcinogen
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc; carcinogen

PROPERTIES: solid, fibrous, crystalline, anistropic

SYNONYMS [CAS#]: actinolite [77536-66-4] or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4].

SAMPLING

SAMPLER: FILTER (0.45- to 1.2-μm cellulose ester membrane, 25-mm diameter; conductive cassette)

FLOW RATE: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust for 100 to 1300 fibers/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, TRANSMISSION ELECTRON (TEM)

ANALYTE: asbestos fibers

SAMPLE PREPARATION: modified Jaffe wick

EQUIPMENT: transmission electron microscope; energy dispersive X-ray system (EDX) analyzer

CALIBRATION: qualitative electron diffraction; calibration of TEM magnification and EDX system

RANGE: 100 to 1300 fibers/mm^2 filter area [1]

ESTIMATED LOD: 1 confirmed asbestos fiber above 95% of expected mean blank value

PRECISION ($\bar{S}_r$): 0.28 when 65% of fibers are asbestos; 0.20 when adjusted fiber count is applied to PCM count [2].

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. This method is used to determine asbestos fibers in the optically visible range and is intended to complement the results obtained by phase contrast microscopy (Method 7400).

INTERFERENCES: Other amphibole particles that have aspect ratios greater than 3:1 and elemental compositions similar to the asbestos minerals may interfere in the TEM analysis. Some non-amphibole minerals may give electron diffraction patterns similar to amphiboles. High concentrations of background dust interfere with fiber identification. Some non-asbestos amphibole minerals may give electron diffraction patterns similar to asbestos amphiboles.

OTHER METHODS: This method is designed for use with Method 7400 (phase contrast microscopy).

REAGENTS:

1. Acetone. (See SPECIAL PRECAUTIONS.)

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl, cellulose ester membrane filter, 0.45- to 1.2-μm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean count is >5 fibers/100 fields. These are defined as laboratory blanks.
   NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects on fiber sampling and during sample shipment. Ground the cowl when possible during sampling.
   NOTE 3: 0.8-μm pore size filters are recommended for personal sampling. 0.45-μm filters are recommended for sampling when performing TEM analysis on the samples because the particles deposit closer to the filter surface. However, the higher pressure drop through these filters normally preclude their use with personal sampling pumps.
2. Personal sampling pump, 0.5 to 16 L/min, with flexible connecting tubing.
3. Microscope, transmission electron, operated at ca. 100 kV, with electron diffraction and energy-dispersive X-ray capabilities, and having a fluorescent screen with inscribed or overlaid calibrated scale (Step 15).
   NOTE: The scale is most efficient if it consists of a series of lines inscribed on the screen or partial circles every 2 cm distant from the center.
4. Diffraction grating replica with known number of lines/mm.
5. Slides, glass, pre-cleaned, 25- x 75-mm.
6. Knife, surgical steel, curved-blade.
7. Tweezers.
8. Grids, 200-mesh TEM copper, (optional: carbon-coated).
9. Petri dishes, 15-mm depth. The top and bottom of the petri dish must fit snugly together. To assure a tight fit, grind the top and bottom pieces together with an abrasive such as carborundum to produce a ground-glass contact surface.
10. Foam, clean polyurethane, spongy, 12-mm thick.
11. Filters, Whatman No. 1 qualitative paper or equivalent, or lens paper.
12. Vacuum evaporator.
13. Cork borer, (about 8-mm).
14. Pen, waterproof, marking.
15. Reinforcement, page, gummed.
16. Asbestos standard bulk materials for reference; e.g. SRM #1866, available from the National Institute of Standards and Technology.
17. Carbon rods, sharpened to 1 mm x 8 mm.
18. Microscope, light, phase contrast (PCM), with Walton-Beckett graticule (see method 7400).
19. Grounding wire, 22-gauge, multi-strand.
20. Tape, shrink- or adhesive-.

SPECIAL PRECAUTIONS: Acetone is extremely flammable (flash point = 0 °F). Take precautions not to ignite it. Heating of acetone must be done in a fume hood using a flameless, spark-free heat source. Asbestos is a confirmed human carcinogen. Handle only in a well-ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. For personal sampling, fasten sampler to worker's lapel near worker's mouth. Remove the top cover from cowl extension ("open-face") and orient sampler face down. Wrap joint between extender and monitor body with tape to help hold the cassette together and provide a marking surface to identify the cassette. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (e.g., closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 0.5 to 16 L/min [3]. Adjust sampling rate, Q (L/min), and time, t (min), to produce fiber density, E, of 100 to 1300 fibers/mm^2 [3.85 · 10^4 to 5 · 10^5 fibers per 25-mm filter with effective collection area (A_c = 385 mm^2)] for optimum accuracy. Do not exceed ca. 0.5 mg total dust loading on the filter. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

   NOTE: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 h (700 to 2800 L) is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes (≤400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust [3].
5. At the end of sampling, replace top cover and small end caps.
6. Ship samples upright with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

7. Remove circular sections from any of three quadrants of each sample and blank filter using a cork borer [4]. The use of three grid preparations reduces the effect of local variations in dust deposit on the filter.
8. Affix the circular filter sections to a clean glass slide with a gummed page reinforcement. Label the slide with a waterproof marking pen.
   NOTE: Up to eight filter sections may be attached to the same slide.
9. Place the slide in a petri dish which contains several paper filters soaked with 2 to 3 mL acetone. Cover the dish. Wait 2 to 4 min for the sample filter(s) to fuse and clear.
   NOTE: The "hot block" clearing technique [5] of Method 7400 or the DMF clearing technique [6] may be used instead of steps 8 and 9.
10. Transfer the slide to a rotating stage inside the bell jar of a vacuum evaporator. Evaporate a 1- by 5-mm section of a graphite rod onto the cleared filter(s). Remove the slide to a clean, dry, covered petri dish [4].
11. Prepare a second petri dish as a Jaffe wick washer with the wicking substrate prepared from filter or lens paper placed on top of a 12-mm thick disk of clean, spongy polyurethane foam [7].

Cut a V-notch on the edge of the foam and filter paper. Use the V-notch as a reservoir for adding solvent.

NOTE: The wicking substrate should be thin enough to fit into the petri dish without touching the lid.

12. Place the TEM grid on the filter or lens paper. Label the grids by marking with a pencil on the filter paper or by putting registration marks on the petri dish halves and marking with a waterproof marker on the dish lid. In a fume hood, fill the dish with acetone until the wicking substrate is saturated.

NOTE: The level of acetone should be just high enough to saturate the filter paper without creating puddles.

13. Remove about a quarter section of the carbon-coated filter from the glass slide using a surgical knife and tweezers. Carefully place the excised filter, carbon side down, on the appropriately-labeled grid in the acetone-saturated petri dish. When all filter sections have been transferred, slowly add more solvent to the wedge-shaped trough to raise the acetone level as high as possible without disturbing the sample preparations. Cover the petri dish. Elevate one side of the petri dish by placing a slide under it (allowing drops of condensed acetone to form near the edge rather than in the center where they would drip onto the grid preparation).

CALIBRATION AND QUALITY CONTROL:

14. Determine the TEM magnification on the fluorescent screen:

a. Define a field of view on the fluorescent screen either by markings or physical boundaries.

NOTE: The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric) [7].

b. Insert a diffraction grating replica into the specimen holder and place into the microscope. Orient the replica so that the grating lines fall perpendicular to the scale on the TEM fluorescent screen. Ensure that goniometer stage tilt is zero.

c. Adjust microscope magnification to 10,000X. Measure the distance (mm) between the same relative positions (e.g., between left edges) of two widely-separated lines on the grating replica. Count the number of spaces between the lines.

NOTE: On most microscopes the magnification is substantially constant only within the central 8- to 10-cm diameter region of the fluorescent screen.

d. Calculate the true magnification (M) on the fluorescent screen:

$$m = \frac{X \cdot G}{Y}$$

where: X = total distance (mm) between the two grating lines;
G = calibration constant of the grating replica (lines/mm);
Y = number of grating replica spaces counted

e. After calibration, note the apparent sizes of 0.25 and 5.0 μm on the fluorescent screen. (These dimensions are the boundary limits for counting asbestos fibers by phase contrast microscopy.)

15. Measure 20 grid openings at random on a 200-mesh copper grid by placing a grid on a glass slide and examining it under the PCM. Use the Walton-Beckett graticule to measure the grid opening dimensions. Calculate an average graticule field dimension from the data and use this number to calculate the graticule field area for an average grid opening.

NOTE: A grid opening is considered as one graticule field.

16. Obtain reference selected area electron diffraction (SAED) or microdiffraction patterns from standard asbestos materials prepared for TEM analysis.

NOTE: This is a visual reference technique. No quantitative SAED analysis is required [7]. Microdiffraction may produce clearer patterns on very small fibers or fibers partially obscured by other material.

a. Set the specimen holder at zero tilt.

b. Center a fiber, focus, and center the smallest field-limiting aperture on the fiber. Obtain a diffraction pattern. Photograph each distinctive pattern and keep the photo for comparison to unknowns.

NOTE: Not all fibers will present diffraction patterns. The objective lens current may need adjustment to give optimum pattern visibility. There are many more amphiboles which give diffraction patterns similar to the analytes named on p. 7402-1. Some, but not all, of these can be eliminated by chemical separations. Also, some non-amphiboles (e.g., pyroxenes, some talc fibers) may interfere.

17. Acquire energy-dispersive X-ray (EDX) spectra on approximately 5 fibers having diameters between 0.25 and 0.5 μm of each asbestos variety obtained from standard reference materials [7].

NOTE: The sample may require tilting to obtain adequate signal. Use same tilt angle for all spectra.

a. Prepare TEM grids of all asbestos varieties.
b. Use acquisition times (at least 100 sec) sufficient to show a silicon peak at least 75% of the monitor screen height at a vertical scale of $\geq$500 counts per channel.
c. Estimate the elemental peak heights visually as follows:
   (1) Normalize all peaks to silicon (assigned an arbitrary value of 10).
   (2) Visually interpret all other peaks present and assign values relative to the silicon peak.
   (3) Determine an elemental profile for the fiber using the elements Na, Mg, Si, Ca, and Fe. Example: 0-4-10-3-<1 [7].
      NOTE: In fibers other than asbestos, determination of Al, K, Ti, S, P, and F may also be required for fiber characterization.
   (4) Determine a typical range of profiles for each asbestos variety and record the profiles for comparison to unknowns.

MEASUREMENT:

18. Perform a diffraction pattern inspection on all sample fibers counted under the TEM, using the procedures given in step 17. Assign the diffraction pattern to one of the following structures:
   a. chrysotile;
   b. amphibole;
   c. ambiguous;
   d. none.

   NOTE: There are some crystalline substances which exhibit diffraction patterns similar to those of asbestos fibers. Many of these, (brucite, halloysite, etc.) can be eliminated from consideration by chemistry. There are, however, several minerals (e.g., pyroxenes, massive amphiboles, and talc fibers) which are chemically similar to asbestos and can be considered interferences. The presence of these substances may warrant the use of more powerful diffraction pattern analysis before positive identification can be made. If interferences are suspected, morphology can play an important role in making positive identification.

19. Obtain EDX spectra in either the TEM or STEM modes from fibers on field samples using the procedure of step 18. Using the diffraction pattern and EDX spectrum, classify the fiber:
   a. For a chrysotile structure, obtain EDX spectra on the first five fibers and one out of ten thereafter. Label the range profiles from 0-5-10-0-0 to 0-10-10-0-0 as "chrysotile."
   b. For an amphibole structure, obtain EDX spectra on the first 10 fibers and one out of ten thereafter. Label profiles ca. 0-2-10-0-7 as "possible amosite"; profiles ca. 1-1-10-0-6 as "possible crocidolite"; profiles ca. 0-4-10-3-<1 as "possible tremolite"; and profiles ca. 0-3-10-0-1 as "possible anthophyllite."
      NOTE: The range of profiles for the amphiboles will vary up to $\pm$ 1 unit for each of the elements present according to the relative detector efficiency of the spectrometer.
   c. For an ambiguous structure, obtain EDX spectra on all fibers. Label profiles similar to the chrysotile profile as "possible chrysotile." Label profiles similar to the various amphiboles as "possible amphiboles." Label all others as "unknown" or "non-asbestos."

20. Counting and Sizing:
    a. Insert the sample grid into the specimen grid holder and scan the grid at zero tilt at low magnification (ca. 300 to 500X). Ensure that the carbon film is intact and unbroken over ca. 75% of the grid openings.
    b. In order to determine how the grids should be sampled, estimate the number of fibers per grid opening during a low-magnification scan (500 to 1000X). This will allow the analyst to cover most of the area of the grids during the fiber count and analysis. Use the following rules when picking grid openings to count [7,8]:
        (1) Light loading (<5 fibers per grid opening): count total of 40 grid openings.
        (2) Moderate loading (5 to 25 fibers per grid opening): count minimum of 40 grid openings or 100 fibers.
        (3) Heavy loading (>25 fibers per opening): count a minimum of 100 fibers and at least 6 grid openings.

        Note that these grid openings should be selected approximately equally among the three grid preparations and as randomly as possible from each grid.
    c. Count only grid openings that have the carbon film intact. At 500 to 1000X magnification, begin counting at one end of the grid and systematically traverse the grid by rows, reversing direction at row ends. Select the number of fields per traverse based on the loading indicated in the initial scan. Count at least 2 field blanks per sample set to document possible contamination of the samples. Count fibers using the following rules:
        (1) Count all particles with diameter greater than 0.25 μm that meet the definition of a fiber (aspect ratio $\geq$3:1, longer than 5 μm). Use the guideline of counting all fibers that would have been counted under phase contrast light microscopy (Method 7400). Use higher magnification (10000X) to determine fiber dimensions and countability under the acceptance criteria. Analyze a minimum of 10% of the fibers, and at least 3 asbestos fibers, by EDX and SAED to confirm the presence of asbestos. Fibers of similar morphology under high magnification can be identified as asbestos without SAED. Particles which are of questionable morphology should be analyzed by SAED and EDX to aid in identification.
        (2) Count fibers which are partially obscured by the grid as half fibers.
            NOTE: If a fiber is partially obscured by the grid bar at the edge of the field of view, count it as a half fiber only if more than 2.5 μm of fiber is visible.
        (3) Size each fiber as it is counted and record the diameter and length:
            (a) Move the fiber to the center of the screen. Read the length of the fiber directly from the scale on the screen.
                NOTE 1: Data can be recorded directly off the screen in μm and later converted to μm by computer.
                NOTE 2: For fibers which extend beyond the field of view, the fiber must be moved and superimposed upon the scale until its entire length has been measured.
            (b) When a fiber has been sized, return to the lower magnification and continue the traverse of the grid area to the next fiber.
    d. Record the following fiber counts:
        (1) f_s, f_b = number of asbestos fibers in the grid openings analyzed on the sample filter and corresponding field blank, respectively.
        (2) F_s, F_b = number of fibers, regardless of identification, in the grid openings analyzed on the sample filter and corresponding field blank, respectively.

CALCULATIONS:

21. Calculate and report the fraction of optically visible asbestos fibers on the filter, $(f_s - f_b)/(F_s - F_b)$. Apply this fraction to fiber counts obtained by PCM on the same filter or on other filters for which the TEM sample is representative. The final result is an asbestos fiber count. The type of asbestos present should also be reported.
22. As an integral part of the report, give the model and manufacturer of the TEM as well as the model and manufacturer of the EDX system.

EVALUATION OF METHOD:

The TEM method, using the direct count of asbestos fibers, has been shown to have a precision of 0.275 (s_r) in an evaluation of mixed amosite and wollastonite fibers. The estimate of the asbestos fraction, however, had a precision of 0.11 (s_r). When this fraction was applied to the PCM count, the overall precision of the combined analysis was 0.20 [2].

REFERENCES:

[1] Walton, W. H. "The Nature, Hazards, and Assessment of Occupational Exposure to Airborne Asbestos Dust: A Review," Ann. Occup. Hyg., 25, 115-247 (1982).

[2] Taylor, D. G., P. A. Baron, S. A. Shulman and J. W. Carter. "Identification and Counting of Asbestos Fibers," Am. Ind. Hyg. Assoc. J. 45(2), 84-88 (1984).

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[7] Yamate, G., S. A. Agarwal, and R. D. Gibbons. "Methodology for the Measurement of Airborne Asbestos by Electron Microscopy," EPA Contract No. 68-02-3266 (in press).

[8] Steel, E. B. and J. A. Small. "Accuracy of Transmission Electron Microcopy for the Analysis of Asbestos in Ambient Environments," Anal. Chem., 57, 209-213 (1985).

METHOD REVISED BY:

Paul A. Baron, Ph.D.; NIOSH/DPSE.

ASPARTAME 5031

$C_{14}H_{18}N_2O_5$ MW: 294.34 CAS: 22839-47-0 RTECS: WM3407000

METHOD: 5031, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: no standard
ACGIH: no standard

PROPERTIES: solid; MP 248-250 °C

SYNONYMS: L-aspartyl-L-phenylalanine methyl ester; 3-amino-N-(alpha-carboxyphenethyl)-succinamic acid N-methyl ester

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (1-μm, 37-mm PTFE)	**TECHNIQUE:**	HPLC, UV DETECTION
FLOW RATE:	1 to 3 L/min	**ANALYTE:**	Aspartame
VOL-MIN:	70 L @ 0.1 mg/m^3	**EXTRACTION:**	2 mL of eluent B.
-MAX:	1200 L	**INJECTION:**	25 μL
SHIPMENT:	routine	**COLUMN:**	C_{18}, 10-μm particle size
SAMPLE STABILITY:	stable at least 30 days at 20 °C [1]	**DETECTOR:**	UV, 220 nm
FIELD BLANKS:	2 to 10 field blanks per set	**MOBILE PHASE:**	60% eluent A/40% eluent B, isocratic
MEDIA BLANKS:	at least 3 per sample set	**CALIBRATION:**	standard solutions of Aspartame in eluent B
ACCURACY		**RANGE:**	7 to 800 μg per sample [1]
RANGE STUDIED:	not studied	**ESTIMATED LOD:**	2 μg per sample [1]
BIAS:	not determined	**PRECISION ($\bar{S}_r$):**	0.026 @ 4.4 to 435 μg per sample [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined		
ACCURACY:	not determined		

APPLICABILITY: The working range is 0.07 to 8 mg/m^3 for a 100-L air sample. The method has been used to analyze personal and area air samples during a health hazard evaluation at a commercial food packaging plant. [1]

INTERFERENCES: Food additives such as flavoring (artificial flavors), stabilizers (ascorbic acid) and food colors (FD&C yellow) collected along with Aspartame sampling, did not affect the analysis. [1]

OTHER METHODS: An HPLC method for the analysis of Aspartame in bulk has been reported. [2]

REAGENTS:

1. Aspartame,™ 96% pure.
2. Water, deionized.
3. Acetonitrile, distilled in glass.
4. Methanol, distilled in glass.
5. 1-Heptanesulfonic acid sodium salt.
6. Monobasic potassium phosphate.
7. Phosphoric acid, reagent grade.
8. Eluent A: Add 2.062 g 1-heptanesulfonic acid sodium salt and 0.45 g monobasic potassium phosphate to 1.0 L deionized water and adjust pH to 2.5 with dilute phosphoric acid.*
9. Eluent B: Add 2.062 g 1-heptanesulfonic acid sodium salt to 1.0 L of 3:2 (v/v) acetonitrile-water, and adjust pH to 3.0 with dilute phosphoric acid.
10. Calibration stock solution: 5 mg/mL. Add 0.05 g Aspartame and dilute with 10 mL eluent B.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 1-μm, 37-mm PTFE filter (Millipore FALP or equivalent) with a cellulose backup pad in a 37-mm polystyrene 2-piece cassette.
2. Personal sampling pump capable of 1 to 3 L/min, with flexible connecting tubing.
3. High-performance liquid chromatograph (HPLC) with UV detector, 220-nm, integrator and C_{18} column (page 5031-1).
4. Syringe filters, 13-mm: 0.45 μm, PTFE.
5. Syringe, 10-mL, disposable.
6. Vials, glass, scintillation, 20-mL with PTFE-lined caps.
7. Syringes, microliter, readable to 0.1 μL.
8. Pipets, various sizes.
9. Tweezers.
10. Ultrasonic water bath.
11. pH meter.

SPECIAL PRECAUTIONS: Phosphoric acid is extremely corrosive. Work with care in a hood using protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front and rear plugs immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately controlled flow rate between 1 and 3 L/min for a sample volume of 70 to 1200 L.
4. At the completion of sampling, replace both plugs and pack the sampler securely for shipment. Include appropriate number of blanks in the shipment.

SAMPLE PREPARATION:

5. Remove the PTFE filter with tweezers and transfer to a 20-mL scintillation vial. Discard the back-up pad. Add 2.0 mL eluent B.
6. Agitate the samples for 1 hour in an ultrasonic water bath.
7. Filter the sample solution using a disposable syringe fitted with a 0.45-μm PTFE filter into a clean vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solutions to eluent B, using serial dilutions as needed to obtain concentrations in the range of 1 to 400 μg /mL.
   b. Analyze with samples and blanks (steps 11 through 13).

c. Prepare a calibration graph (peak area vs. mass of Aspartame, μg per sample).

9. Determine the recovery at least once for each lot of filters used for sampling in the range of interest. Prepare six filters at each of three levels plus three media blanks.
   a. Add known amounts of Aspartame in methanol to the filters.
   b. Cover filters. Allow to stand overnight for solvent evaporation.
   c. Prepare samples (step 5 through 7), and analyze (step 11 through 13) together with standards.
   d. Determine recovery (R). Construct a graph of R vs. μg Aspartame recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 5031-1.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak areas.

CALCULATIONS:

14. Determine the mass, μg (corrected for recovery) of Aspartame found on the sample filter (W) and the average blank filter (B).
15. Calculate concentration, C, of Aspartame in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

A calibration curve constructed from nine standards over the range 0.5 to 463 μg/mL Aspartame in solution was linear and indicated a limit of detection (LOD) of 2 μg per filter and a limit of quantitation (LOQ) of 7 μg per filter. Test samples were prepared by spiking filters with known amounts of Aspartame from a solution in methanol at levels between 4.4 μg per filter and 434 μg per filter. At each level, three filters were subjected to each of the following studies (Table 1):

a. To evaluate extraction efficiency, the filters were analyzed immediately.
b. To assess storage stability, spiked filters were stored for 1 month prior to analysis.
c. To investigate the stability of the material on the filter during sampling, spiked filters were attached to a sampling pump and 1000 L of laboratory air was drawn through them at 2.5 L/min before analysis.

TABLE 1: Average Percent Recovery (n=3) of Aspartame

Spiked Amount (μg) (n=3)	Extraction Efficiency (%RSD)	Sampling Stability (%RSD)	Storage Stability @ 30 days (%RSD)
4.4	100 (2.3)	100 (1.3)	–
43.5	103 (4.8)	98 (3.1)	102 (2.7)
217	101 (1.8)	100 (2.4)	–
435	101 (1.3)	101 (1.3)	–

REFERENCES:

[1] Albrecht, W., G. Burr, and C. Neumeister. Sampling and Analytical Method for Workplace Monitoring of Aspartame in Air., App. Ind. Hyg., 4:9 (1989).

[2] Verzella, G., F. Bagnasco, and A. Mangia. Ion-Pair High-Performance Liquid Chromatographic Analysis of Aspartame and Related Products., J. Chromatogr., 349, 83 (1985).

METHOD WRITTEN BY:

Charles Neumeister, NIOSH/DPSE.

AZELAIC ACID 5019

$HOOC(CH_2)_7COOH$ MW: 188.25 CAS: 123-99-9 RTECS: CM1980000

METHOD: 5019, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solid; d 1.225 g/mL @ 25 °C; MP 106.5 °C; BP >360 °C (decomposes)

SYNONYMS: nonanedioic acid; 1,7-heptanedicarboxylic acid; lepargylic acid

SAMPLING

SAMPLER: FILTER (5-μm PVC membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 200 L @ 5 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: bis(trimethylsilyl)ester of azelaic acid

EXTRACTION: 5 mL ethanol; stand 20 min @ 70 °C; evaporate to dryness, derivatize and redissolve in pyridine

DERIVATIZATION: BSTFA/TMCS in pyridine; 20 min @ 70 °C

INJECTION VOLUME: 1 μL

TEMPERATURE-INJECTION: 250 °C;
-DETECTOR: 250 °C;
-COLUMN: 190 to 250 °C; 6 °C/min or 200 °C isothermal

CARRIER GAS: He, 39 mL/min

COLUMN: 3 m x 2-mm ID; 6% methyl silicone on 60/80 mesh Chromosorb WAW DMCS

CALIBRATION: analyte in pyridine

RANGE: 1 to 10 mg per sample

ESTIMATED LOD: 0.001 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.02 @ 1 to 10 mg per sample [1]

APPLICABILITY: The working range is 2 to 20 mg/m^3 for a 500-L air sample. The measurement range can be lowered if adequate recoveries are found. The method may be applicable to other straight-chain aliphatic dicarboxylic acids.

INTERFERENCES: Moisture decomposes both the trimethylsilyl reagents and their corresponding derivatives.

OTHER METHODS: This is P&CAM 256 [2] in a revised format.

REAGENTS:

1. N,O-bis(trimethylsilyl)trifluoro-acetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) obtainable from chromatography products suppliers.
   NOTE: Store in desiccator.
2. Pyridine, spectroquality grade.*
3. Ethanol, spectroquality grade.
4. Azelaic acid, highest purity available.
5. Helium, purified.
6. Hydrogen, purified.
7. Air, "zero grade."

* See Special Precautions

EQUIPMENT:

1. Sampler: PVC membrane filter, 5-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 5019-1).
4. Vacuum oven or hotplate.
5. Analytical balance, 0.01 mg.
6. Waterbath, 70 °C.
7. Vials, glass, 20-mL, PTFE-lined screw caps.
8. Pipets, 1- and 5-mL.
9. Syringes, 10-μL.
10. Tweezers, microspatula, weighing paper and an applicator stick.

SPECIAL PRECAUTIONS: Pyridine may cause central nervous system depression and irritation of the skin and respiratory tract [3]. Work must be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 200 to 1000 L.
3. Cap the samplers with plastic plugs and pack securely for shipment.

SAMPLE PREPARATION:

4. Remove filter from cassette holder with tweezers and insert in a glass vial. Push it gently to the bottom of the vial.
5. Pipet 5.0 mL ethanol into the vial. Cap the vial.
6. Place the vial in a 70 °C waterbath for 20 min. Shake the vial every 5 min.
   NOTE: Use of an ultrasonic bath is not recommended because it breaks up the PVC filter.
7. Lift the filter with tweezers so it is above the ethanol level in the vial. Rinse the filter with ten 1-mL aliquots of ethanol. Discard the filter.
8. Place the vial in a vacuum oven or on a hotplate at 45 to 50 °C. Evaporate to dryness.
9. Derivatize.
   a. Add 1 mL pyridine to the vial to dissolve the residue.
   b. Add 1 mL BSTFA mixture to the vial. Shake the vial for 1 min.
   NOTE: Avoid working in a humid atmosphere because water decomposes the trimethylsilyl reagent and derivative.
   c. Cap the vial. Place the vial in a waterbath at 70 °C for 20 min. Shake the contents of the vial every 5 min.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.001 to 10 mg azelaic acid per sample.
    a. Add weighed amounts of azelaic acid to marked vials containing 5 mL ethanol.
    b. Evaporate and derivatize (steps 8 and 9).

c. Analyze together with samples and blanks (steps 12 and 13).
d. Prepare calibration graph (peak area vs. mg azelaic acid).
NOTE: If azelaic acid is not 100% pure, correct the mass of azelaic acid standards before preparation of calibration graph.

11. Determine the recovery of azelaic acid from PVC filters at least once for each lot of filters used.
a. Weigh various amounts of azelaic acid to cover the range of interest onto PVC filters in marked vials.
b. Treat as in steps 5 through 9 and 12 and 13.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5019-1. Inject a 1-μL sample.
13. Measure peak area after each injection. Calculate the mean area.
NOTE: Remove daily the white flakes which accumulate on the FID.

CALCULATIONS:

14. Determine the mass, mg, of azelaic acid (W) per filter and the average media blank (B) from the calibration graph.
15. Calculate the concentration, C, of azelaic acid in the air volume sampled, V (L):

$$C = \frac{W - B}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The measurement precision, $\bar{S}_r$, of this method was determined to be 0.02 using standards in the range 1 to 10 mg per sample. The average recovery of azelaic acid from spiked PVC filters in the range 2 to 10 mg per filter was 94.9 ± 4.3% [1].

REFERENCES:

[1] Palassis, J. The Sampling and Determination of Azelaic Acid in Air, Am. Ind. Hyg. Assoc. J., 39, 731-736 (1978).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, USDHHS Publ. (NIOSH) 81-123 (1981).

METHOD REVISED BY:

John Palassis, NIOSH/DTMD.

BARIUM, soluble compounds 7056

Ba MW: 137.34 CAS: 7440-39-3 RTECS: CQ8370000

METHOD: 7056, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.5 mg/m^3
NIOSH: 0.5 mg/m^3
ACGIH: 0.5 mg/m^3

PROPERTIES: solubility @ 100 °C:
$BaCO_3$: 0.006 g/100 g H_2O;
$BaCl_2$: 59 g/100 g H_2O;
$Ba(NO_3)_2$: 34 g/100 g H_2O;
BaO: 91 g/100 g H_2O

SYNONYMS: vary depending upon compound

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 50 L @ 0.5 mg/m^3
-MAX: 2000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.28 to 1.08 mg/m^3 [1] (168-L samples)

BIAS: − 0.55%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.054 [1]

ACCURACY: ± 10.81%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: barium ion (Ba^{2+})

EXTRACTION: hot water leach, 10 mL, 10 min, twice; conc. HCl, 3 drops; evaporate to dryness

FINAL SOLUTION: 5% HCl/1.1 mg/mL Na^+, 5 mL

FLAME: nitrous oxide-acetylene reducing

WAVELENGTH: 553.6 nm

CALIBRATION: standard solutions of Ba^{2+} in 5% HCl/1.1 mg/mL Na^+

RANGE: 25 to 200 μg per sample [1]

ESTIMATED LOD: 2 μg per sample [1]

PRECISION ($\hat{S}_r$): 0.025 @ 43 to 180 μg per sample [1]

APPLICABILITY: The working range is 0.13 to 10 mg/m^3 for a 200-L air sample. This method determines Ba^{2+} in water-soluble barium compounds. Insoluble barium compounds (e.g., $BaSO_4$) require an ashing procedure.

INTERFERENCES: Ionization of barium in the flame is controlled by addition of sodium chloride to samples and standards. Calcium, at >0.1%, gives a positive interference unless background correction is used.

OTHER METHODS: This revises Method S198 [2].

REAGENTS:

1. Water, distilled or deionized.
2. Nitric acid (HNO_3), conc.*
3. Hydrochloric acid (HCl), conc.*
4. Sodium chloride (NaCl).
5. 5% HCl (v/v)/1.1 mg/mL Na^+: Dilute 5 mL conc. HCl and 0.28 g NaCl to 100 mL with deionized water.
6. Calibration stock solution, 1000 μg Ba/mL. Commercially available or dissolve 1.437 g $BaCO_3$ in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl.
7. Nitrous oxide, 98%.
8. Acetylene, 99.6%.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with nitrous oxide-acetylene burner head and barium hollow cathode lamp.
   NOTE: Background correction (e.g., D_2 or H_2 lamp) needed for samples with >0.1% (w/v) Ca^{2+}.
4. Regulators, two-stage, for nitrous oxide and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Pipets, 4- to 400-μL, and 5-mL.
8. Hotplate, surface temperature 140 °C.
9. Forceps or tweezers, plastic-tipped.
10. Centrifuge, and centrifuge tubes, 50-mL.

* Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Nitric and hydrochloric acids are corrosive liquids. Wear protective clothing and work in a fume head.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 50 to 2000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Open cassette filter holders and transfer samples and blanks to clean beakers.
4. Add 10 mL boiling distilled water. Let stand 10 min with occasional swirling. Decant extract to a centrifuge tube.
5. Wash filter and beaker twice with ca. 2 mL hot distilled water and add to centrifuge tube.
6. Repeat extraction and washing (steps 4 and 5), adding the solutions to the centrifuge tube.
7. Remove filter with forceps and rinse with stream of hot distilled water into centrifuge tube.
8. Rinse original beaker three times with ca. 2 mL hot distilled water and add to centrifuge tube. Centrifuge and decant the solution to a second beaker.
9. Add three drops conc. HCl to sample and evaporate until ca. 0.5 mL liquid remains.
10. Cool each beaker. Pipet 5.0 mL 5% HCl/1.1 mg/mL Na^+ solution into each beaker. Swirl to dissolve residue.

CALIBRATION AND QUALITY CONTROL:

11. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with 5% HCl/1.1 mg/mL Na^+ solution to produce Ba^{2+} concentrations in the range 0.4 to 40 μg/mL (0.002 to 0.2 mg per sample). Prepare fresh daily.
12. Analyze working standards with the blanks and samples (steps 17 and 18).
13. Prepare calibration graph (absorbance vs. solution concentration, μg/mL).
14. Aspirate a standard for every ten samples to check instrument drift.
15. Check recoveries with at least one spiked media blank per ten samples.
16. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7056-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If absorbance values for samples are above the linear range of the standards, dilute with 5% HCl/1.1 mg/mL Na^+ solution, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of barium in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of barium, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S198 was validated using atomized aqueous solutions of barium chloride to generate atmospheres at approximately 0.3 to 1.1 mg/m^3 [1]. Samples taken at 1.4 L/min showed 100% collection efficiency. Recovery of barium chloride standards spiked on filters was 102% with $\bar{S}_r$ = 1.4% in the range 0.043 to 0.18 mg barium per sample.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S198, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S198, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

BENZENE by portable GC 3700

C_6H_6 MW: 78.11 CAS: 71-43-2 RTECS: CY1400000

METHOD: 3700, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1 ppm; STEL 5 ppm
NIOSH: 0.1 ppm; C 1ppm/15 min (suspect carcinogen)
ACGIH: 10 ppm; (suspect carcinogen)
(1 ppm = 3.19 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.879 g/mL @ 20 °C; BP 80.1 °C; MP 5.5 °C; VP 12.7 kPa (95.2 mm Hg; 12.5% v/v) @25 °C; explosive range 1.3 to 7.1% v/v

SYNONYMS: benzol; cyclohexatriene

SAMPLING		MEASUREMENT	
SAMPLER:	AIR BAG (Tedlar)	**TECHNIQUE:**	GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR
FLOW RATE:	0.02 (or lower) to 5 L/min (or higher); fill bag to ≤80% of capacity; spot samples possible (step 2.a.)	**ANALYTE:**	benzene
SAMPLE STABILITY:	bags should be analyzed as soon after collection as possible (≤4 h).	**COLUMN:**	CPSil 5CB Macrobore capillary column operated isothermally at 30 °C (other columns and detectors shown in field study to be acceptable).
FIELD BLANKS:	clean air, either in bag or from a non-work area.	**CALIBRATION:**	bag standards or calibrated gas mixtures
		RANGE:	lower limit 0.02 to 1 ppm (see Interferences section below); upper limit 500 ppm.
		ESTIMATED LOD:	0.01 ppm for a 1-mL injection.
ACCURACY		**PRECISION ($\hat{S}_r$):**	0.127
RANGE STUDIED:	0.03 to 100 ppm [1]		
BIAS:	not significant		
OVERALL PRECISION ($\hat{S}_{rT}$):	0.136		
ACCURACY:	> ± 27%		

APPLICABILITY: The working range is 0.02 to 500 ppm (0.06 to 1600 mg/m^3) (see EVALUATION OF METHOD).

INTERFERENCES: Any compounds having the same or nearly the same retention time as benzene on the column in use are potential interferences. Such compounds cause positive interferences, however, and the actual benzene concentration will be less than or equal to the total of the benzene plus these compounds. The presence of a large number of compounds with retention time similar to benzene will cause a high background resulting in decreased sensitivity, possibly to the point where the LOQ approaches 1 ppm. Butane, styrene, toluene and xylenes have been shown not to affect this method [1]. Acceptable estimates of benzene concentration in diesel and gasoline vapors have been made with this method [2].

OTHER METHODS: Methods 1500 (Hydrocarbons, BP 36 - 126 °C) and 1501 (Hydrocarbons, aromatic) use activated charcoal sampler tubes.

REAGENTS:

1. Benzene* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure benzene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 5 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
   NOTE: Pumps lubricated with petroleum products should not be used.
3. Sample bags, Tedlar, 1- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labeling bags.

SPECIAL PRECAUTIONS: Benzene is a suspect carcinogen [3,4]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING:

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. Spot sample. Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections, if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.
   b. Integrated air sample for TWA determination.
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags. Alternatively, purge used bags at least two times with clean air, then fill with clean air and analyze for benzene as in step (4) below.
      (2) Attach the sample bag to the outlet port of a personal sampling pump with a minimum length of flexible tubing. To the inlet port of the pump attach a length of Teflon tubing sufficient to reach the desired site. Alternatively, a rubber squeeze bulb can be used in place of a personal sampling pump when sample size is small. In either case, tubing and pump/bulb should be flushed with sample air prior to, and clean air subsequent to, sample collection.

NOTE: Tygon tubing has been shown to adsorb some materials in complex hydrocarbon mixtures and to off-gas during later sample collection causing an increase in hydrocarbon concentration in those subsequent samples.

(3) Pump the air sample into the bag at a rate calculated to fill ≤80% of the sample bag capacity over the sampling period.
NOTE: The flow rate must be constant throughout the sampling period.

(4) Within 4 h after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2.a).

3. Obtain the benzene peak height or area of the injected sample.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph with at least three replicate determinations of at least six working standards. Plot peak height or area vs. mass or concentration of benzene.
   b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
   c. Determine the ability of the GC column to separate the benzene peak from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph (peak height vs. mass or concentration of benzene) with triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of benzene in sample by comparison of sample peak height with daily calibration graph (step 5). Determine concentration, C, of benzene in the injected sample, V (mL):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

NOTE: Some GCs will perform this calculation electronically.

EVALUATION OF METHOD:

This method was evaluated over the range 0.03 to 100 ppm benzene using a Photovac 10S portable GC. Certified standard gas mixtures of benzene in air were obtained from Scott Specialty Gases Inc., and these were used to establish the calibration graph. Once this graph was established, bias was assessed by analyzing a bag sample containing an unknown concentration and comparing the concentration obtained with that obtained from analysis of replicate charcoal tube sample taken from the same bag. Additionally, a field evaluation was subsequently conducted in which results obtained using this method were compared with results obtained using conventional laboratory GC analysis and with results obtained using laboratory GC/MS analysis. Instruments used in the field evaluation include the Photovac 10S, the Sentex Scentoscreen and the MSI-301B by Microsensor Systems, Inc.

Previous issues of this method discussed the use of portable GC with ambient temperature packed columns. That technique was considered to be limited in its ability to separate the analyte from any interferences present. Evaluation of this method, which uses a capillary column, indicates that benzene can be separated from butane, styrene, toluene and xylenes, and that a response corresponding to benzene can be identified in such complex mixtures as gasoline and diesel vapors [1].

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[1] Burroughs, G.E. and W.J. Woodfin. "On-Site Screening for Benzene in Complex Environments." A report to the U.S. Coast Guard, Research and Development Center, Groton, CT, in partial fulfillment of MIPR No. Z51100-2-E00528, August, 1993.
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[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, US DHHS (NIOSH) Publ. 81-123 (1981).
[4] Criteria for a Recommended Standard...Occupational Exposure to Benzene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 74-137 (1974); as revised in August, 1976, and by E. J. Baier, NIOSH Testimony to U.S. Department of Labor, July, 1977.

METHOD WRITTEN BY:

G.E. Burroughs and J.C. Posner, Ph.D., NIOSH/DPSE.

BENZIDINE

$(C_6H_4NH_2)_2$ MW: 184.23 CAS: 92-87-5 RTECS: DC9625000

METHOD: 5509, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : carcinogen (29 CFR 1910.1010)
NIOSH: carcinogen (29 CFR 1910.1010)
ACGIH: carcinogen (skin)

PROPERTIES: solid; MP 127 °C; BP 400 °C

SYNONYMS: [1,1'-biphenyl]-4,4'-diamine; p-diaminodiphenyl.

SAMPLING

SAMPLER: FILTER (13-mm glass fiber)

FLOW RATE: 0.2 L/min

VOL-MIN: 20 L @ 10 $\mu g/m^3$
-MAX: 100 L

SHIPMENT: ship benzidine samples in dry ice

SAMPLE STABILITY: 11 days @ −15 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 21 to 63 $\mu g/m^3$ [1]

BIAS: − 3.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 [1]

ACCURACY: ± 13.7%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: benzidine or 3,3'-dichlorobenzidine

DESORPTION: 0.5 mL 0.17% (v/v) triethylamine in methanol; stand 60 min

INJECTION VOLUME: 10 μL

MOBILE PHASE: 60% methanol/40% water;

FLOW RATE: 1.5 mL/min; ambient temperature

COLUMN: μBondapak C_{18}, 10-μm particles, 30 cm x 4-mm

DETECTOR: UV, 254 nm

CALIBRATION: solutions of analyte(s) in eluent

RANGE: 0.2 to 7 μg per sample

ESTIMATED LOD: 0.05 μg per sample [1]

PRECISION ($\bar{S}_r$): ≤0.07 [1]

APPLICABILITY: The working range for benzidine or 3,3'-dichlorobenzidine is 4 to 200 $\mu g/m^3$ for a 50-L air sample. Benzidinium sulfate and 3,3'-dichlorobenzidine dihydrochloride will be collected and converted to benzidine and 3,3'-dichlorobenzidine, respectively, during sample preparation.

INTERFERENCES: Aniline interferes in the determination of benzidine but may be resolved [2]. 4,4'-Methylenebis(2-chloroaniline) interferes in the determination of 3,3'-dichlorobenzidine [1]. A number of compounds were shown not to interfere [1,2] (see NOTE 2, step 12).

OTHER METHODS: This combines and replaces P&CAM 243 and P&CAM 246 [3].

REAGENTS:

1. Methanol, HPLC grade.
2. Acetonitrile, HPLC grade.
3. Triethylamine.
4. Water, distilled, deionized.
5. Benzidine.*
6. 3,3'-Dichlorobenzidine.*
7. Eluent: 0.17% (v/v) triethylamine in methanol. Dilute 170 μL triethylamine to 100 mL with methanol.
8. Calibration stock solution, 0.5 μg/μL. Dissolve 50 mg analyte in 100 mL eluent.
9. Recovery (R) stock solution, 0.5 μg/μL. Dissolve 50 mg analyte in 100 mL methanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 13-mm, Type AE, glass fiber filter (Gelman, or equivalent) in a 13-mm filter holder (Swinney, Gelman, or equivalent).
2. Personal sampling pump, 0.2 L/min, with flexible connecting tubing.
3. High-performance liquid chromatograph, UV detector, integrator and column (page 5509-1).
4. Test tubes, 1-mL, with polyethylene stoppers.
5. Syringes, glass, 10- and 25-μL, readable to 0.1 μL.
6. Pipets, delivery, 0.5- and 5-mL, graduated in 0.1 mL.
7. Flasks, volumetric, 10- and 100-mL.
8. Centrifuge.
9. Test tube shaker, vortex type.

SPECIAL PRECAUTIONS: Benzidine is a recognized human carcinogen and can be absorbed through the skin [4,5,6]. 3,3'-Dichlorobenzidine is a carcinogen [4,6]. Take appropriate precautions to avoid personal and area contamination.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.2 L/min for a total sample size of 20 to 100 L.
3. Cap the sampler.
4. Ship and store samples at −15 °C if benzidine may be present.
   NOTE: Samples may be stored at room temperature if only 3,3'-dichlorobenzidine is present.

SAMPLE PREPARATION:

5. Place glass fiber filter in a test tube.
6. Add 0.5 mL eluent to each test tube. Seal each test tube and shake them on a test tube shaker.
7. Allow samples to stand for 1 h with intermittent shaking.
8. Centrifuge each sample for 10 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.05 to 7 μg analyte per sample.
   a. Deliver aliquots of calibration stock solution with microliter syringe to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 12 through 14).
   c. Prepare calibration graph (peak area vs. μg analyte).
10. Determine recovery (R) at least once per year for each lot of filters. Prepare four filters at each of five levels, plus three media blank filters.
    a. Place sample filters into separate test tubes.
    b. Inject an aliquot of R stock solution, or a dilution thereof in methanol, directly onto the filter.
    c. Cap the test tubes. Allow to stand overnight.
    d. Prepare (steps 5 through 8) and analyze (steps 12 through 14) with working standards.

e. Prepare a graph of R for each filter vs. μg analyte recovered.

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and R graphs are in control.

MEASUREMENT:

12. Set the liquid chromatograph to conditions given on page 5509-1 for analyte of interest.
    NOTE 1: If aniline is present, use a Waters Radial Pak A (C_{18}) column, or equivalent, and follow the procedures found in reference [2].
    NOTE 2: The following compounds were found not to interfere with the determination of either compound: o-, p- and m-chloroaniline; 4,4'-methylenedianiline and ß-naphthylamine. 2-Chloro-4-methylaniline; 3,3'-dichlorobenzidine; 4,4'-methylenebis(2-chloroaniline); hydrazobenzene; and 1,2- and 1,4-naphthoquinone do not interfere in the determination of benzidine. Benzidine, aniline, N-methylaniline, 2-toluidine and 3,3'-dimethylbenzidine will not interfere in the determination of 3,3'-dichlorobenzidine [1].
13. Inject an aliquot (see page 5509-1 for appropriate size).
14. Measure peak area.

CALCULATIONS:

15. Read the mass, μg (corrected for R), of analyte found on the sample filter (W) and on the media blank filter (B) from the calibration graph.
16. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 21 to 63 μg/m^3 for benzidine and the range 20 to 130 μg/m^3 for 3,3'-dichlorobenzidine. The generated atmospheres for both compounds were at 30 °C and 80% relative humidity. The sampling rate was 0.8 L/min. The pooled overall precision ($\hat{S}_{rT}$) was 0.07 for 29 benzidine samples and 0.07 for 28 3,3'-dichlorobenzidine samples. The sampling methods were evaluated for effects of temperature (25, 30, and 35 °C) and relative humidity (20 and 80%). No detectable quantities of either benzidine or 3,3'-dichlorobenzidine were found on backup silica gel tubes [1]. At 180 °C, vapors of these carried by a stream of dry nitrogen at 0.3 L/min did not break through the backup silica gel in 3 h [1].

The average recovery of benzidine from filters was determined to be 97% over the range 0.2 to 2.0 μg when stored at -15 °C for 11 days. Recoveries dropped to 89% and 75% after 15 days and 21 days, respectively. Recoveries of benzidine and benzidinium sulfate from filters and silica gel indicated that the compounds were unstable in these matrices at ambient temperature. Recoveries over the range of 0.5 to 5 μg 3,3'-dichlorobenzidine and its dihydrochloride were 96% after 21 days from both filters silica gel and stored at -15 °C and at ambient temperature [1].

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[2] Kennedy, E. R. and M. J. Seymour. ACS Symposium Series, No. 149, Chemical Hazards in the Workplace - Measurement and Control, 21-35, American Chemical Society, Washington, DC (1981).

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[6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY: M. J. Seymour, NIOSH/DPSE.

BENZIDINE in urine 8306

$C_{12}H_{12}N_2$ MW: 184.24 CAS: 92-87-5 RTECS: DC9625000

METHOD: 8306, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposures to benzidine and benzidine-based azo dyes.

SYNONYMS: [1,1'-biphenyl]-4,4'-diamine

BIOLOGICAL SAMPLING		MEASUREMENT	
SPECIMEN:	urine, 2 to 3 h after exposure	**TECHNIQUE:**	GAS CHROMATOGRAPHY, ECD
VOLUME:	100 mL in polyethylene bottle	**ANALYTE:**	N,N'-diheptafluorobutyryl benzidine
PRESERVATIVE:	2 drops 12 N HCl after collection	**INJECTION VOLUME:**	3 µL, Grob type-splitless
SHIPMENT:	frozen and shipped in dry ice	**COLUMN:**	15 m × 0.25-mm I.D. capillary; WCOT-SE-54
SAMPLE STABILITY:	unknown	**CARRIER GAS:**	5 % methane in argon, 1 mL/min
CONTROLS:	at least 3 urine specimens from non-exposed individuals per study; 1 per 10 samples	**TEMPERATURE-INJECTOR:**	260°C
		-DETECTOR:	350°C
		-COLUMN:	120°C for 2 min; 40°/min to 280°; hold 6 min
		CALIBRATION:	solutions of benzidine in benzene with internal standard
		QUALITY CONTROL:	spiked urine corrected for creatine content
		RANGE:	10 to 1000 µg/L
		RECOVERY:	92%
		ESTIMATED LOD:	5 µg/L
		PRECISION ($\bar{S}_r$):	0.11
		ACCURACY:	± 29%

APPLICABILITY: This procedure is useful for monitoring exposures to benzidine or benzidine-based azo dyes which are absorbed via the skin, lung, or gastrointestinal tract, and whose metabolites are benzidine or acetylbenzidine. This procedure quantitates benzidine, N-acetylbenzidine, N,N'-diacetylbenzidine, as conjugates of benzidine. Maximum urinary levels occur 2 to 3 h after exposure [1].

INTERFERENCES: None known.

OTHER METHODS: This method is based on references [2] and [3].

REAGENTS:

1. Hydrochloric acid, conc. (sp. gr. 1.18).
2. Sodium hydroxide, 10 N. Dissolve 400 g NaOH in 1:1 methanol:water (v/v) to make 1 L solution.
   CAUTION: EXOTHERMIC REACTION.
3. Sodium hydroxide, 5 N. Dilute 10 N with 1:1 methanol:water
4. Acetone, hexane, methanol, and benzene*, pesticide grade.
5. Hexane:benzene, 3:2 (v/v).
6. Sodium sulfate (anhydrous) extracted in Soxhlet extractor for 24 h with benzene.
7. Trimethylamine stock solution.
   a. Dissolve 2 g $(CH_3)_3NHCl$ in 5 mL 5 N NaOH.
      CAUTION: EXOTHERMIC REACTION
   b. Extract four times with 5-mL portions of benzene.
   c. Percolate each 5 mL extract through a 2-cm anhydrous sodium sulfate column.
   d. Keep in the dark and refrigerated when not in use. Reagent stability unknown.
8. Trimethylamine working solution.
   Dilute trimethylamine stock solution 1:20 with benzene. Reagent stability unknown.
9. Benzidine stock solution, 100 µg/mL.* Dissolve 10 mg benzidine, accurately weighed, in benzene to make 100 mL solution. Refrigerate. Discard if a color develops.
10. Methylene dianiline stock solution, 100 µg/mL. Dissolve 10 mg methylenedianiline,, accurately weighed, in benzene to make 100 mL solution. Refrigerate. Discard if color develops.
11. Derivatized methylenedianiline stock solution, 1 µg/mL.
    a. Add 0.1 mL methylenedianiline stock solution to 1.5 mL benzene and 0.5 mL trimethylamine working solution.
    b. Derivatize and wash (steps 12 and 13).
    c. Percolate the solution through 2 cm anhydrous sodium sulfate.
    d. Dilute to 10.0 mL with benzene. Stable at least one month.
12. Florisil, PR grade, 60/100 mesh; activated at 650°C.
    a. Extract 24 h in a Soxhlet extractor with benzene.
    b. Heat to 130°C for 24 h.
    c. Cool and add 10 g distilled water/100g Florisil. Shake overnight.

EQUIPMENT:

1. Bottles, polyethylene, 125-mL.
2. Gas chromatograph with $_{28}Ni^{63}$ electron capture detector, temperature programming, capillary column option, Grob-type injection system, and electronic integrator.
3. Shaker and rotator.
4. Evaporator and vortex mixer.
5. Centrifuge (refrigerated optional).
6. Waterbath with a temperature range 30 to 100°C.
7. Soxhlet extractor.
8. Culture tubes, 25 × 200-mm, 20 × 125-mm, and 16 × 150-mm, with PTFE-lined screw caps.**
9. Pipettes, 1-, 5- and 10-mL and Pasteur (disposable).**
10. Graduated centrifuge tubes, 15-mL, glass-stoppered.**
11. Volumetric flasks.**

** Wash with detergent, clean with chromic acid, rinse with distilled water, acetone, and benzene.

13. Buffer. Dissolve 136 g KH_2PO_4 in 900 mL H_2O. Adjust to pH 6 with 10 N NaOH. Dilute to 1 L with H_2O and extract once with 100 mL benzene.
14. Paraffin oil.
15. Heptafluorobutyric anhydride.
16. Nitrogen gas, compressed, purified.

* See SPECIAL PRECAUTIONS.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. Benzidine and benzene are documented human carcinogens and must be handled in compliance with 29 CFR 1910.1005 and 1910.1028.

SAMPLING:

1. Collect a spot urine sample in a polyethylene bottle. Add 2 drops 12 N HCl as a preservative.
2. Freeze the samples and ship in an insulated container with dry ice.
3. Keep the samples frozen until analysis.

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the sample (e.g., [4]).
5. Pipet 10 mL of the urine specimen into a 50-mL culture tube containing 10 mL 10 N NaOH.
6. Seal the tube and incubate 2 h at 80 °C.
7. Cool to room temperature, add 20 mL benzene, seal, and shake 1 h.
8. Remove the benzene layer and percolate it through a 2-cm column of anhydrous sodium sulfate. Collect the eluate in a 25 × 200-mm culture tube.
9. Repeat step 8 twice. Combine the extracts.
10. Add three or four drops of paraffin oil to the extracts and concentrate the extracts to near dryness under a gentle stream of nitrogen.
11. Add 1.5 mL benzene and 0.5 mL trimethylamine working solution.
12. Add 50 µL heptafluorobutyric anhydride. Seal and place in a 50 °C waterbath for 20 min. Cool to room temperature.
13. Wash the derivatized extract.
    a. Add 2 mL pH 6 buffer solution. Seal and shake 2 min.
    b. Centrifuge 2 min. Discard the bottom (aqueous) layer.
    c. Repeat the washing with two additional 2-mL portions of pH 6 buffer.
14. Place a small glass wool plug in a chromatographic column and add 1.6 g Florisil. Top with 2 cm anhydrous sodium sulfate. Wash the column with 50 mL hexane.
15. Add the buffer-washed, derivatized extract to the Florisil column. Rinse the culture tube twice with ca. 2 mL benzene and add the rinsings to the Florisil column.
16. When the top of the extract is in the sodium sulfate layer, add 10 mL 3:2 (v/v) hexane:benzene. Discard the eluate.
17. Elute the N,N'-diheptafluorobutyryl benzidine with 15 mL benzene.
18. Add 0.5 mL derivatized methylenedianiline stock solution to the eluate. Concentrate to 10 mL under a gentle stream of nitrogen.

CALIBRATION AND QUALITY CONTROL:

19. Prepare six working standards containing between 0 and 10 μg benzidine.
    a. Add aliquots of benzidine stock solution to 1.5 mL benzene and 0.5 mL trimethylamine working solution.
    b. Perform steps 12 and 13.
    c. Percolate the benzene layer through 2 cm anhydrous sodium sulfate.
    d. Add 0.5 mL derivatized methylenedianiline stock solution.
    e. Dilute to 10.0 mL with benzene.
    f. Analyze the working standards together with samples and blanks (step 21 and 22).
    g. Prepare calibration graph (concentration of standards vs. ratio of peak areas of benzidine to methylenedianiline).
20. Analyze a spiked urine for every 10 samples (minimum three per study).

MEASUREMENT:

21. Set the chromatograph according to manufacturer's recommendations and conditions given on page 8306-1.
22. Inject 3 μL derivatized sample extract (step 18). Measure peak areas of both methylenedianiline and benzidine. Calculate the ratio of peak areas (benzidine to methylenedianiline). The t_r of methylenedianiline is 7.6 min while the t_r of benzidine is 8.0 min under these conditions.

CALCULATIONS:

23. Determine benzidine urine concentrations (μg/mL) by comparing the ratio of benzidine methylenedianiline peak areas for the samples to those obtained for standards on the calibration graph. Report the results as μg benzidine/g creatinine.

GUIDES FOR INTERPRETATION:

Benzidine is an OSHA-regulated human carcinogen. Although no specific standard has been set, the fact that benzidine is a human carcinogen means it or its metabolites should not be detected in urine or any other physiological fluid. However, a level of 0.010 μg/mL has been suggested as an indicator of excessive exposure [1].

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[1] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, 43, Biomedical Publications, Davis, CA (1980).
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METHOD REVISED BY:

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BENZOYL PEROXIDE

$(C_6H_5CO)_2O_2$ MW: 242.22 CAS: 94-36-0 RTECS: DM8575000

METHOD: 5009, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3
ACGIH: 5 mg/m^3

PROPERTIES: solid; MP 103 °C; d 1.334 g/mL @ 25 °C
VP not significant; autoignition temperature 80 °C

SYNONYMS: dibenzoyl peroxide, benzoyl superoxide

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 40 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 9% loss from filter after 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3 to 19 mg/m^3 [1] (90-L samples)

BIAS: − 0.52%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.060 [1]

ACCURACY: ± 11.82%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: benzoyl peroxide

EXTRACTION: ethyl ether, 10 mL

INJECTION VOLUME: 20 μL

PRESSURE-COLUMN: 9000 kPa (1300 psi)

MOBILE PHASE: 70/30 methanol/water; 1.6 mL/min

DETECTOR: UV photometer @ 254 nm

COLUMN: 250 mm x 3 mm-ID stainless steel; Spherisorb ODS (spherical silica particles with 5% bonded coating of octadecyl groups) or equivalent

CALIBRATION: benzoyl peroxide in ethyl ether

RANGE: 0.2 to 1.7 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 2 to 19 mg/m^3 for a 90-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S253 [3] in a revised format. A non-specific gravimetric method and a non-specific colorimetric method appear in the criteria document [4].

REAGENTS:

1. Benzoyl peroxide, 99% pure.*
2. Ethyl ether, purified, without stabilizer.*
3. Methanol, distilled in glass.
4. Water, deionized and distilled.
5. Calibration stock solution, 10 mg/mL. Dissolve 250 mg benzoyl peroxide in ethyl ether and dilute to 25 mL. Stable at least one week at 4 °C.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, with backup pad in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Refrigerated, bagged ("Blue Ice," or equivalent).
4. Vials, 20-mL, PTFE-lined caps.
5. High performance liquid chromatograph, 254-nm UV detector, sample injection valve with a 20-μL external sample loop, syringe filter, integrator and column (page 5009-1).
6. Tweezers.
7. Microliter syringes, 10- and 100-μL.
8. Volumetric flasks, 10- and 25-mL, assorted sizes.
9. Pipet, 10-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Benzoyl peroxide is a flammable solid and may explode when heated; it will attack some plastics, rubber, and coatings [4]. Ethyl ether is highly flammable and forms explosive peroxides on exposure to air.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 40 to 400 L. Do not exceed 2 mg particulate loading on the filter.
3. Ship samples in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

4. Immediately upon receipt at laboratory, refrigerate the samples.
5. As soon as possible after receipt, transfer each filter to a clean vial with tweezers.
6. Pipet 10 mL ethyl ether into each vial; screw on cap. Swirl to mix.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards covering the range 0.01 to 1.7 mg per sample.
   a. Add calibration stock solution with a microliter syringe to ethyl ether in a 10-mL volumetric flask and dilute to the mark.
   b. Analyze together with samples, blanks and control samples (steps 10 through 12).
   c. Prepare calibration graph of peak area vs. mass (mg) of benzoyl peroxide per sample.
8. Determine recovery of benzoyl peroxide from filters at least once for each lot of samplers in the calibration range (step 7). Prepare three filters at each of five levels plus media blanks.
   a. Add aliquot of calibration stock solution with a microliter syringe directly onto a media blank filter in a vial.
   b. Prepare and analyze together with working standards (steps 5, 6 and 10 through 12).
   c. Prepare a graph of recovery vs. mg benzoyl peroxide recovered.
9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

10. Set high performance liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5009-1.
11. Flush sample loop thoroughly with sample (0.1 mL) and inject sample.
12. Measure peak area.

CALCULATIONS:

13. Read mass, mg (corrected for recovery), of benzoyl peroxide found on sample filters, W (mg), and on average blank filters, B (mg), from calibration graph.
14. Calculate concentration, C (mg/m^3), of benzoyl peroxide in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S253 was issued on January 21, 1977 [3], and validated over the range 3.1 to 19.1 mg/m^3 at 26 °C and 764 mm Hg, using 90-L samples [1,5]. The collection efficiency of the filter was determined to be 1.00, since no benzoyl peroxide was detected on a backup filter mounted directly behind the front filter. Storage stability studies on the filters held in the filter cassettes indicated a 9.3% decrease in the amount of benzoyl peroxide recovered after one week. Benzoyl peroxide was stable in ethyl ether at room temperature for at least one week. Overall precision, $\hat{S}_{rT}$, was 0.060. Recovery was 0.97 in the range 0.225 to 0.900 mg per sample for 18 spiked samples.

REFERENCES:

[1] NIOSH Backup Data Report, S253, for Benzoyl Peroxide, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield, VA 22161.
[2] UBTL Memorandum, UBTL Analytical Laboratory Report for Benzoyl Peroxide, Sequence #2182-J (unpublished, February 29, 1980).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S253, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Criteria for a Recommended Standard...Occupational Exposure to Benzoyl Peroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-166 (1977).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; S253 originally validated under NIOSH Contract 210-76-0123.

BENZYL CHLORIDE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

BERYLLIUM and compounds, as Be 7102

Be MW: 9.01 CAS: 7440-41-7 RTECS: DS1750000

METHOD: 7102, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 $\mu g/m^3$; C 5 $\mu g/m^3$; P 25 $\mu g/m^3$/30 min
NIOSH: not to exceed 0.5 $\mu g/m^3$ (suspect carcinogen)
ACGIH: 2 $\mu g/m^3$ (suspect carcinogen)

PROPERTIES: hard, light metal; valence +2; MP 1284 to 1300 °C

SYNONYMS: Vary as to compound.

SAMPLING

SAMPLER: FILTER (0.8 μm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 25 L @ 2 $\mu g/m^3$
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.7 to 11.8 $\mu g/m^3$ [1] (40-L samples)

BIAS: − 0.39%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.064 [1]

ACCURACY: ± 12.42%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: beryllium

ASHING REAGENTS: HNO_3, 10 mL; H_2SO_4, 1 mL

CONDITIONS: 150 °C until brown fumes disappear; 400 °C to dense fumes of H_2SO_4

FINAL SOLUTION: 2% Na_2SO_4/3% H_2SO_4; 10 mL

GRAPHITE FURNACE: 110 °C dry 20 sec; 900 °C char 10 sec; 2800 °C atomize 18 sec

WAVELENGTH: 234.9 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

INJECTION VOLUME: 10 μL

CALIBRATION: Be^{2+} in 2% Na_2SO_4/3% H_2SO_4

RANGE: 0.05 to 1 μg per sample [2]
ESTIMATED LOD: 0.005 μg per sample [2]
PRECISION ($\bar{S}_r$): 0.008 [2]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 90-L air sample. The method is applicable to ceiling measurements using a 25-L air sample.

INTERFERENCES: Calcium interference is masked by 3% (v/v) sulfuric acid. Sodium, potassium, and aluminum enhance beryllium absorbance; this effect is overcome by addition of 2% (w/v) sodium sulfate to both standards and samples. Perchloric, phosphoric, and hydrofluoric acids produce interfering non-atomic peaks. These must be removed by digesting to dryness.

OTHER METHODS: This revises Method P&CAM 288 [2], which replaced Method S339 [3]. Flame atomic absorption and plasma emission (ICP-AES) are not sensitive enough for beryllium at these concentrations.

REAGENTS:

1. Nitric acid, conc., reagent grade or better.
2. Sulfuric acid, conc., reagent grade or better.
3. Sodium sulfate, reagent grade.
4. Sodium sulfate, 2% (w/v)/3% sulfuric acid (v/v). Add 10 g sodium sulfate and 15 mL H_2SO_4 to deionized water. Dilute to 500 mL.
5. Calibration stock solution, 1000 μg Be/mL,* commercially available, or dissolve 1.000 g Be metal in a minimum volume of 1:1 HCl, dilute to 1 L with 1% (v/v) HCl
6. Argon, prepurified.
7. Water, distilled or deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter in two-piece cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace and background corrector.
4. Beryllium hollow cathode lamp.
5. Pressure regulator, two-stage, for Argon.
6. Beakers, Phillips, 125-mL.*
7. Watchglasses.*
8. Volumetric flasks, 10-mL.*
9. Pipets, 10-mL volumetric, with pipet bulb.*
10. Automatic pipettor with tips, 10-μL and assorted sizes for standards.
11. Hotplate, 150 to 400 °C.
12. Waterbath, 60 to 70 °C.
13. Bottles, polyethylene, 25-mL.

* Clean all glassware with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Beryllium is very toxic and a suspected human carcinogen [4]. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 25 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open cassettes and transfer filters to clean Phillips beakers.
4. Add 10 mL conc. HNO_3 and 1 mL conc. H_2SO_4. Cover with watchglass.
5. Heat in fume hood on hotplate (150 °C) until brown fumes of HNO_3 disappear, then at 400 °C until dense fumes of H_2SO_4 appear.
   NOTE: Verify that the compounds in the samples are soluble with this ashing procedure, e.g., ore or mining samples will require HF in the digestion. If additional ashing acids are used (e.g., HF, $HClO_4$, or H_3PO_4), evaporate to complete dryness at this point.
6. Cool and rinse watchglass and sides of beaker with distilled water and evaporate just to dryness. Remove beaker immediately and air-cool.
7. Pipet 10.0 mL 2% Na_2SO_4/3% H_2SO_4 solution into beaker and cover.
   NOTE: Start sulfate reagent blanks at this step.
8. Heat in 60 to 70 °C waterbath for 10 min. Allow to stand overnight before analysis to ensure complete dissolution of $BeSO_4$.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.005 to 1 μg Be per sample.
   a. Use serial dilutions of known amounts of calibration stock solution in 2% Na_2SO_4/ 3% H_2SO_4 to prepare working standards. Store in polyethylene bottles. Stable at least four weeks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   NOTE: Analyze working standards alternately with the samples to compensate for the increasing Be signal as the graphite tube ages.
10. Analyze three quality control blind spikes and three analyst spikes.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations and to conditions on page 7102-1.
12. Inject 10-μL aliquots of samples into graphite tube. Record absorbance (peak height mode).

CALCULATIONS:

13. Read absorbance of samples, A; average media blanks, A_b; average sulfate reagent blanks, A_r; and working standards, A_s.
14. Using the working standard, C_s (μg/mL), analyzed adjacent to the sample of interest, calculate concentration, C ($\mu g/m^3$), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) \cdot C_s \cdot 10^4}{(A_s - A_r)V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was evaluated using NTIS Standard Reference Material No. 2675 for Be over the range of 0.1 to 0.4 μg Be/filter (equivalent to one-half to two times the OSHA PEL). Beryllium recovery was 98.2% with a measurement precision, $\bar{S}_r$, of 0.008 [2]. This method is an improvement of S339 [3], which was validated over the range of 2.68 to 11.84 mg/m^3 using a 40-L sample. Mean recovery was 106.9% with overall precision of 0.064 [1].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S339, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 288, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Ibid., V. 3, S339, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Criteria for a Recommended Standard...Occupational Exposure to Beryllium, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 72-10268 (1972); and as revised in August, 1977 in NIOSH testimony at OSHA hearing.

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE; S339 validated under NIOSH Contract CDC-99-74-45.

BORON CARBIDE

B_4C MW: 55.26 CAS: 12069-32-8 RTECS: None

METHOD: 7506, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: no standard
ACGIH: no standard

PROPERTIES: solid; d 2.51 g/mL; MP 2350 °C

SYNONYMS: None

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm cyclone, Higgins-Dewell (HD) + 5-μm PVC membrane)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 100 L @ 1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: boron carbide

ASH: RF plasma asher

SUSPEND: in 2-propanol

REDEPOSIT: 0.45-μm Ag membrane filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° receiving slit
Graphite monochromator; scintillation detector
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: standard suspensions of B_4C in 2-propanol

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.05 mg per sample

PRECISION ($\bar{S}_r$): 0.04 [1]

APPLICABILITY: The working range is 0.2 to 4 mg/m^3 for a 500-L air sample. The method is specific for determining respirable boron carbide among other mine dusts.

INTERFERENCES: Titanium dioxide, silver, titanium diboride, niobium oxide, silver chloride interfere; also see APPENDIX A.

OTHER METHODS: This revises P&CAM 324 [1].

REAGENTS:

1. Boron carbide, ACS grade, <10-μm particle size.
   a. Wet-sieve ultrasonically with a 10-μm sieve to approximate respirable dust. Evaporate the alcohol. Dry the sieved material in an oven at 110 °C for 1 h, cool, and store in a desiccator.
2. 2-Propanol.
3. Desiccant.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferrably, conductive) held together by tape or cellulose shrink band.
      NOTE: Test PVC filter for THF digestion (see Step 4).
   b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Bulk sampler: PVC membrane filter, 37-mm, 5-μm pore size in two-piece filter cassette. Sample closed face at 4 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-μm pore size. Filters commercially available (e.g., Poretics Corp., Millipore Corp.)
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Filtration apparatus and side-arm vacuum flask with 25- and 37-mm filter holders.
8. Sieve, 10-μm pore size, for wet sieving.
9. Analytical balance (0.01 mg).
10. Magnetic stirrer with thermally-insulated top.
11. Ultrasonic bath or probe.
12. Pipets, 2- to 20-mL.
13. Flask, volumetric, 1-L.
14. Desiccator.
15. Bottles, 1-L, with ground glass stoppers.
16. Drying oven.
17. Polyethylene wash bottle.
18. Beakers, borosilicate, 50-mL, and matching watchglasses.
19. Glue or tape for securing Ag filters to XRD sample holder.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with a nylon cyclone or 2.2 ± 5% with a HD cyclone for a total sample size of 100 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: For determination of total boron carbide, sample on the PVC filter, without cyclone, at 1 to 4 L/min.
3. Take a bulk dust sample (e.g., 1 m^3 at 4 L/min).

SAMPLE PREPARATION:

4. Prepare the high-volume respirable dust or settled dust sample for qualitative analysis. Transfer to a filter and XRD sample holder by: (1) ashing and redepositing as described below for personal samples, (2) removing part of the dust from a thickly-coated sample and redepositing it, or (3) mounting all or part of the collection filter on the holder. The settled dust may be ground and/or wet sieved to best match the airborne dust exposure. Wet-sieving is done with a 10-μm sieve, 2-propanol, and an ultrasonic bath, followed by evaporation of excess alcohol, drying in an oven for 2 h, and overnight storage in a dessicator. Deposit the end product on a filter or pack in a conventional XRD powder holder and follow step 10.
   NOTE: For quantitative determination of percent boron carbide, weigh out, in triplicate, 2 mg of the respirable or sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with steps 6 and 7.
5. Place the filters in 50-mL beakers in the low temperature asher. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker.
6. Cover the beaker with a watchglass. Agitate in an ultrasonic bath for at least 3 min (until agglomerated particles are broken up). Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel. Control filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

8. Select six silver membrane filters randomly from the same box of filters used for depositing the samples. These will be used as media blanks to correct for sample self-absorption. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove and let dry. Determine the net normalized intensity for the silver peak, $\hat{I}^{\circ}_{Ag}$, for each media blank (step 11). Average the values for the six media blanks.
9. Prepare and analyze working standard filters.
   a. Weigh 10- and 100-mg portions of boron carbide to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
   b. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer and add a stirring bar. Cool to room temperature before use.
   c. Mount a silver filter on the filtration apparatus. Place 2 to 4 mL 2-propanol on the filter. Turn off the stirrer and shake the suspension vigorously by hand. Immediately withdraw an aliquot from the center of the suspension. Do not adjust volume in the pipet by expelling

part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter, keeping the tip of the pipet just above the surface of the delivered suspension.

d. Rinse the pipet with several portions of 2-propanol, draining the rinses into the funnel.
e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Prepare working standard filters in triplicate by this technique at, e.g., 50, 100, 200, 500, 1000, and 2000 μg boron carbide.
f. Analyze by XRD (step 11). Use the same diffraction peaks and instrumental conditions as for samples. Designate the net and normalized XRD intensities for the working standard filters as I_x° (step 11.d) and $\hat{I}_x^\circ$ (step 11.e), respectively. Correct $\hat{I}_x^\circ$ for matrix absorption for standards containing >200 μg B_4C (steps 11.f and 12).
g. Prepare calibration graph ($\hat{I}_x^\circ$ vs. μg B_4C) using $1/\sigma^2$ weighted least squares.
h. Determine the slope, m (counts/μg), of the calibration graph. The intercept, b, of the line with the $\hat{I}_x^\circ$ axis should be zero ± 5 μg.

MEASUREMENT:

10. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2-θ) of the settled dust bulk or high-volume respirable sample to determine the presence of boron carbide and any matrix interference (see APPENDIX). The expected diffraction peaks are:

	Peak (Degrees 2-θ)	
	Primary	Secondary
Boron carbide	37.80°	34.91°
Silver	38.12°	44.28°

11. Mount the filter (sample, standard or blank) in the X-ray diffractometer and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N (approximately equal to the net count for the reference specimen peak). Use this value of N for all analyses.
       NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently measured reference specimen intensity.
    b. Measure the area of the most intense, interference-free diffraction peak of B_4C. Scan times must be long, e.g., 15 min.
    c. Determine the position of the background for each sample. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain total background.
    d. Calculate net intensity, I_x (peak count minus total background count).
    e. Calculate the normalized intensity, $\hat{I}_x = I_x \cdot N/I_r$.
    f. Determine the net normalized intensity, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-θ range used for B_4C and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

12. Calculate the concentration of boron carbide, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(T) - b}{m \cdot V}, \ mg/m^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration curve ($\hat{I}_x^\circ$ vs. W)
m = initial slope of calibration curve, counts μg

$f(T) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

$R = \sin(\theta_{Ag})/\sin(\theta_x)$
$T = \hat{I}_{Ag}/(\text{average } \hat{I}_{Ag}^\circ)$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}_{Ag}^\circ$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [2] and [3].

EVALUATION OF METHOD:

The method was developed using the secondary B_4C peak because the primary B_4C peak interferred with the primary peak of AgCl, which is usually found on silver filters [1]. B_4C that was previously ground, sieved through a 10-μm sieve and dried, was used to prepare 30 working standards on 25-mm silver filters in the range 20 to 2000 μg per filter (10 levels, three at each level). The detection limit was 50 μg per filter. The limit of quantitation was 100 μg per filter. The calibration graph had a linear correlation coefficient of 0.9999 and a pooled relative standard deviation of 0.04 (n = 24). Recovery was 0.92 with s_r = 0.02 from five FWS-B (MSA Co.) filters spiked at the 600 μg level; the filters were ashed in a low temperature asher and were treated as described in SAMPLE PREPARATION.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 324, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[2] Leroux, J. and C. Powers. Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters, Occup. Health Rev., 21, 26 (1970).
[3] Williams, D. D. Direct Quantitative Diffractometric Analysis, Anal. Chem., 31, 1841 (1959).

METHOD WRITTEN BY:

J. Palassis, NIOSH/DTMD.

APPENDIX:

INTERFERENCES

When using copper Kα X-radiation, titanium dioxide (anatase) and the primary peak of silver interfere with the primary boron carbide peak; therefore, no measurements can be done with either the primary boron carbide or the silver peak. The secondary boron carbide peak is chosen as the analytical peak if no other interferences are present.

The secondary titanium diboride peak interferes to a small extent with the secondary boron carbide peak. The primary titanium diboride peak interferes with the secondary silver peak.

Niobium oxide interferes with the tertiary boron carbide peak.

Silver chloride, found as an impurity in the silver filter, may interfere with some low-intensity boron carbide peaks.

When peak overlaps are not severe, a smaller receiving slit or chromium X-radiation may be used; however, a new calibration graph will be necessary.

The presence of some elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This can be minimized by a diffracted beam monochromator.

The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made (step 12 and Table 1).

Table 1. Matrix absorption correction factors, boron carbide/silver peak, degrees 2θ.

Boron Carbide	34.91	23.54	22.11		34.91	23.54	21.11
Silver	44.28	44.28	44.28		44.28	44.28	44.28
T	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)
1.00	1.000	1.000	1.000	0.74	1.2011	1.3038	1.3249
0.99	1.0063	1.0093	1.0099	0.73	1.2107	1.3187	1.3409
0.98	1.0127	1.0188	1.0200	0.72	1.2205	1.3340	1.3573
0.97	1.0193	1.0284	1.0302	0.71	1.2305	1.3495	1.3740
0.96	1.0259	1.0382	1.0407	0.70	1.2407	1.3654	1.3911
0.95	1.0326	1.0481	1.0513	0.69	1.2512	1.3816	1.4086
0.94	1.0394	1.0582	1.0620	0.68	1.2618	1.3982	1.4264
0.93	1.0463	1.0685	1.0730	0.67	1.2726	1.4152	1.4447
0.92	1.0533	1.0790	1.0842	0.66	1.2836	1.4325	1.4633
0.91	1.0604	1.0897	1.0955	0.65	1.2949	1.4502	1.4824
0.90	1.0676	1.1005	1.1071	0.64	1.3064	1.4683	1.5019
0.89	1.0750	1.1115	1.1189	0.63	1.3182	1.4868	1.5218
0.88	1.0825	1.1227	1.1309	0.62	1.3302	1.5058	1.5423
0.87	1.0900	1.1342	1.1431	0.61	1.3425	1.5252	1.5632
0.86	1.0977	1.1458	1.1555	0.60	1.3550	1.5450	1.5846
0.85	1.1056	1.1576	1.1682	0.59	1.3678	1.5654	1.6066
0.84	1.1135	1.1697	1.1811	0.58	1.3809	1.5862	1.6290
0.83	1.1216	1.1820	1.1943	0.57	1.3944	1.6076	1.6521
0.82	1.1298	1.1945	1.2077	0.56	1.4081	1.6295	1.6757
0.81	1.1382	1.2073	1.2213	0.55	1.4221	1.6519	1.7000
0.80	1.1467	1.2203	1.2353	0.54	1.4365	1.6750	1.7249
0.79	1.1554	1.2335	1.2495	0.53	1.4513	1.6986	1.7504
0.78	1.1642	1.2470	1.2640	0.52	1.4664	1.7229	1.7766
0.77	1.1732	1.2608	1.2787	0.51	1.4819	1.7478	1.8036
0.76	1.1823	1.2749	1.2938	0.50	1.4979	1.7734	1.8312
0.75	1.1916	1.2892	1.3092				

T = sample transmittance (step 12).
f(T) = sample correction factor (step 12).

BROMINE 6011

See CHLORINE, Method 6011, for procedure

Br_2 MW: 159.82 CAS: 7726-95-6 RTECS: EF9100000

METHOD: 6011, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm; STEL 0.3 ppm
ACGIH: 0.1 ppm; STEL 0.3 ppm
(1 ppm = 6.53 mg/m^3)

PROPERTIES: liquid; d 3.119 g/mL @ 20 °C; BP 58.78 °C; VP 23.3 kPa (175 mm Hg) @ 20 °C vapor density (air=1) 5.5

SYNONYMS: None.

SAMPLING

SAMPLER: PREFILTER + FILTER (PTFE, 0.5-μm + silver membrane, 25-mm, 0.45-μm)

FLOW RATE: 0.3 to 1 L/min

VOL-MIN: 8 L @ 0.1 ppm
-MAX: 360 L

SHIPMENT: routine, protect from light

SAMPLE STABILITY: ≥30 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.07 to 1.42 mg/m^3 (72-L samples)

BIAS: − 1.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069 [1]

ACCURACY: ± 13.6%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY

ANALYTE: bromide ion (Br^-)

EXTRACTION: 3 mL 6 mM $Na_2S_2O_3$, 10 min

INJECTION VOLUME: 50 μL

COLUMN: Dionex HPIC-AG4A guard, HPIC-AS4A separator, MFC-1 precolumn, AMMS anion suppressor

DETECTOR SETTING: 10 μS full scale

ELUENT: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol, 2 mL/min

CALIBRATION: standard solutions of Br^- in deionized water

RANGE: 5 to 150 μg Br^- per sample [1]

ESTIMATED LOD: 1.6 μg Br^- per sample [1]

PRECISION ($\bar{S}_r$): 0.045 @ 5 to 100 μg per sample [1]

APPLICABILITY: The working ranges for Br_2 and Cl_2 are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m^3) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m^3) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference upon a maximum of 15 μg per sample. HBr gives a positive interference as it is sampled continuously [1].

OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

BROMOFORM

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

(1) BROMOXYNIL and (2) BROMOXYNIL OCTANOATE 5010

(1) $C_7H_3Br_2NO$ MW: (1) 276.93 CAS: (1) 1689-84-5 RTECS: (1) DI3150000
(2) $C_{15}H_{17}Br_2NO_2$ (2) 403.13 (2) 1689-99-2 (2) DI3325000

METHOD: 5010, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: (1) liquid; BP 194 to 195 °C;
(2) solid; MP 45 to 47 °C

SYNONYMS: (1): 2,6-dibromo-4-cyanophenol; 3,5-dibromo-4-hydroxybenzonitrile;
(2): 2,6-dibromo-4-cyanophenyl octanoate.

SAMPLING

SAMPLER: FILTER
(2-μm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 0.1 mg/m^3
-MAX: 400 L

SHIPMENT: refrigerated; protect from light

SAMPLE STABILITY: at least 25 days @ 4 °C in the dark [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Bromoxynil; Bromoxynil octanoate

EXTRACTION: 3 mL acetonitrile; 60 min

MOBILE PHASE: acetonitrile/water gradient; 1 mL/min

COLUMN: μ-Bondapack C_{18}, 25 cm x 4.6 mm-ID reverse phase or equivalent

DETECTOR: UV detector @ 254 nm

CALIBRATION: solutions of analytes in acetonitrile

RANGE: 2 to 30 μg per sample [1]

ESTIMATED LOD: (1) 0.6 and (2) 0.3 μg per sample [1]

PRECISION ($\bar{S}_r$): (1) 0.011 @ 18 μg per sample [1]
(2) 0.042 @ 35 μg per sample [1]

APPLICABILITY: The working range is 0.02 to 0.3 mg/m^3 for a 100-L air sample. This method permits the simultaneous determination of both analytes.

INTERFERENCES: None known. Both analytes photodecompose.

OTHER METHODS: A gas chromatographic method has been described [2].

REAGENTS:

1. Bromoxynil.
2. Bromoxynil octanoate.
3. Acetonitrile, HPLC grade.
4. Water, distilled, deionized.
5. Calibration stock solution, 1 mg/mL. Dissolve 0.100 g each of Bromoxynil and Bromoxynil octanoate in acetonitrile; dilute to 100 mL in a volumetric flask. Prepare daily, in duplicate.

EQUIPMENT:

1. Sampler: PTFE-coated glass fiber (Pallflex T60A20) or 2-μm PTFE membrane (GHIA), 37-mm diameter. (Filters commercially available).
   NOTE: Use opaque or light-protected cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Jars, ointment, 60-mL, squat form, with PTFE-lined screw caps.
4. Volumetric flasks, 10- and 100-mL
5. Pipet, 3-mL.
6. Vials (for autosampler).
7. Liquid chromatograph with gradient capability, UV detector (254 nm) and column, (see page 5010-1).
8. Syringes, 5-mL.
9. Syringe filters, PTFE; or Swinnex adaptor with luer fitting containing 0.5-μm PTFE filter, 13-mm.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 20 to 400 L. Do not exceed 2 mg total dust loading on filter.
3. After sampling, cap the filter holders, ship at 4 °C and protect from light.

SAMPLE PREPARATION:

4. Transfer the filter to a jar. Add 3.0 mL acetonitrile and desorb with occasional swirling for at least 1 h.
5. Filter an aliquot through a PTFE syringe filter or a 0.5-μm PTFE filter using a syringe with a Swinnex adaptor to remove particulate. Transfer the aliquot to a sample vial and seal.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.6 to 30 μg of both analytes per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg analyte).
      NOTE: Before processing any samples, demonstrate, through the analysis of a solvent blank, that all glassware and reagents are interference-free. Each time a new set of samples is analyzed or there is a change in reagents, process a solvent blank as a safeguard against chronic laboratory contamination.

MEASUREMENT:

7. Set the liquid chromatograph to the conditions on page 5010-1 using the following mobile phase gradient: 50% CH_3CN/50% H_2O for 10 min; 10 min gradient to 100% CH_3N; hold 10 min; 2 min gradient to 50% CH_3CN/50% H_2O; hold 15 min.
8. Inject 100 μL sample extract with a high-pressure syringe or a sampling loop. Record the volume injected to the nearest 0.5 μL. Under these conditions, the retention times are 3.6 min for Bromoxynil and 33 min for Bromoxynil octanoate.
9. Measure peak area.
   NOTE: If the peak area exceeds the linear range of the system, dilute with acetonitrile and reanalyze. If the peak area measurement is hindered by the presence of interferences, other chromatographic conditions may be required.

CALCULATIONS:

10. Read the mass of analytes (including appropriate aliquot factors) in the sample extract, W (μg), and average media blank, B (μg), from the calibration graph.
11. Determine the concentrations, C (mg/m^3), of each analyte in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was developed with laboratory samples during the period June to September, 1983 [1]. PTFE-coated glass fiber filters were spiked with 50 μg Bromoxynil and 90 μg Bromoxynil octanoate, after which 90 L of clean air at 80% RH was drawn through the filters. Recoveries averaged 93% for Bromoxynil and 100% for Bromoxynil octanoate with relative standard deviations, $\bar{S}_r$, of 0.046 and 0.020, respectively. Storage at ambient conditions for 14 days gave recoveries of 70 to 80% for both compounds, while storage under refrigeration for 25 days or at ambient conditions for two days followed by refrigeration for 23 days gave recoveries in the range 95 to 98%.

REFERENCES:

[1] Arthur D. Little, Inc., Backup Data Report prepared under NIOSH Contract 200-82-2528 (unpublished, October 7, 1983).
[2] Thrun, K., J. Harris, and V. Grady. "Sampling and Analysis Procedures for Pesticide Manufacturing Wastes," Report, EPA Contract No. 68-02-3111 (1982).

METHOD WRITTEN BY:

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1,3-BUTADIENE

$H_2C=CHHC=CH_2$ MW: 54.09 CAS: 106-99-0 RTECS: EI9275000

METHOD: 1024, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : 1000 ppm
NIOSH: lowest feasible; suspect carcinogen
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 2.21 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.9 (air = 1); BP −4.4 °C; explosive range 2.0 to 11.5% v/v in air

SYNONYMS: butadiene; biethylene; divinyl

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut charcoal, 400- and 200-mg in separate tubes)

FLOW RATE: 0.01 to 0.5 L/min

VOL-MIN: 5 L @ 100 ppm
-MAX: 25 L

SHIPMENT: separate front and back tubes, chill below −4 °C

SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.19 to 19 mg/m^3 (25-L samples)
BIAS:	0.1%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.060
ACCURACY:	± 11.32%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-butadiene

DESORPTION: 4 mL methylene chloride; 30 min

INJECTION: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: see APPENDIX A

CARRIER GAS: helium

MAKEUP GAS: nitrogen, 30 mL/min

COLUMNS: fused silica, 10 m x 0.50-mm ID 1.8-µm CP WAX 57 CB (backflushable pre-column), and 50 m x 0.32-mm ID Al_2O_3/KCl PLOT (see APPENDIX A)

CALIBRATION: vapor-spiked sampling media

RANGE: 1 to 480 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION ($\bar{S}_r$): 0.025

APPLICABILITY: The working range is 0.02 to 100 ppm (0.04 to 220 mg/m^3) for a 25-L air sample. At the higher levels, desorbed samples may require dilution. Below 0.9 mg/m^3 (0.4 ppm), the desorption efficiency falls below 75% and allowance should be made for decreased accuracy.

INTERFERENCES: Pentane, methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels. High humidity (>80% RH) or other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.

OTHER METHODS: This revises Method S91 [1].

REAGENTS:

1. Methylene chloride,* chromatographic quality with hydrocarbon (cyclohexene) preservative.
2. 1,3-Butadiene,* 99.5%, in cylinder equipped for gas withdrawal, with needle valve.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, purified.
6. Nitrogen, purified.
7. Water, distilled.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Tandem charcoal tubes. Each tube is flame-sealed glass (8.5 cm long, 8-mm OD, 6-mm ID), has plastic caps for resealing, and contains activated coconut shell charcoal (such as SKC Lot 120) preceded by silylated glass wool and followed by a 3-mm urethane foam plug. The front tube holds 400 mg charcoal. The back tube holds 200 mg.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., Blue Ice or dry ice), and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
5. Ice, wet.
6. Vials, 5-mL, 2-mL, 1-mL, and other convenient sizes, with PTFE-lined septum caps.
7. Pipettes, TD, 4-, 2-, and 1-mL.
8. Syringes, gas-tight, 250-, 100-, 25-, and 10-μL.
9. Beaker, 150-mL.
10. Gas drying tube with serum cap to fit stem and 2-cm piece of plastic tubing to fit over serum cap.

SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential carcinogen, teratogen, and reproductive hazard [2]. Methylene chloride is toxic, very volatile, and a suspect carcinogen [3]. Work should be performed in a well-ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.5 L/min for a sample size of 5 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below -4 °C during shipment and storage.

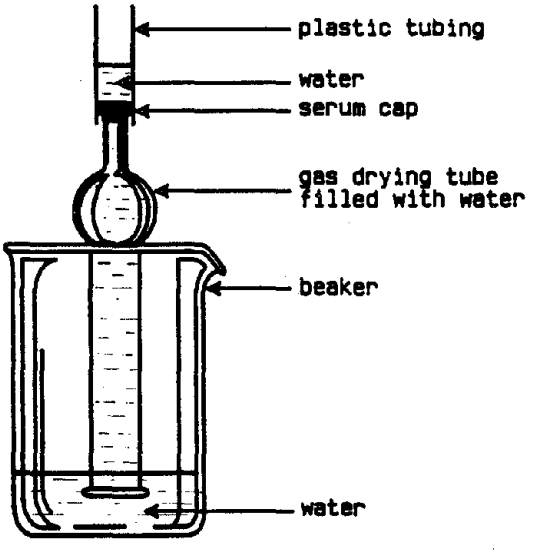
SAMPLE PREPARATION:

5. Add 4.0 mL methylene chloride to 5-mL vials and 2.0 mL to 2-mL vials. Loosely cap vials and thoroughly chill in ice.
6. Place front sorbent sections in 5-mL vials and back sections in 2-mL vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Remove from ice and allow to stand 30 min with occasional agitation.
8. Transfer sample solution to appropriate vial and cap if using an autosampler. Thoroughly chill solution and vial before making transfer.

CALIBRATION AND QUALITY CONTROL:

NOTE: The accurate measurement of pure 1,3-butadiene gas by gas-tight syringe is a critical step in the calibration. Even a slight obstruction (e.g., flakes of PTFE from the plunger tip which obstruct the needle) can cause 1,3-butadiene to be liquified as the plunger is depressed, making delivery incomplete. Bracketing gas samples with water, as described below, allows the volume taken to be approximately verified, and assures complete delivery. The precision of the analysis of multiple independent standards is another indicator of the accuracy of the volumes taken.

9. Make up stock solutions in triplicate at three concentration levels, e.g., 200 μL of 1,3-butadiene gas in 1 mL solution, and both 200 and 50 μL of gas in 4 mL solution:
   a. Prepare a beaker and drying tube assembly as shown. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



   b. Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
   c. Take a known amount (50 or 200 μL) of 1,3-butadiene from the drying tube with a 100- or 250-μL gas-tight syringe. Bracket the gas in the syringe with small amounts of water (5 to 10% of syringe volume) taken from the area above the serum cap before and after withdrawing the gas. Do not take water from inside the drying tube, since it may contain a significant amount of dissolved 1,3-butadiene.
   d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
   e. Agitate and continue to chill the vial to complete dissolution.

10. Calibrate daily with media blanks and triplicate independent media standards of at least six levels ranging from, e.g., 0.5 to 200 μL 1,3-butadiene gas per sample:
   a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
   b. Take pure gas (50 or 200 μL, as in step 9.c) for the higher levels, or 40 μL of stock solution for lower levels.
   c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
   d. Seal tube with plastic caps.
   e. Store at temperature below -4 °C overnight, then desorb (steps 5 through 8).
   f. Analyze media standards and blanks together with samples (steps 13 and 14).
   g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in μg/mL).

11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    a. Dilute the stock solutions (step 9) with methylene chloride to extend the range of standards down to 0.1 μg/mL. Avoid including water in the portions diluted.
    b. Transfer solutions as in step 8 if using an autosampler, and analyze together with media standards (steps 13 and 14).
    c. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare DE calibration graph of peak area or height vs. μg/mL 1,3-butadiene.
    d. Read the concentrations, μg/mL, in media standards and blanks from DE calibration graph and multiply by the desorption volume to calculate the masses recovered.
    e. Prepare a graph of DE vs. μg taken. DE = (mass found - blank mass)/(mass taken).
12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1024-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If detector response is above range of working standards, dilute with methylene chloride, reanalyze, and apply appropriate dilution factor in calculations.
14. Measure peak area or height.
    NOTE: Vinylidene chloride, an impurity in methylene chloride, elutes just after 1,3-butadiene and may be used as an internal standard.

CALCULATIONS:

15. Determine the concentration, μg/mL, of 1,3-butadiene found in each sample front (W_f) and back (W_b) sorbent section from calibration graph (step 10), and multiply by desorption volume, D, mL, and dilution factor, if any, to calculate the mass, μg, found.
    NOTE 1: This calibration method corrects for media blank and DE. Do not duplicate corrections.
    NOTE 2: For any sampler with $W_b > W_f/10$, report breakthrough and possible sample loss.

$$C = \frac{(W_f + W_b) \cdot D}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The detector responses determined for triplicate standard solutions at each of five levels were linear over the range 0.3 to 440 μg per sample. The pooled $\bar{S}_r$ was 0.038. The estimated LOD was 0.02 μg/mL.

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 56 ppm 1,3-butadiene. When exposed to 0.7 and 2.5 mL of pure 1,3-butadiene gas followed by 80% RH air, breakthrough occurred after 35 L and 28.5 L, respectively. The corresponding respective time-weighted average concentrations were 20 and 88 ppm.

For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480 μg per sample, the pooled $\bar{S}_r$ was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%, respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 μg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4 °C. Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the frozen samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125 μg 1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the $\bar{S}_r$ of the response was 0.016. Subsequently, simulated samples were exposed to known amounts of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463 μg per sample was 101.6% versus media standards and 91.3% versus standard solutions; the $\bar{S}_r$ of the response was 0.047. At 45.3 μg per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the $\bar{S}_r$ of the response was 0.048. At 4.64 μg per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the $\bar{S}_r$ of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 μg, with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the $\bar{S}_r$ of the response was 0.023. The $\bar{S}_r$ of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision ($\hat{S}_{rT}$) of the total sampling and analytical method was 0.060. For levels at and above 45 μg (0.8 ppm in 25 L), apparent biases may be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed significant breakthrough ($W_b > W_f/10$). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441 μg per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were -0.002 $\pm$ 0.003, 0.000 $\pm$ 0.003, -0.020 ± 0.002, 0.002 $\pm$ 0.002, and -0.019 ± 0.002, respectively. For the media standards, the respective pooled S_r for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 $\pm$ 0.4, 66.4 $\pm$ 0.3, 70.5 $\pm$ 0.2, 86.2 $\pm$ 0.3, and 91.2 $\pm$ 0.2.

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below -4 °C, and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 μg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092, 0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 $\pm$ 0.032, 0.961 $\pm$ 0.014, 0.994 $\pm$ 0.008, 1.029 $\pm$ 0.015, 1.064 $\pm$ 0.021, and 1.074 $\pm$ 0.021. Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the

2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080, 0.005 ± 0.128, -0.003 ± 0.092, 0.060 ± 0.179, 0.249 ± 0.188, and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per μg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable -- the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

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[4] Grubbs, F. E. "Procedures for Detecting Outlying Observations in Samples," Technometrics, 11(1), 1-21, (February, 1969).
[5] MacCallum, R. N., and J. J. McKetta. "Low Pressure Z_s of C_4 Hydrocarbons," Hydrocarbon Process. Petrol. Refiner, 42(5), 191-194 (1963).

METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., Yvonne T. Gagnon, NIOSH/DPSE and John Palassis, NIOSH/DTMD.

APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [1] is 6 m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C_4 to C_6 hydrocarbons are present, interferences are likely. For the development of this method, a 50 m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al_2O_3/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10 m x 0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

Set the initial oven temperature to 50 °C and the "C" backpressure regulator to 185 kPa. With the solenoid valves activated (inject mode), set the "C" flow control to 20 mL/min and the "B" controls so that the effluent from the analytical column and the "C" split vent total 10 mL/min. Then, with the solenoid valves deactivated (backflush or normal mode), adjust the "B" backpressure regulator until the flow from the "C" split vent returns to the value previously measured. This establishes a reverse flow of 10 mL/min through the pre-column. Program the oven to hold the initial temperature (50 °C) for 2 min, then rise to 120 °C at 20 °C/min, and hold for 8 min. Adjust the time from injection to backflush by injecting standards and progressively decreasing the time from 2 min until the methylene chloride peak is removed without attenuating the butadiene peak. It may be necessary to clear higher hydrocarbons from the analytical column by programming the oven to 200 °C at 30 °C/min and holding 4 min. Program the solenoid valves to be activated after each run to prepare for the next injection.

Using the backflushable pre-column, there remains a slight problem with retention drift. While in inject mode, the pre-column strips residual water from the carrier gas. This activates the aluminum oxide surface of the analytical column and causes retention to increase. The effect is most noticeable when starting up after the system has been idle. When beginning a sequence of samples, it is advisable to analyze solvent blanks until the retention drift (e.g., of vinylidene chloride) becomes tolerable.

APPENDIX B. CONVERSION OF 1,3-BUTADIENE VOLUME TO MASS:

MacCallum and McKetta [5] determined the compressibility factor, Z, which corrects for non-ideal behavior, for 1,3-butadiene at temperatures, T, ranging from 10 to 75 °C, and pressures, P, from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against P, PT, and PT^2, yields the following equation (standard error of the estimated Z is 0.000635 for 13 degrees of freedom):

$$Z = a + bP + cPT + dPT^2.$$

where: $a = 1.00095$, $b = -4.84089 \times 10^{-5}$, $c = 4.44816 \times 10^{-7}$, $d = -1.15744 \times 10^{-9}$

The mass, M, of 1,3-butadiene, corrected for compressibility and the presence of water vapor (when the gas is stored above water), may be calculated by the following equation:

$$M = \frac{(P - P_v) \cdot V \cdot 54.09}{Z \cdot 62.36 \cdot (T + 273.2)}, \ \mu g.$$

where: P_v = vapor pressure of water @ T °C (mm Hg)
V = volume of 1,3-butadiene (μL)
54.09 = molecular weight of 1,3-butadiene ($g \cdot mol^{-1}$)
62.36 = gas constant ($mm\ Hg \cdot L \cdot mol^{-1} \cdot K^{-1}$)
273.2 = absolute temperature of 0 °C (K)

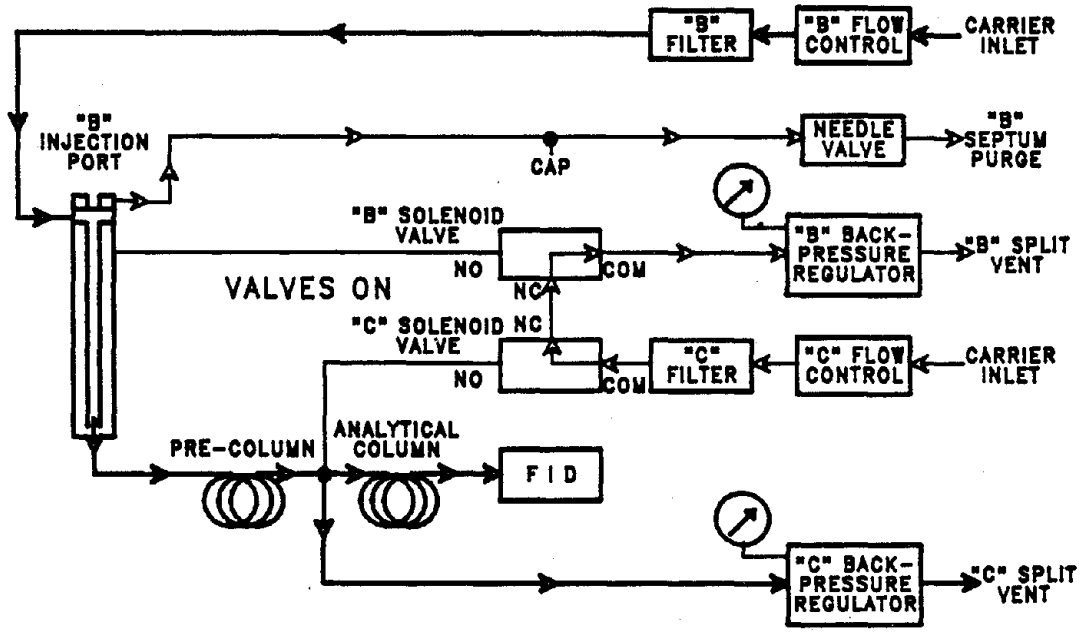

Figure 1. Flow diagram for pre-column system in inject mode.

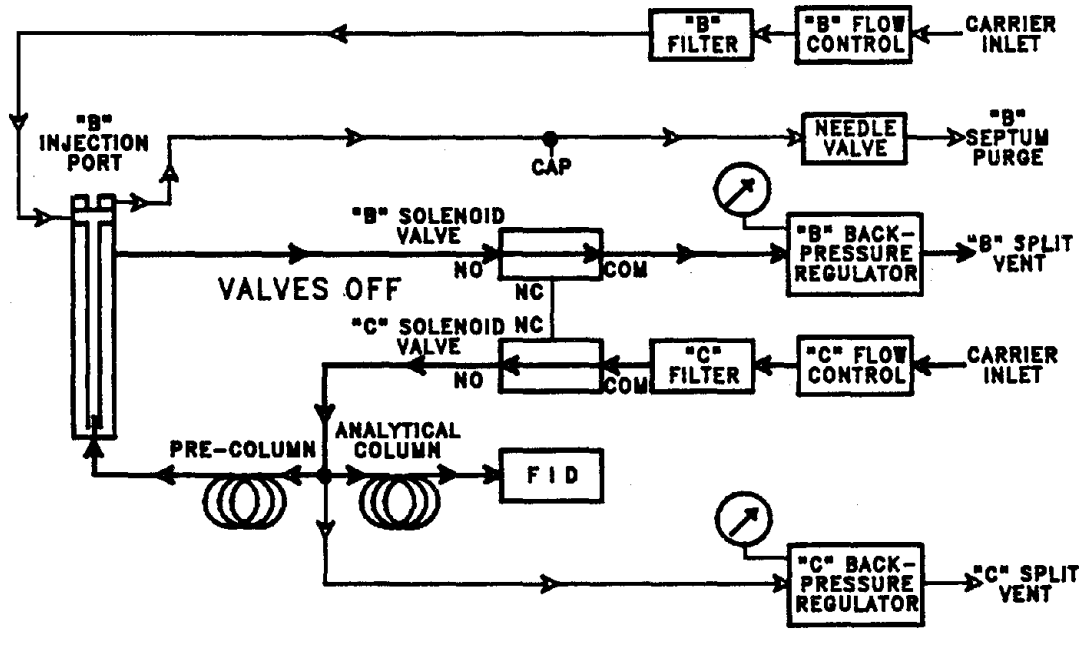

Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

2-BUTOXYETHANOL

See ALCOHOLS IV (Method 1403) for procedure

n-BUTYL ACETATE

See ESTERS I (Method 1450) for procedure

sec-BUTYL ACETATE

See ESTERS I (Method 1450) for procedure

t-BUTYL ACETATE

See ESTERS I (Method 1450) for procedure

n-BUTYL ALCOHOL

See ALCOHOLS II (Method 1401) for procedure

sec-BUTYL ALCOHOL

See ALCOHOLS II (Method 1401) for procedure

tert-BUTYL ALCOHOL

See ALCOHOLS I (Method 1400) for procedure

n-BUTYLAMINE 2012

$CH_3(CH_2)_3NH_2$ MW: 73.16 CAS: 109-73-9 RTECS: EO2975000

METHOD: 2012, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 5 ppm (skin) ceiling
NIOSH: 5 ppm (skin) ceiling
ACGIH: 5 ppm (skin) ceiling
(1 ppm = 2.99 mg/m^3 @ NTP)

PROPERTIES: liquid, ammoniacal odor; MP −49 °C; BP 77.8 °C; d = 0.7327 g/mL @ 25 °C; VP 10.9 kPa (82 mm Hg) @ 20 °C; vapor density 2.5 (air = 1)

SYNONYMS: butylamine, 1-aminobutane, NBA

SAMPLING

SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel tube 150 mg/75 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 2 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 8.09 to 35.5 mg/m^3 [1] (15-L samples)

BIAS: − 5.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.092 [1]

ACCURACY: ± 23.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: n-butylamine

EXTRACTION: 1 mL 50% methanol; neutralize a 500µL aliquot with 1 N KOH

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 195 °C
-COLUMN: 90 °C

CARRIER GAS: N_2, 20 mL/min

COLUMN: 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B, 6 ft x 1/4"-O.D.

CALIBRATION: standard solutions of butylamine in aqueous methanol

RANGE: 0.03 to 1 mg per sample [1]

ESTIMATED LOD: 0.012 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.0490 [1]

APPLICABILITY: The working range is 0.7 to 144 ppm (2 to 430 mg/m^3) for a 15-L air sample. Using a nitrogen-specific detector instead of a FID will greatly increase sensitivity. This alternate detector has been used for amines with a 30-m x 0.25-mm x 0.25-µm film DB-5 (5% methyl, phenyl-50% dimethyl-polysiloxane) fused-silica capillary column with a liner packed with KOH-coated glass wool.

INTERFERENCES: Both concentrated sulfuric acid and silica gel are desiccants, so in sampling atmospheres above 60% relative humidity the sorbent tube may have lowered capacity.[1]

OTHER METHODS: This revises Method S138 [3]. Method 2010 for aliphatic amines may also be used for determination of n-butylamine.

REAGENTS:

1. n-Butylamine,* ACS reagent grade.
2. Potassium hydroxide,* (KOH) 1N, ACS reagent grade.
3. Water, deionized.
4. n-Butyl alcohol, for internal standard.
5. Methanol, distilled in glass.
6. 50% methanol in water (v/v).
7. Calibration stock solution.

* See Special Precautions

EQUIPMENT:

1. Sampler: 150 mg/75 mg sulfuric acid coated (20/40 mesh) silica gel tube. See Appendix for instruction on preparation. (Tubes are commercially available, but have a designated shelf life).
2. Personal sampling pump, 0.01 to 1 L/min, with flexible polyethylene or PTFE tubing.
3. Hygrometer or other suitable device for measuring relative humidity.
4. Vials, glass, 2-mL with PTFE-lined caps.
5. Gas chromatograph with a flame ionization detector, recorder, integrator and column (page 2012-1).
6. Tweezers.
7. Syringes, 10- and 500-μL.
8. Volumetric flasks, 10-mL.
9. Pipets, 1- and 10-mL glass, delivery, with pipet bulb.

SPECIAL PRECAUTIONS: Butylamine vapor can cause irritation to the eyes, nose, and throat. Inhalation can cause headache and flushing of skin. Contact with the liquid may produce severe injury to eyes and skin [4]. Potassium hydroxide is a strong caustic, corrosive to tissue. Handle with gloves. Work in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the silica gel tube immediately prior to sampling. Attach outlet of tube to the sampling pump with flexible tubing.
3. Sample 2 to 100 L of air at an accurately known flow rate in the range 0.01 to 1.0 L/min.
4. The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded.
5. Cap and seal the sample tube for shipment and place in a suitable container in order to prevent damage during transit.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section's vial.
8. Add 1 mL 50% methanol to the vial. Tightly cap the vial. Agitate the vial for 2 hours.
9. Neutralization of the sample solution. Allow the silica gel particles to settle. Transfer a 500 μL aliquot to a clean vial and add 500 μL of 1.0 N KOH.

   NOTE 1: If the internal standard is to be used, add the internal standard solution made up in 1.0 N KOH.

   NOTE 2: Analyze samples immediately to avoid loss of amine as free base.

CALIBRATION AND QUALITY CONTROL:

10. Prepare working standards (12 to 1000 μg/mL aqueous methanol) by adding appropriate aliquots of calibration stock solution to 50% methanol. Follow neutralization procedure in step 9.
11. Analyze working standards together with samples and blanks (steps 14 through 16). Prepare a calibration graph of area vs. μg of n-butylamine.
12. Determine recovery for each lot of silica gel used for sampling in the concentration range of interest. Prepare four silica gel tubes at each of five levels plus three media blanks.
    a. Remove and discard 75 mg back sorbent section of an unused sorbent tube.
    b. Spike aliquot of calibration solution onto front section sorbent section of silica gel tube with a microliter syringe.
    c. Cap and let stand overnight.
    d. Desorb following (steps 7 through 9) and analyze along with working standards and blanks (steps 14 through 16).
    e. Prepare graph of recovery vs. μg n-butylamine.
13. Analyze three quality control spikes and three analyst spikes to ensure that calibration graph and recovery graph are in control.

MEASUREMENT:

14. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2012-1.
15. Inject 5-μL sample aliquot.
    NOTE: If peak area is above the linear range of the working standards, dilute with 50% methanol, reanalyze, and apply the appropriate dilution factor in calculations.
16. Measure peak area.

CALCULATIONS:

17. Determine mass, μg (corrected for recovery), of n-butylamine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample less.
18. Calculate concentration of n-butylamine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 8.09 to 35.5 mg/m^3 at 24 °C and pressure of 769 mm Hg using 15-L samples [1,3]. Sampling and measurement precision, $\bar{S}_r$, was 0.049, with average recovery of 91.4%, representing a non-significant bias. Sample stability during storage was evaluated at 270 μg n-butylamine per sample. Samples showed 98.4% recovery after one day of storage at ambient conditions compared to 95.2% recovery for seven-day old samples.

REFERENCES:

[1] Backup Data Report for n-butylamine, prepared under NIOSH Contract 210-76-0123 (1978).
[2] NIOSH/DPSE Analytical Sequence #4975, Measurement Research Support Branch, NIOSH, Cincinnati, Ohio (unpublished, 1986).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S138, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[4] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Paula Fey O'Connor, NIOSH/DPSE.

APPENDIX: PREPARATION OF SULFURIC ACID-TREATED SILICA GEL.

Place a known amount of 20/40 mesh silica gel in a drying oven set at 125 °C for one hour. Cool the silica gel to a constant weight (W). Add reagent grade concentrated sulfuric acid dropwise by means of a pipet to 1.25 (W) or 25% by weight of the acid. Return the treated silica gel to the drying oven for one hour with intermittent mixing. Store the treated silica gel in an airtight container.

n-BUTYL GLYCIDYL ETHER 1616

$C_7H_{14}O_2$ MW: 130.19 CAS: 2426-08-6 RTECS: TX4200000

METHOD: 1616, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 50 ppm
NIOSH: C 5.6 ppm; 15 min
ACGIH: 25 ppm
(1 ppm = 5.32 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.9087 g/mL @ 20 °C; BP 164 °C; VP 0.43 kPa (3.2 mm Hg, 4200 ppm) @ 20 °C

SYNONYMS: 1,2-epoxy-3-butoxypropane; butoxymethyloxirane; BGE

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 15 L @ 25 ppm
-MAX: 30 L

SHIPMENT: routine (refrigerate at lab)

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 133 to 542 mg/m^3 [1] (10-L samples)

BIAS: −16.1% @ 133 mg/m^3 [1]
−1.0% @ 259 to 542 mg/m^3

OVERALL PRECISION ($\hat{S}_{rT}$): 0.074 [1]

ACCURACY: ±15.5% @ 259 to 592 mg/m^3
±30.6% @ 133 mg/m^3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: n-butyl glycidyl ether

DESORPTION: 0.5 mL CS_2, 30 min

TEMPERATURE-INJECTION: 180 °C
-DETECTOR: 275 °C
-COLUMN: 130 °C

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2, 50 mL/min

COLUMN: stainless steel, 3.2-mm ID x 3 m, packed with 10% FFAP on 80/100 mesh Chromosorb W-AW DMCS

CALIBRATION: standard solutions of n-butyl glycidyl ether in CS_2

RANGE: 1.6 to 6.4 mg per sample

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.016 [1]

APPLICABILITY: The working range is 15 to 60 ppm (80 to 320 mg/m^3) for a 20-L air sample. Because of unexpected bias at the lowest test level and the possibility of poor desorption efficiency at low loadings, a sample volume of at least 15 L is recommended. This method has not been evaluated for short-term exposures at 5.6 ppm. An appropriate capillary column may be used for better resolution and sensitivity.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S81 [2] in a revised format.

REAGENTS:

1. Carbon disulfide* (CS_2), chromatographic quality.
2. n-Butyl glycidyl ether*, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 7.0 cm long, 6-mm OD, 4-mm ID; flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 100 mg; back = 50 mg) separated by a urethane foam plug. A silanized glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1.0 L/min air flow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1616-1).
4. Vials, 2-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Flasks, volumetric, 10-mL.
7. Pipets, 0.5-mL.

SPECIAL PRECAUTIONS: Both n-butyl glycidyl ether and CS_2 are toxic. In addition, CS_2 is a serious fire and explosion hazard (flash point = −30 °C). All work with these compounds must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 15 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 0.5 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.1 to 8 mg n-butyl glycidyl ether per sample.
   a. Add a known amount of n-butyl glycidyl ether to CS_2 in 10-mL volumetric flask and dilute to the mark. Use serial dilutions as needed for smaller concentrations.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (n-butyl glycidyl ether peak area vs. mg n-butyl glycidyl ether).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject known amount (1 to 20 μL) of n-butyl glycidyl ether or standard solution of n-butyl glycidyl ether in CS_2 directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg n-butyl glycidyl ether recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1616-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of n-butyl glycidyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of n-butyl glycidyl ether in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S81 was issued on February 14, 1975 [2] and validated over the range 133 to 542 mg/m^3 for 10-L air samples from dynamically generated test atmospheres [1]. The n-butyl glycidyl ether concentrations were independently measured by means of a total hydrocarbon analyzer. The average recoveries for sets of six samples taken at concentrations of 542 and 259 mg/m^3 were 99.8% and 98.2%, respectively. A different method was used to generate concentrations of about 133 mg/m^3. For two sets of six samples taken at the latter concentration, the average recovery was 83.9%. The reason for the low recovery was not determined. Breakthrough was not observed after sampling 44 L from a test atmosphere containing 30 mg/m^3 of n-butyl glycidyl ether. The desorption efficiency decreased from 93.1 to 82.6% as loadings decreased of 6.4 to 1.6 mg per sample. Sample stability was not determined; however, refrigeration of the samples upon receipt by the laboratory is recommended.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S81, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977). Available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S81, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

R.A. Glaser, NIOSH/DPSE. Method S81 was originally validated under NIOSH Contract CDC-99-74-45.

p-tert-BUTYLTOLUENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

CADMIUM and compounds, as Cd 7048

Cd **MW:** 112.40 (Cd); 128.40 (CdO) **CAS:** 7440-43-9 (Cd); 1306-19-0 (CdO) **RTECS:** EU9800000 (Cd) EV1930000(CdO)

METHOD: 7048, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 0.1 mg/m^3, C 0.3 (fume); 0.2, C 0.6 (dust)
NIOSH: lowest feasible; carcinogen
ACGIH: 0.01 mg/m^3 (total dust); 0.002 mg/m^3 (respirable); carcinogen

PROPERTIES: soft metal; valence +2; BP 765 °C; MP 320.9 °C

SYNONYMS: Vary depending upon the compound.

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 25 L @ 0.1 mg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 0.98 mg/m^3 [1] (25-L samples)

BIAS: − 1.57%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1]

ACCURACY: ± 13.23%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: cadmium

ASHING: conc. HNO_3, 6 mL; 140 °C
conc. HCl, 6 mL; 400 °C

FINAL SOLUTION: 0.5 N HCl; 25 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 228.8 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

CALIBRATION: Standard solutions of Cd in 0.5 N HCl

RANGE: 2.5 to 30 μg per sample

ESTIMATED LOD: 0.05 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.05 @ 3 to 23 μg per sample [1,3,4]

APPLICABILITY: The working range is 0.1 to 2 mg/m^3 for a 25-L air sample, and 0.01 to 0.2 mg/m^3 for a 250-L air sample. This is an elemental analysis and it will not distinguish Cd fume from Cd dust. Aliquots of the ashed samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is required to control molecular or flame absorption. Iron does not interfere at 20 parts Fe to 1 part Cd [1].

OTHER METHODS: This method combines and replaces P&CAM 173 [5], S312 [4], and S313 [6]. A similar method appears in the criteria document [7]. Method 7300 (ICP-AES) is an alternate, multielement measurement method with approximately the same sensitivity. Aliquots of the ashed samples can be analyzed by graphite furnace atomic absorption with greatly increased sensitivity.

REAGENTS:

1. Nitric acid, conc., ultrapure.
2. Hydrochloric acid, conc., ultrapure.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water; dilute to 1 L.
4. Calibration stock solution, 100 μg Cd/mL.* Commercially available or dissolve 0.100 g Cd metal in minimum volume of (1:1) HCl. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head , cadmium hollow cathode lamp, and background correction.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 300 μL.*
8. Hotplate, surface temperature 400 °C.

* Clean with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

Cadmium compounds are very toxic and should be considered carcinogens [3,7]. Handle with extra care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 2 and 3 L/min for 15 min (30 to 45 L) for ceiling measurements, or at 1 to 3 L/min for a total sample size of 25 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted.

3. Open the cassette filter holders and transfer the samples and blanks to separate clean beakers.
4. Add 2 mL conc. HNO_3, cover with a watchglass, and heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Start reagent blanks at this point.
5. Repeat 2 more times using 2 mL conc. HNO_3 each time.
6. Add 2 mL conc. HCl, cover with a watchglass, and heat on hotplate (400 °C) until the volume is reduced to ca. 0.5 mL.
7. Repeat 2 more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
8. Cool solution and add 10 mL distilled water.
9. Transfer the solution quantitatively to a 25-mL volumetric flask.
10. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards. Add known amounts, covering the range 0 to 30 μg Cd per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 0.5 N HCl.
12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
14. Aspirate a standard after every 10 samples to check for instrument drift.
15. Check recoveries with at least 2 spiked media blanks per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7048-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 0.5 N HCl, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of cadmium in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of cadmium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S312 was issued on June 12, 1976 [4], and validated over the range 0.12 to 0.98 mg/m^3 for a 25-L sample of CdO dust [1]. Method S313 was issued on November 26, 1976 [6], and validated over the range 0.12 to 0.57 mg/m^3 for a 25-L sample of Cd fume, and over the range 0.04 to 0.18 mg/m^3 for a 140-L sample of Cd fume [1].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S312 and S313, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Seq. #3990-M (unpublished, November 29, 1983).
[3] Current Intelligence Bulletin 42: Cadmium. U.S. Department of Health and Human Services, Publ. (NIOSH) 84-116 (Sept. 27, 1984).
[4] NIOSH Manual of Analytical Methods, V. 3, Method S312, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Ibid, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

[6] Ibid, Method S313.
[7] Criteria for a Recommended Standard...Occupational Exposure to Cadmium, Appendix II, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-192 (1976).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S312 and S313 originally validated under NIOSH Contract CDC-94-74-45.

CALCIUM and compounds, as Ca 7020

Ca MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 7020, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: soft, reactive metal; valence 2; MP 848 °C; VP not significant

SYNONYMS: Quicklime (CaO); limestone ($CaCO_3$); marble ($CaCO_3$); hydrated lime ($Ca(OH)_2$)

SAMPLING

SAMPLER:	FILTER (0.8-μm cellulose ester membrane)
FLOW RATE:	1 to 3 L/min
VOL-MIN:	20 L @ 5 mg/m^3
-MAX:	400 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	2.6 to 10.2 mg/m^3 [1] (85-L samples)
BIAS:	− 0.39%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.063 [1]
ACCURACY:	± 11.5%

MEASUREMENT

TECHNIQUE:	ATOMIC ABSORPTION, FLAME
ANALYTE:	calcium
ASHING:	conc. HNO_3, 6 mL; 140 °C 60% (w/v) $HClO_4$, 2 mL; 400 °C
FINAL SOLUTION:	5% HCl; 100 mL 1000 μg/mL Cs; 1000 μg/mL La
FLAME:	air-acetylene, reducing
WAVELENGTH:	422.7 nm
BACKGROUND CORRECTION:	none used
CALIBRATION:	Ca^{2+} in 5% HCl
RANGE:	0.08 to 1.7 mg per sample [2]
ESTIMATED LOD:	0.001 mg per sample [3]
PRECISION ($\check{S}_r$):	0.02 [1,3]

APPLICABILITY: The working range is 1 to 20 mg/m^3 for an 85-L air sample. This is an elemental analysis, not compound specific. Verify that the compounds in the samples are soluble with the ashing procedure. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: The use of 1000 μg/mL Cs controls ionization in the flame caused by metals such as Na, K, Li, and Mg. The presence of Si, Al, or H_3PO_4 require the use of 1% (w/w) La as a releasing agent.

OTHER METHODS: This method combines and replaces P&CAM 173 [4] and S205 [2]. Method 7300 (ICP-AES) is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 5% (v/v). Add 50 mL conc. HCl to 500 mL water; dilute to 1 L.
4. Calibration stock solution, 1000 μg Ca/mL. Commercially available or add 50 mL deionized water and minimum volume of HCl (20 mL) to dissolve 2.498 g $CaCO_3$. Dilute to 1 L with deionized water.
5. Cs solution, 50 mg/mL. Dissolve 73.40 g $CsNO_3$ in water to make 1 L solution.
6. La solution, 50 mg/mL. Dissolve 156 g $La(NO_3)_3 \cdot 6H_2O$ in water to make 1 L solution.
7. Distilled or deionized water.
8. Air, filtered.
9. Acetylene.
10. Perchloric acid, 60% w/v.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and calcium hollow cathode lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 500 μL.*
8. Hotplate, surface temperature 140 and 400 °C.

* Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 20 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to separate clean beakers.
4. Add 5 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Add 2 mL conc. HNO_3 and 1 mL 60% $HClO_4$.
7. Heat on 400 °C hotplate until dense fumes of perchloric acid appear.
8. Remove watchglass and rinse into the beaker with distilled water.
9. Place the beakers on the 400 °C hotplate and allow to go to dryness.
10. Cool each beaker and dissolve the residues in 5 mL 5% HCl.
11. Transfer the solution quantitatively to a 100-mL volumetric flask containing 2 mL of 50 mg/mL Cs solution and 2 mL of 50 mg/mL La solution.
    NOTE: Dilute to a smaller volume (e.g., 10 mL) with proportionally less Cs and La if required for sensitivity of analysis for other metals in the sample.
12. Dilute to volume with 5% HCl.

CALIBRATION AND QUALITY CONTROL:

13. Add known amounts, covering the range 0 to 500 μg Ca per sample, of calibration stock solution to 100-mL volumetric flasks containing 2 mL each of the 50 mg/mL Cs and La solutions and dilute to volume with 5% HCl.
14. Analyze the working standards along with the samples and blanks (steps 19 and 20).
15. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
16. Aspirate a standard for every 10 samples to check instrument drift.
17. Check recoveries with at least one spiked media blank per 10 samples.
18. Use method of additions occasionally to check for interferences.

MEASUREMENT:

19. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7020-1.
20. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HCl and an appropriate amount of the 50 mg/mL Cs and La solutions, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

21. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of calcium in the sample, C_s, and average media blank, C_b, from the calibration graph.
22. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of calcium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S205 [2] was issued on September 26, 1975, and validated over the range 2.6 to 10.2 mg/m^3 using an 85-L air sample by lab testing with spiked filters and generated atmospheres of CaO, verified by EDTA titration [1]. Collection efficiency of 1.00 was determined for the sampling device. Precision and accuracy data are given on page 7020-1. An additional check showed an estimated LOD of 1 μg Ca per sample [3].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] V. 3, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1979).
[3] User check, UBTL, NIOSH Seq. #3990-Q (unpublished, November 29, 1983).
[4] Ibid, NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S205 originally validated under NIOSH Contract CDC-99-74-45.

TABLE 1: General Information

FORMULA	M.W.	CAS #	RTECS #	EXPOSURE LIMITS (mg/m^3) OSHA	NIOSH	ACGIH
Ca	40.08	7440-70-2	EV8040000	--	--	--
CaO	56.08	1305-78-8	EW3100000	5	2	2
$Ca(OH)_2$	74.10	1305-62-0	EW2800000	None	5	5
$Ca(CO_3)_2$ total dust	100.09	471-34-1	EV9580000	15 (total); 5 (resp.)	10 (total); 5 (resp.)	10

CAMPHOR

See KETONES II (Method 1301) for procedure

CARBARYL 5006

$C_{10}H_7OC(=O)NHCH_3$ MW: 201.22 CAS: 63-25-2 RTECS: FC5950000

METHOD: 5006, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group II Pesticide
ACGIH: 5 mg/m^3

PROPERTIES: solid; crystal; d 1.230 g/mL @ 20 °C; BP decomposes; MP 142 °C; VP <0.005 Pa (<4 x 10-5 mm Hg; <0.4 mg/m^3) @ 20 °C

SYNONYMS: Sevin; 1-naphthalenol N-methylcarbamate; 1-Naphthyl-N-methylcarbamate

SAMPLING

SAMPLER:	FILTER (glass fiber)
FLOW RATE:	1 to 3 L/min
VOL-MIN:	20 L @ 5 mg/m^3
-MAX:	400 L
SHIPMENT:	ship filters in 25-mL scintillation vials
SAMPLE STABILITY:	at least 7 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	2 to 13 mg/m^3 [1] (90-L samples)
BIAS:	- 0.73%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.057 [1]
ACCURACY:	± 11.3%

MEASUREMENT

TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
ANALYTE:	p-nitrobenzenediazonium tetrafluoroborate complex
SAMPLE WORKUP:	20 mL 0.1 M methanolic potassium hydroxide; to 2-mL aliquot, add 17 mL glacial acetic acid; add 1 mL p-nitrobenzenediazonium tetrafluorobate
WAVELENGTH:	475 nm
CALIBRATION:	Carbaryl in methylene chloride
RANGE:	0.1 to 1.0 mg per sample [2]
ESTIMATED LOD:	0.03 mg per sample [3,4]
PRECISION ($\bar{S}_r$):	0.015 [1]

APPLICABILITY: The working range is 0.5 to 20 mg/m^3 for a 200-L air sample.

INTERFERENCES: Phenols such as 1-naphthol will give a positive interference [2]. Interferences from other aromatic carbamates and phenoxyacetic acid pesticides may occur but have not been documented.

OTHER METHODS: This revises Method S273 [2].

REAGENTS:

1. Carbaryl, reagent grade.*
2. Methanol, absolute.*
3. Methylene chloride, distilled in glass.*
4. 0.1 M KOH in absolute methanol. Dissolve 0.1 mole (5.612 g) in 10 mL methanol in a 1-L volumetric flask; dilute to mark with methanol.
5. Glacial acetic acid.*
6. p-Nitrobenzenediazoniumtetrafluoroborate. Dissolve 25 mg in 5 mL methanol. Add 20 mL glacial acetic acid. Prepare just before use. Keep in an ice bath (4 °C) during use. Discard if the solution becomes deep yellow.
7. Calibration stock solution, 2 mg/mL.* Dissolve an accurately weighed 20-mg portion of Carbaryl in methylene chloride to make 10 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm Type A/E glass fiber filter (Gelman Sciences, or equivalent).
   NOTE: The filter must be free of organic binders.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Spectrophotometer capable of measuring at 475 nm with matched glass cuvettes (1-cm path length).
4. Vials, scintillation, 25-mL, with PTFE-lined screw caps.
5. Tweezers.
6. Syringe, Luer-Lok glass, 10-mL, with 13-mm stainless steel filter holder and PTFE filters.
7. Shaker, mechanical wrist-action.
8. Flasks, volumetric, 10-mL and 1 L.
9. Pipets, 1-, 2-, 17- and 20-mL with pipet bulb.
10. Syringes or micropipets, 10-, 25- and 50-μL.
11. Timer, 5- and 20-min.
12. Ice bath.

SPECIAL PRECAUTIONS: Carbaryl is a cholinesterase inhibitor; use precautions to prevent skin contamination [5,6]. Methylene chloride is toxic; use only in a hood. Methylene chloride is a suspect human carcinogen. Methanol is flammable and toxic (flash point = 11 °C); use only in a hood. Glacial acetic acid is corrosive; handle only with gloves and facial splash protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 20 to 400 L.
3. Within 1 h after sampling, remove the filter carefully to prevent sample loss and place it in a vial. Handle filter only with tweezers.

SAMPLE PREPARATION:

NOTE: Process the samples, blanks, recovery spikes, and working standards in small groups (e.g., two to four) to maintain consistent timing for all analyses. Include a reagent blank in each small group for use in the reference cell of the spectrophotometer.

4. Add 20 mL methanolic 0.1 M KOH to the vial containing the filter.
5. Place the vial on a shaker for 5 min.
6. Transfer 2 mL sample solution to another vial. Start reagent blank at this step.
   NOTE: For filter samples containing >1 g Carbaryl, dilute the sample solution with methanolic 0.1 M KOH prior to this step.
7. Add 17.0 mL glacial acetic acid to the 2 mL of sample solution and cover vial with a PTFE-lined screw cap. Mix by swirling.
8. Add 1 mL p-nitrobenzenediazonium tetrafluoroborate solution. Mix by swirling. Start a 20-min timer for each vial at this point.
9. Use a syringe fitted with a PTFE in-line filter to transfer the solution from the sample vial to the cuvette. Proceed directly to step 15 after exactly 20 min from step 8.

NOTE 1: The color degrades steadily with time. All samples, blanks, recovery spikes, and working standards must have exactly the same time for color development.
NOTE 2: The PTFE in-line filter removes glass fibers from the samples. (Standards do not have to be filtered.)

CALIBRATION AND QUALITY CONTROL:

10. Calibrate with at least six working standards over the range 0.05 to 1.0 mg Carbaryl per sample.
    a. Add known amounts of calibration stock solution to methanolic 0.1 M KOH in vials to make 20 mL of solution.
    b. After 5 min, transfer 2.0 mL of each solution into a clean vial.
    c. Prepare as in steps 7 through 9.
    d. Analyze together with samples and blanks (steps 13 through 15).
    e. Prepare calibration graph (absorbance vs. mg Carbaryl).
11. Check recovery with at least three spiked media blanks per sample set.
    a. Add aliquot of calibration stock solution with a microliter syringe directly to a representative filter. Air dry.
    b. Prepare and analyze together with working standards (steps 4 through 9 and 13 through 15).
    c. Calculate recovery [(mg recovered - mg blank)/mg added].
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

13. Set spectrophotometer at 475 nm.
14. Adjust baseline to zero with distilled water in both cells.
15. Read the absorbance of the sample against the absorbance of the reagent blank.
    NOTE 1: Prepare a fresh reagent blank with each small group of samples. The absorbance of reagent blanks increases with time [5].
    NOTE 2: If absorbance of the sample is >1.0, dilute the filter extract (step 4) with methanolic 0.1 M KOH, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, mg of Carbaryl found on the filter, W, and average media blank, B, from the calibration graph.
17. Calculate the concentration, C (mg/m^3), of Carbaryl in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, mg/m^3.$$

EVALUATION OF METHOD:

Method S273 [2] was issued on February 27, 1976, and validated over the range of 1.96 to 13.4 mg/m^3 at 24 °C and 763 mm Hg [1]. Overall precision, $\hat{S}_{rT}$, was 0.057 with an average recovery of 102%, representing a non-significant bias. The concentration of Carbaryl was independently verified by a Thermo Systems particle mass monitor. Generated atmospheres were produced by nebulization of a toluene solution of a commercial formulation of Sevin containing 15% Carbaryl by weight. No Carbaryl was detected in bubblers (containing 0.1 M KOH in methanol) placed behind the glass fiber filters when 90-L air samples were taken of an atmosphere containing 15 mg/m^3 Carbaryl. Thus, it was concluded that Carbaryl vapor was not a significant factor.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] User check, UBTL, Inc., NIOSH Sequence #4213-V (unpublished, August 16, 1984).
[4] User check, Kettering Laboratory, University of Cincinnati (NIOSH, unpublished, November 5, 1984).
[5] NIOSH Criteria for a Recommended Standard...Occupational Exposure to Carbaryl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-107 (1976).
[6] NIOSH Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (July, 1978).

METHOD REVISED BY:

P. Fey O'Connor, NIOSH/DPSE; S273 originally validated under NIOSH Contract 99-74-45.

CARBON BLACK

C MW: 12.01 CAS: 1333-86-4 RTECS: FF5800000

METHOD: 5000, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : 3.5 mg/m^3
NIOSH: 3.5 mg/m^3 (in presence of PAHs: carcinogen/PAHs to 0.1 mg/m^3, cyclohexane extractable fraction)
ACGIH: 3.5 mg/m^3

PROPERTIES: solid; may contain polynuclear aromatic hydrocarbons (PAH)

SYNONYMS: acetylene black; amorphous carbon; furnace black; lamp black

SAMPLING

SAMPLER: FILTER (tared 5-μm PVC membrane)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 30 L @ 3.5 mg/m^3
-MAX: 570 L

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 8 mg/m^3 (100-L samples)

BIAS: 0.01%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056 [1]

ACCURACY: ± 11.0%

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: airborne particulate material

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology, Class S-1.1 weights or ASTM Class 1 weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.03 mg per sample

PRECISION ($\bar{S}_r$): 0.025 @ 3.5 mg/m^3 [1, 2]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample. This method is not applicable for the determination of "cyclohexane-solubles" [3]. This analysis is simple but the method is nonspecific. Information on any other particulate materials present should be assessed. The method may be extended to higher air concentrations (e.g., nuisance dust levels) by collecting a smaller sample volume [4].

INTERFERENCES: The presence of any other particulate material in the air being sampled will be a positive interference since this is a gravimetric method.

OTHER METHODS: This is Method S262 [5] in a revised format. It is similar, except for collecting device, to the method described in the carbon black criteria document [3].

EQUIPMENT:

1. Sampler: 37-mm, 5-μm pore size PVC filter and stainless steel support screen in 37-mm, cassette filter holder (preferably, conductive).
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Microbalance capable of weighing to 0.001 mg.
4. Static neutralizer; e.g. Po-210; replace nine months after production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance (e.g. 20 ± 1 °C and 50 ± 5% RH).

SPECIAL PRECAUTIONS: Carbon black containing polynuclear aromatic hydrocarbons (cyclohexane extractable materials) in excess of 0.1% (w/w) should be treated as a suspect carcinogen [3].

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
   NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weights, W_1, (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry, and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 30 to 570 L. Do not exceed a filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedures.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust.
   NOTE: If the filter adheres to underside of cassette top, gently lift using the dull side of scalpel blade. Take care not to tear the filter.

CALIBRATION AND QUALITY CONTROL:

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
11. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [6] or in the field [7]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. Calculate precision from these replicates and record $\bar{S}_r$ on control charts. Take corrective action when the precision is out of control [6].

MEASUREMENT:

12. Weigh each filter, including field blanks. Record the post-sampling weight, W_2 (mg). Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.).

CALCULATIONS:

13. Calculate the concentration, C (mg/m^3), of carbon black in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3, \ mg/m^3.$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = tare weight of blank filter (mg)
B_2 = post-sampling weight of blank filter (mg)

EVALUATION OF METHOD:

Method S262 [5] was issued on January 30, 1976, and validated over the range 1.9 to 7.7 mg/m^3 for a 200-L sample and over the range 7.8 to 28 mg/m^3 for a 100-L sample using Vulcan XC72 (0.03-μm particle size; Cabot Corp.) in a Wright Dust Feeder [1]. Overall precision, $\hat{S}_{rT}$, was 0.056. Collection efficiency was between 99 and 100%.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.
[3] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Carbon Black, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-204, 80-88 (1978).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S262, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

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METHOD REVISED BY:

Frank Hearl, P.E., NIOSH/DRDS; S262 and S349 originally validated under NIOSH Contract CDC-99-74-45.

CARBON DIOXIDE 6603

CO_2 MW: 44.01 CAS: 124-38-9 RTECS: FF6400000

METHOD: 6603 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 5000 ppm; STEL 30000 ppm
NIOSH: 5000 ppm
ACGIH: 5000 ppm
(1 ppm = 1.800 mg/m^3)

PROPERTIES: gas; sublimes @ – 78.5 °C

SYNONYMS: carbonic acid; dry ice

SAMPLING

SAMPLER: GAS SAMPLING BAG

FLOW RATE: 0.02 to 0.1 L/min; fill bag ≤ 80% of capacity; spot samples (step 2.a.) or TWA samples (step 2.b.)

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

FIELD BLANKS: in bag from a non-work area

ACCURACY

RANGE STUDIED: 2270 - 10000 ppm [3] (3.5-L samples)

ACCURACY: ± 5.3% [1]

BIAS: −2.5% [3]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.014 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), TCD

ANALYTE: carbon dioxide

TEMPERATURE-INJECTION: ambient
-DETECTOR: 70 °C
-COLUMN: ambient

CARRIER GAS: He, 100 mL/min

COLUMN: 1.5 m x 6-mm ID stainless steel, packed with 80/100 mesh Poropak QS

DETECTOR: thermal conductivity

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 500 - 15000 ppm [2]

ESTIMATED LOD: 1 ppm

PRECISION ($\hat{S}_r$): 0.005 [1]

APPLICABILITY: The working range is 500 to 15000 ppm (900 to 2700 mg/m^3) in relatively non-complex atmospheres.

INTERFERENCES: Any compound having the same or nearly the same retention time as carbon dioxide on the column in use.

OTHER METHODS: This is method S249 in a revised format [2].

REAGENTS:

1. Carbon dioxide,* 99% or higher purity
2. Nitrogen,* purified
3. Helium,* purified
4. Air*, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with thermal conductivity detector, column (p. 6603-1), and 5-mL gas sampling loop.
2. Strip chart recorder, if appropriate. (Many GCs have built-in data-handling capabilities)
3. Personal sampling pump, 0.02 to 0.1 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
4. Sample bags, five-layer, 2- to 20- L, or other appropriate sizes, fitted with a metal valve and hose bib (Calibrated Instruments, 731 Saw Mill Rd., Ardsley, NY 10502, or equivalent).
5. Gas-tight syringes, 10 mL and other convenient sizes for making standards and GC injections if GC is not equipped with gas sampling loop.
6. Calibrated rotameters, for standards preparation.
7. Label tape and marking pens for labelling bags.

SPECIAL PRECAUTIONS: Shipment of compressed must comply with 49 CFR 171-177, DOT regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC and recorder (if applicable) and allow to warm up according to manufacturer's instructions.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. **Spot sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.
   b. **Integrated air sample for TWA determination.**
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to the outlet port of the personal sampling pump with a minimum length of flexible tubing.
      (3) Pump the air sample into the bag at a rate calculated to fill $\leq$80% of the sample bag capacity over the sampling period.
      NOTE: The flow rate must be known to $\pm$5% throughout the sampling period.
      (4) Within 24 hours after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2a).
3. Obtain the carbon dioxide peak height of the injected sample.
   NOTE: Under these conditions, carbon dioxide elutes at about 2 min, after oxygen and nitrogen.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph with at least three replicate determinations of at least five working standards. Plot peak height vs. mass of carbon dioxide.
   b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
   c. Determine the ability of the GC column to separate the carbon dioxide peak from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph (peak height vs. mass of carbon dioxide with triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of carbon dioxide in the sample by comparison of the sample peak height with the daily calibration graph (step 5). Determine the concentration, C, of carbon dioxide in the injected sample, V (mL):

$$C = W/V \quad (mg/m^3)$$

NOTE: Some GCs will perform this calculation electronically.

EVALUATION OF METHOD:

This method for carbon dioxide was evaluated in accordance with the criteria for validation described in Reference [3]. Evaluation was over the range 2270-10000 ppm using a Fisher-Hamilton Gas Partitioner Model 29 gas chromatograph with a thermal conductivity detector and a 5-mL gas sampling loop [1,2]. Recovery after storage of CO_2 at 5800 ppm for 7 days was 92.5% (Saran or Tedlar bags), and 99.5% (5-layer bags). Other GCs and columns other than the one used this evaluation are available for use for the determination of carbon dioxide.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S249, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S249, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 77-157-C (1977).
[3] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD WRITTEN BY:

M. L. Woebkenberg, NIOSH/DPSE

CARBON DISULFIDE 1600

CS_2 MW: 76.14 CAS: 75-15-0 RTECS: FF6650000

METHOD: 1600, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 20 ppm; C 30 ppm; P 100 ppm
NIOSH: 1 ppm; STEL 10 ppm (skin)
ACGIH: 10 ppm (skin)
(1 ppm = 3.11 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.263 g/mL @ 20 °C
BP 46.5 °C; MP −112 °C; VP 40 kPa
(300 mm Hg; 40% v/v) @ 20 °C;
explosive range 1 to 50% v/v in air

SYNONYMS: dithiocarbonic anhydride

SAMPLING

SAMPLER: SOLID SORBENT TUBE + DRYING TUBE (coconut shell charcoal, 100 mg/50 mg, and sodium sulfate, 270 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 10 ppm
-MAX: 25 L

SHIPMENT: dryer attached to charcoal, refrigerated

SAMPLE STABILITY: 1 week @ 25 °C
6 weeks @ 0 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 46 to 183 mg/m^3 [2] (6-L samples)

BIAS: − 0.78%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.059 [1]

ACCURACY: ± 12.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR FPD

ANALYTE: sulfur

DESORPTION: 1 mL toluene; stand 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 145 °C
-COLUMN: 30 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: glass, 2 m x 6-mm OD, 5% OV-17 on 80/100 mesh GasChrom Q or equivalent

CALIBRATION: standard solutions of CS_2 in toluene

RANGE: 0.05 to 0.5 mg per sample

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.052 @ 0.28 to 1.1 mg per sample [1]

APPLICABILITY: The working range is 10 to 200 mg/m^3 (3 to 64 ppm) for a 5-L air sample and is applicable to ceiling determinations. Better sensitivity may be obtained by using higher sampling rates if high humidity is not present [3,4]. This method has been used extensively in the viscose rayon industry and at carbon disulfide production facilities.

INTERFERENCES: No interference occurs from hydrogen sulfide [4]. Water vapor is a potential sampling interferant [4] which is removed by the drying tube. Alternate GC columns, e.g., 5% OV-210 on Chromosorb G-HP or DB-5 fused silica capillary, aid in resolution of chromatographic interferences.

OTHER METHODS: This revises Method S248 [5] and Method 1600 (dated 2/15/84). The criteria document method [3] uses a higher sampling rate. This method replaces P&CAM 179 which uses a similar collection method but extraction-atomic absorption for measurement [6].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Toluene, chromatographic quality.
3. Calibration stock solution, 0.0253 mg/μL. Dilute 0.253 g CS_2 (0.200 mL at 20 °C) to 10 mL with toluene. Prepare in duplicate.
4. Oxygen, purified.
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Drying tube: glass tube, 7 cm long, 6-mm OD, 4-mm ID; single 270-mg section of granular anhydrous sodium sulfate between two silylated glass wool plugs. This removes moisture equivalent to 6 L of air at 100% RH and 22 °C.
   b. Sorbent tube: glass tube, 7 cm long, 6-mm OD, with flame-sealed ends and plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Available commercially.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tubing, 5-mm ID.
4. Refrigerant, bagged (0 °C).
5. Gas chromatograph, FPD with sulfur filter, integrator and column (see page 1600-1).
   NOTE: A valve to vent the solvent peak when it elutes from the column is useful to protect the detector.
6. Vials, glass, 25-mL, PTFE-lined caps.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-μL, readable to 0.1 μL.
9. Delivery pipets, 1- to 100-μL and 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C) [3,7]; work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing. Connect the drying tube to the front section of the charcoal tube with a 20-mm section of PTFE tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 25 L.
   NOTE: Samples may be taken up to 1 L/min if ambient humidity is low [3,4].
4. Keep the drying tube connected to the charcoal tube during shipping. Refrigerate (0 °C) to prevent CS_2 migration to the back section. Cap the open ends. Pack securely for shipment.
   NOTE: Store samples away from any source of CS_2 to avoid contamination.

SAMPLE PREPARATION:

5. Detach and discard drying tube. Place front and back sorbent sections of sampler tube in separate vials. Discard glass wool and foam plugs.
6. Pipet 1.0 mL toluene into each vial. Cap each vial.
7. Allow to stand 60 min with occasional agitation.
   NOTE: Keep desorbed samples and standards away from sources of CS_2 to avoid contamination.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark to prepare solutions in the range 0.02 to 0.5 mg CS_2/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph ([peak area]$^{1/2}$ vs. mg CS_2).
   NOTE: The FPD has a small linear range. Additional working standards may be required [9].
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg CS_2 recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.
    NOTE: At low levels (<0.1 mg CS_2 per sample), DE may be low and variable.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1600-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The retention time for toluene is ca. 30 min, which may be shortened by temperature programming.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of desorbed sample with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass (corrected for DE), mg, of CS_2 found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of CS_2 in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method modifies S248, in that 1 mL toluene (instead of 10 mL benzene) is used to desorb samples, resulting in a better desorption efficiency at low levels and safer working conditions for the analyst [8]. Method S248 [5] was issued on January 30, 1976, and validated over the range 15 to 59 mg/m^3 using a 6-L sample with spiked samplers and atmospheres generated by syringe pump/triple air dilution and verified by total hydrocarbon analyzer [1]. Overall precision, $\hat{S}_{rT}$, was 0.059 with "found" concentrations 0.8% lower than "true" concentrations for 18 samples tested, representing a non-significant bias. Breakthrough (with drying tube preceding charcoal tube) occurred at 162 min (100% RH, 40 ppm CS_2, 0.2 L/min sampling rate) = 32.4 L; DE (0.28 to 1.12 mg/sample) = 0.86; storage stability (0.56 mg/sample) = 85% recovery after one week at 25 °C. At a 1 L/min sampling rate, breakthrough occurred at 19 L at 100 mg/m^3 [4]. A user check of this method gave an estimated LOD of 0.02 mg CS_2 per sample [2].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] User check, UBTL, Inc., NIOSH Sequence #3990-L (unpublished, November 9, 1983).
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[4] McCammon, C.S., P.M. Quinn and R. Kupel. A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide, Am. Ind. Hyg. Assoc. J., 36, 618-624 (1975).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
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[7] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[8] Foley, G. D. NIOSH/DPSE (internal memo, April 17, 1985).
[9] Quincoces, C.E. and M.G. Gonzaleg. Characterization of the Flame Photometric Detector in the Sulfur Mode, Chromatographia 20:371 (1985).

METHOD REVISED BY:

Mary Lynn Woebkenberg, NIOSH/DPSE; S248 originally validated under NIOSH Contract CDC-99-74-45.

CARBON TETRACHLORIDE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

CHLORDANE

$C_{10}H_6Cl_8$ MW: 409.80 CAS: 57-74-9 RTECS: PB9800000

METHOD: 5510, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); carcinogen; Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin), suspect human carcinogen

PROPERTIES: liquid; d 1.59 to 1.63 g/mL @ 25 °C; BP 175 °C; VP 0.0013 Pa (1.0 x 10^{-5} mm Hg) @ 20 °C

SYNONYMS: 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane and isomers; Toxichlor; Octachlor

SAMPLING

SAMPLER: FILTER AND SOLID SORBENT TUBE (0.8-μm cellulose ester membrane; Chromosorb 102, 100/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 10 L @ 0.5 mg/m^3
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: > 1 week @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 2 per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 0.16 to 1.17 mg/m^3 [1,2] (120-L samples)

BIAS: 3.0%

OVERALL PRECISION ($\hat{S}_{r}$): 0.070 [1,2]

ACCURACY: ± 15.3%

MEASUREMENT

TECHNIQUE: GAS CHROMOTOGRAPHY, ELECTRON CAPTURE DETECTOR (GC/ECD)

ANALYTE: Chlordane

EXTRACTION: 10 mL toluene, stand 30 min

INJECTION VOLUME: 2 μL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 205 °C

CARRIER GASES: 95% argon/5% methane @ 75 mL/min

COLUMN: 2 m x 4-mm ID glass packed with 1.5%, SP2250/1.95% SP2401 on 100/120 mesh

CALIBRATION: solution of analyte in toluene or hexane with internal standard

RANGE: 5 to 150 μg per sample [2]

ESTIMATED LOD: 0.1 μg per sample [3]

PRECISION ($\bar{S}_{r}$): 0.02 @ 6 to 120 μg per sample [2]

APPLICABILITY: The working range is 0.04 to 1.2 mg/m^3 for a 120-L sample. Chlordane, accompanied by a mixture of penta-, hexa-, hepta-, and nonachlorinated compounds, is defined by a group of five chromatographic peaks. It is necessary to determine the percentage of Chlordane and its isomers in the standards used.

INTERFERENCES: None identified; an alternate column is 2 m x 2-mm ID glass packed with 3% QF-1 on 100/120 mesh Chrom Q.

OTHER METHODS: This is NIOSH method S278 in a revised format. [2]

REAGENTS:

1. Toluene, distilled in glass.
2. Hexane, distilled in glass.
3. Chlordane, 95%.*
4. Calibration stock solution, ca. 6 mg/mL. Dissolve 10 mg Chlordane in 1 mL toluene. NOTE: Since Chlordane is available only as a mixture, standardize the solution as follows:
   a. Dilute 10 μL calibration stock solution to 10 mL.
   b. Analyze by steps 11-13.
   c. Divide combined area of Chlordane peaks (Fig. 1) by total area of all peaks to determine fraction Chlordane, f.
5. Internal standard, p,p'-DDT, 98%.*
6. 95% Argon/5% methane mixture, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 0.8-μm pore size cellulose ester membrane filter supported by a stainless steel screen in a two-piece filter cassette holder plus a 10 cm x 8-mm OD x 6-mm ID, 20/40 Chromosorb 102 tube (front = 100 mg; back = 50 mg), separated by 3-mm silanized glass wool plug, flame sealed ends with plastic caps. Pressure drop across the tube at 1 L/min must not exceed 2.5 mm Hg. Filters and tubes are commercially available.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator and column (page 5510-1).
4. Vials, scintillation, 20-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Flasks, volumetric 10-mL.
7. Bottles, 60 mL, 40-mm ID, straight-sided with a PTFE-lined cap for extracting filter holder and screen.
8. Stopwatch.
9. Manometer.
10. Pipets, 1- and 10-mL an other convenient sizes for preparing standards.
11. Tweezers.

SPECIAL PRECAUTIONS: Chlordane and p,p'-DDT are toxic and rapidly absorbed through the skin [4]. Use gloves and eyeglasses to avoid direct contact with these compounds. Handle these chemicals and organic solvents with care in the laboratory hood. Chlordane is a potential human carcinogen [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Assemble the sampler and connect the sorbent tube (ends broken just before the connection) to the sampling pump with backup section nearest the sampling pump. Keep the sampler in a vertical position during sampling.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 10 to 200 L.
4. Remove the sorbent tube from the outlet of the cassette and connect it to the inlet side of the cassette. Cap the open end of the sorbent tube and plug the outlet of the cassette. Ship sampler with appropriate blanks to laboratory.
5. In separate package, ship bulk sample of the suspected material.

SAMPLE PREPARATION:

6. Separate the sampler components for extraction as follows:
   a. Into a bottle, transfer the filter, front sorbent section and glass wool plugs. Add 10.0 mL toluene. After desorption is complete, dilute a 1-mL aliquot to 10 mL for analysis.
   b. Into a second bottle, transfer the stainless steel screen. Using a 10-mL volumetric pipet, rinse the inner surfaces of the cassette into the bottle with hexane.
   c. Into a scintillation vial, transfer the back sorbent section. Add 10.0 mL toluene.
7. Cap each container and allow to stand 30 min. with occasional swirling.
   NOTE: A suitable internal standard such as p,p'-DDT may be added, at 0.4 μg/mL, at this point.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to toluene containing internal standard in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain Chlordane concentrations in the range 0.01 to 15 μg/mL.
   b. Analyze the samples and blanks (steps 11 through 13).
   c. Prepare a calibration graph (ratio of the total Chlordane peak areas to peak area of internal standard vs. μg Chlordane).
9. Determine recovery at least once for each lot of filters and Chromosorb 102 used. Prepare three samplers at each of five levels plus three media blanks.
   a. Place cellulose ester membrane filter and 100 mg of Chromosorb 102 in a bottle.
   b. Add calibration stock solution to the filter and Chromosorb 102 in the container with a microliter syringe. Prepare parallel blank samples with no added analyte.
   c. Cap the bottle. Allow to stand overnight.
   d. Desorb (steps 6 and 7) and analyze with working standards (steps 11 through 13).
   e. Prepare a graph of recovery vs. μg Chlordane recovered.
10. Check recovery at two levels for each sample set in duplicate. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5510-1.
12. Inject 2-μL sample aliquot using solvent flush technique or with autosampler. Make duplicate injections of samples and standards.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the solution, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak areas. Divide the total Chlordane peak area (sum of five peaks; see Fig. 1) by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

14. Determine the mass, μg (corrected for recovery), of Chlordane found in the filter plus front sorbent section (W_f), back sorbent section (W_b), extract from cassette and screen (W_c), and average media blank filter plus front sorbent section (B_f) and back sorbent section (B_b).
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate the concentration, C, of Chlordane in the volume of air sampled, V (L):

$$C = \frac{(W_f + W_b + W_c - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S278 was validated on June 8, 1979, [1,2,6]. The substance used to dynamically generate test atmospheres at 25 °C and 760 mm Hg was Ortho-Klor-72 (40% Chlordane), Velsicol Chemical Corporation. Collection efficiencies and recoveries were close to 1.00 in the range 6 to 120 μg per sample. No significant breakthrough was observed after 240 min of sampling an atmosphere of 1.1 mg/m^3 Chlordane at a flow rate of approximately 1 L/min. Samples spiked with Chlordane, extracted with toluene, and stored one week at room temperature gave recoveries of 96 to 100%. Overall precision ($\hat{S}_{rT}$) was 0.07. No significant bias was found.

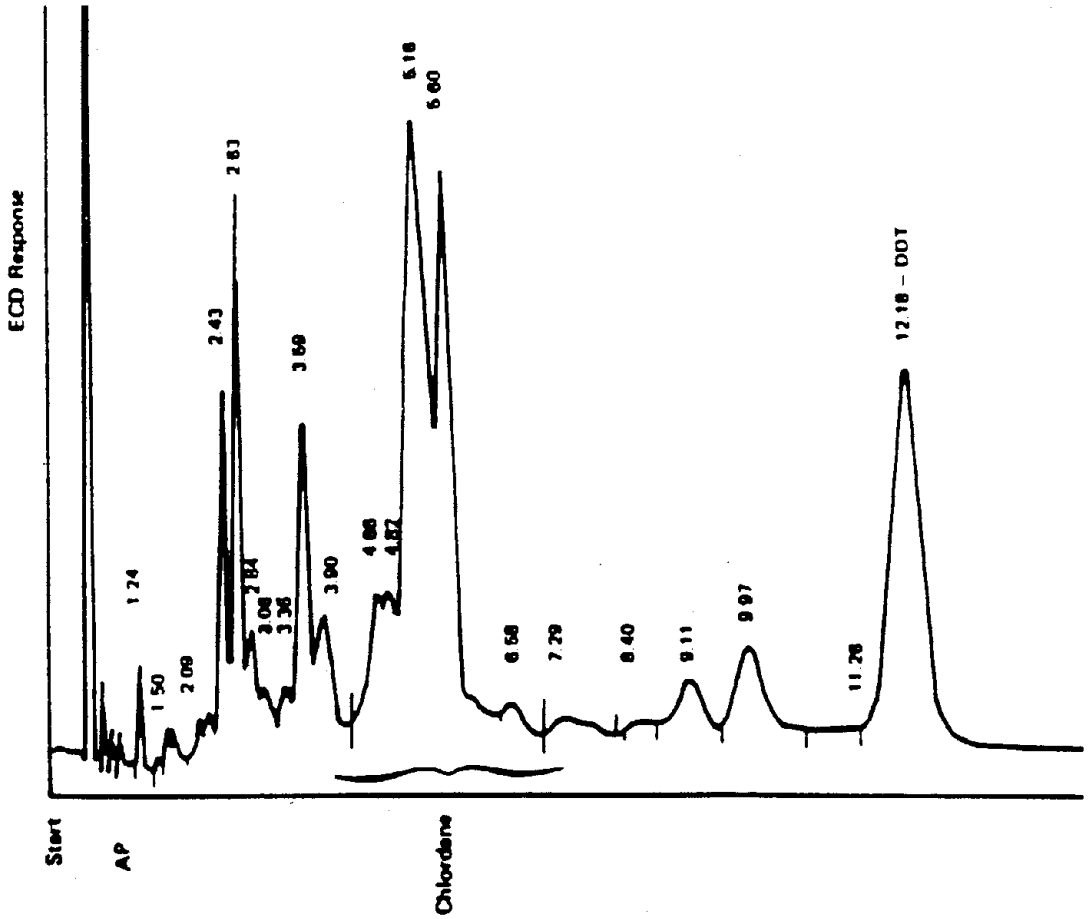
REFERENCES:

[1] NIOSH Backup Data Report S278 (June 8, 1979) for Chlordane prepared under NIOSH Contract No. 210-76-0123 (1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S278, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] UBTL, Inc. NIOSH Seq. Report 4-999-K (July 19, 1985, unpubl).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 from NTIS, Springfield, VA 22161.
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., ATSDR; S278 originally validated under NIOSH Contract No. 210-76-0123.

Figure 1. Chromatogram of Chlordane analytical standard.



CHLORINATED CAMPHENE 5039

$C_{10}H_{10}Cl_8$ (average) MW: 414 (average) CAS: 8001-35-2 RTECS: XW5250000

METHOD: 5039, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 0.5 mg/m^3 (skin)
NIOSH: lowest feasible (skin), carcinogen, Class I Pesticide
ACGIH: 0.5 mg/m^3 (skin); STEL 1 mg/m^3 (skin)
(1 ppm = 16.9 mg/m^3 @ NTP)

PROPERTIES: solid; MP 70 °C to 95 °C; BP (760 mm Hg) decomposes; sp. gr. 1.63; VP 0.03 to 0.05 kPa (0.2 to 0.4 mm Hg) @ 20 °C

SYNONYMS: toxaphene

SAMPLING

SAMPLER: FILTER
(0.8-μm cellulose ester membrane)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 2 L @ 0.5 mg/m^3
-MAX: 30 L

SHIPMENT: place filter and backup pad in screw cap vial; ship separate bulk sample

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.225 to 1.16 mg/m^3 [1] (15-L samples)
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	0.076 [1]
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: chlorinated camphene

DESORPTION: 10 mL petroleum ether

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 250 °C
-COLUMN: 205 °C

CARRIER GAS: nitrogen, 50 mL/min

COLUMN: glass, 1.8 m x 6-mm OD, packed with 3% OV-1 on 100/120 mesh Gas Chrom Q

CALIBRATION: chlorinated camphene in petroleum ether

RANGE: 0.7 to 14 μg per sample [1]

ESTIMATED LOD: 0.14 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.024 (3 to 14 μg per sample) [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 for a 15-L air sample.

INTERFERENCES: Other pesticides such as aldrin, parathion, dieldrin, DDT and its metabolites, and polychlorinated biphenyls elute in the retention time band for chlorinated camphene.

OTHER METHODS: This is Method S67 [2] in a revised format. Toxaphene in air has been collected on Chromosorb 102 with acceptable recovery [3].

REAGENTS:

1. Chlorinated camphene* (toxaphene).
2. Petroleum ether*, 30 to 60 °C, suitable for pesticide residue analysis.
3. Nitrogen, purified.
4. Calibration stock solution, 0.1 mg/mL. Dissolve 5 mg of chlorinated camphene in 50 mL petroleum ether.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm cellulose ester membrane filter (0.8-μm pore size) supported by a cellulose backup pad in a three-piece filter holder. Do not use tenite filter holders.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni ECD, integrator, and column (page 5039-1).
4. Vials, 20-mL with PTFE-lined screw caps for shipping filters and pads.
5. Syringes, 10-μL and larger sizes for preparation of standard solutions.
6. Pipet, 10-mL.
7. Volumetric flasks, 10-mL.
8. Tweezers, stainless steel.

SPECIAL PRECAUTIONS: Petroleum ether is highly flammable. Prepare samples and standards in well-ventilated hood. Overexposure to chlorinated camphene may cause nausea, mental confusion, and unconsciousness; contact with chlorinated camphene solutions may cause skin irritation [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.2 and 1 L/min for a sample size of 2 to 30 L.
3. Carefully transfer the filter and backup pad to a screw cap vial by means of tweezers.

SAMPLE PREPARATION:

4. Pipet 10 mL petroleum ether into each vial and seal.
5. Gently swirl the vial to wet the filter and backup pad. Allow to stand 30 min.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to petroleum ether in 10-mL volumetric flasks and dilute to the mark to obtain concentrations in the range 0.14 to 14 μg chlorinated camphene/10 mL.
   b. Analyze with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (sum of peak areas in the retention time band vs. μg chlorinated camphene).
7. Determine recovery (R) at least once for each batch of filters used for sampling in the working range. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of calibration stock solution onto the filter. Allow filters to air dry.
   b. Store samples overnight in vials.
   c. Prepare (steps 4 and 5) and analyze with samples (steps 8 and 9).
   d. Prepare a graph of R vs. μg chlorinated camphene recovered.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5039-1. Inject 5-μL aliquots manually using solvent flush technique or with autosampler.
   NOTE: If peak areas are outside the calibration range, make dilution of sample or standard solution, analyze and apply the dilution factor in calculations.
10. Sum the peak areas in the retention time band. Use bulk sample to identify the appropriate retention time band.

CALCULATIONS:

11. Determine the mass, μg (corrected for R), of chlorinated camphene found in each sample (W) and average media blank (B).
12. Calculate concentration, C, of chlorinated camphene in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 0.22 to 1.2 mg/m^3 at 22 °C and 761 mm Hg using 15-L samples [1]. No reference method was used. The collection efficiency for the filters was found to be 1.0 using a challenge concentration of 1.3 mg/m^3 for 30 L. Average recoveries of chlorinated camphene from cellulose ester filters were 91% to 98% in the range 0.7 to 14 μg per sample. Cassettes were found to be unsuitable for storage of 0.7 μg chlorinated camphene on filters for 1 day at room temperature.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S67, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S67, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Thomas, Thomas C.; Nishioka, Yoshimi A., "Sampling of Airborne Pesticides using Chromosorb 102," Bull. Environ. Contam. Toxicol., 35(4), 460-5 (1985).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock No. PB 83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; Method S67 originally developed under NIOSH Contract CDC-99-74-45.

CHLORINATED DIPHENYL OXIDE 5025

$C_{12}H_4Cl_6O$ MW: 376.88 CAS: 55720-99-5 RTECS: KO4200000

METHOD: 5025, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : 0.5 mg/m^3
NIOSH: 0.5 mg/m^3
ACGIH: 0.5 mg/m^3

PROPERTIES: Table 1

SYNONYMS: chlorinated diphenyl ether; hexachlorodiphenyl oxide

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 8 L @ 0.5 mg/m^3
-MAX: 200 L

SHIPMENT: within 1 h of sampling, transfer filter and backup pad to screw-cap bottle; otherwise, routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; for proper identification of analytes

ACCURACY

RANGE STUDIED: 0.1 to 1 mg/m^3 [1] (90-L samples)

BIAS: − 0.21%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.070 [1]

ACCURACY: ± 13.76%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTION

ANALYTE: chlorinated diphenyl oxide

DESORPTION: 10 mL isooctane, stand 2 hours

INJECTION VOLUME: 15 μL

TEMPERATURE-FURNACE: 760 °C
-TRANSFER LINE: 225 °C
-VENT: 250 °C
-COLUMN: 210 °C

GASES-FURNACE: H_2, 150 mL/min
-CARRIER: N_2, 150 mL/min

COLUMN: 1.5 m x 2-mm ID glass; 5% SE-30 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of chlorinated diphenyl oxide in isooctane

RANGE: 4 to 150 μg per sample [2]

ESTIMATED LOD: 0.2 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.019 @ 0.02 to 0.09 mg per sample [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 for a 90-L air sample. The method has been evaluated only for the hexachloro derivative. The sampler may not be adequate for the monochloro or dichloro derivatives, which have higher vapor pressures.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S119 [2].

REAGENTS:

1. Isooctane, chromatographic quality.
2. Calibration stock solution, 2 μg/μL chlorinated diphenyl oxide* in isooctane. Prepare in duplicate.
3. Nitrogen, purified.
4. Hydrogen, prepurified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, supported by cellulose backup pad in two-piece polystyrene filter holder.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Gas chromatograph, electrolytic conductivity detector, effluent vent, integrator and column (page 5025-1).
4. Vials, 20-mL, PTFE-lined caps, for shipping filters.
5. Syringes, 25-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, 10-mL.
8. Tweezers.

SPECIAL PRECAUTIONS: Prolonged skin contact with chlorinated diphenyl oxide can cause chloracne; acute and chronic exposure can cause liver damage [3,4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 8 to 200 L.
3. Within 1 h of sampling, using tweezers, carefully transfer the filter and backup pad to a vial.

SAMPLE PREPARATION:

4. Pipet 10.0 mL isooctane into each vial containing a sample or blank filter and backup pad. Seal and gently swirl the vial to wet the filter and backup pad. Allow to stand 2 h.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to isooctane in 10-mL volumetric flasks and dilute to the mark to obtain concentrations in the range 0.4 to 15 μg chlorinated diphenyl oxide/mL.
   b. Analyze with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (sum of areas of selected peaks vs. μg chlorinated diphenyl oxide).
6. Determine recovery (R) at least once for each batch of filters used for sampling in the calibration range. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of calibration stock solution onto the filter. Allow filters to air dry.
   b. Store samples overnight in vials.
   c. Prepare (step 4) and analyze with working standards (steps 8 and 9).
   d. Graph R vs. μg chlorinated diphenyl oxide.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

8. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5025-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Open the effluent vent to keep the solvent from passing into the detector. Close the effluent vent after the solvent peak has eluted.
   NOTE: Under conditions given, the solvent elutes in about 20 sec. The large quantity of solvent injected may cause malfunction of the conductivity cell, unless it is vented.
9. Sum the areas of selected peaks.
   NOTE: Use a bulk sample if necessary to identify the appropriate chromatographic peaks.

CALCULATIONS:

10. Determine the mass, μg (corrected for R) of chlorinated diphenyl oxide found in the sample (W) and in the average media blank (B) from the calibration graph.
11. Calculate concentration, C, of chlorinated diphenyl oxide in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S119 was evaluated over the range 0.1 to 1 mg/m^3 hexachlorodiphenyl oxide at 22 °C and 767 mm Hg using 90-L samples [1]. Overall precision, $\hat{S}_{rT}$, was 0.070; no reference method was used. The test atmospheres were generated from solutions (0.25 to 0.5% w/v) of chlorinated diphenyl oxide (Chem Samples) in toluene, using a fluid aspirator, cyclone and an impactor. Sampling with two filters in series was conducted in an atmosphere containing 1 mg/m^3 chlorinated diphenyl oxide. Chlorinated diphenyl oxide was found only on the front filters (with LOD = 0.002 mg/m^3). Filters enriched with 100 μg chlorinated diphenyl oxide were analyzed after passing 100 L of air through them. The resulting recovery of the analyte was 99.75% with $\bar{S}_r$ = 0.017%. The recovery of chlorinated diphenyl oxide from enriched filters through which no air was drawn was 1.012 in the range 23 to 90 μg per sample. Storage stability of the sample was not tested.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S119, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S119, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[4] Occupational Diseases, A Guide to Their Recognition, revised ed., 255-256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-181 (1978).
[5] Patty, F. A. Industrial Hygiene and Toxicology, 2nd ed, Vol. 2, 1706-1707, Interscience, New York (1963).

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S119 originally developed under NIOSH Contract CDC-99-74-45.

Table 1. Properties of chlorinated diphenyl oxide [3,5].

Compound	BP, °C (8 mm Hg)	d, g/mL 25 °C	Vapor Pressure @ 25 °C Pa	mm Hg	mg/m^3	1 ppm in mg/m^3 @ NTP
Monochloro-	153	1.19	0.93	0.007	77	8.37
Dichloro-	168.2	1.32	0.08	0.0006	8	9.78
Hexachloro-	230 to 260	1.57 @ 20 °C	<0.008	<0.00006	<1	15.41

CHLORINATED TERPHENYL (60% CHLORINE) 5014

$C_{18}H_{4.65}Cl_{9.35}$ MW: 552 (average) CAS: 11126-42-4 RTECS: TQ1390000

METHOD: 5014, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm ≈ 23 mg/m^3 @ NTP)

PROPERTIES: solid; d 1.67 g/mL @ 25 °C; BP 280 to 335 °C @ 5 mm Hg (0.67 kPa); softening point 98 to 105.5 °C

SYNONYMS: chlorinated triphenyl, polychloroterphenyl, PCT, Aroclor 5460

SAMPLING

SAMPLER: FILTER (glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 100 L @ 10 μg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.01 to 1.0 mg/m^3 [1] (100-L samples)

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: chlorinated terphenyl

DESORPTION: 4 mL isooctane, 30 min ultrasonic agitation

INJECTION VOLUME: 2 μL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 300 °C
-COLUMN: 240 °C

GASES-CARRIER: nitrogen, 40 mL/min
-PURGE: nitrogen

COLUMN: 2.0 m x 2-mm ID glass; 3% QF-1 on 80/100 mesh Gas Chrom Q or equivalent

CALIBRATION: chlorinated terphenyl in isooctane

RANGE: 1 to 100 μg per sample [1]

ESTIMATED LOD: not determined

PRECISION ($\hat{S}_r$): 0.081 [1]

APPLICABILITY: The working range is 0.01 to 1 mg/m^3 for a 100-L air sample.

INTERFERENCES: Presence of other chlorinated terphenyls, e.g., Aroclor 5442 (42% chlorine), or other substances with similar retention and detection characteristics may interfere with the analysis.

OTHER METHODS: None evaluated by NIOSH.

REAGENTS:

1. Isooctane (2,2,4-trimethylpentane), distilled in glass.*
2. Hexane, distilled in glass.*
3. Chlorinated terphenyl (60% chlorine).*
4. Calibration stock solution, 1 mg/mL. Dilute an accurately weighed 100-mg portion of chlorinated terphenyl to 100 mL with hexane.
5. Nitrogen, 99.999%.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm glass fiber filter (Gelman #64877 or equivalent) supported by a backup pad in a closed-face polystyrene cassette (Gelman #4338 or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni ECD, integrator and column (page 5014-1).
4. Tweezers, stainless steel.
5. Vials, glass, 5-mL, crimp seals or caps, silicone rubber septa lined with polyperfluoroethylene.
6. Pipets, 1-, 2- and 4-mL, with pipet bulb.
7. Ultrasonic bath.
8. Balance, readable to 0.1 mg.
9. Volumetric flasks, 5-, 10-, 25- and 100-mL.
10. Syringe, 10-μL.

SPECIAL PRECAUTIONS: Hexane (flash point = −22 °C) and isooctane (flash point = 4 °C) are highly flammable. Prepare samples and standards in well-ventilated hood.

Chlorinated terphenyls may be similar to chlorinated biphenyls in toxicity. Use protective clothing to avoid skin contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 100 to 1500 L.

SAMPLE PREPARATION:

3. Transfer filter to 5-mL vial using tweezers. Discard backup pad.
4. Pipet 4.0 mL of isooctane into vial and seal immediately.
5. Agitate vial in ultrasonic bath for 30 min to complete extraction.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 1 to 100 μg chlorinated terphenyl per sample.
   a. Add known amounts of calibration stock solution to hexane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (detector response vs. μg chlorinated terphenyl per sample).
7. Prepare two control samples at each of two levels for checking analysis of field samples.
   a. For each control sample, inject calibration stock solution directly onto filter. Mount filter in cassette and draw ca. 30 L of analyte-free air through (to evaporate hexane). Seal cassette and store overnight.

b. Desorb filters as in steps 3 through 5, and analyze as in steps 9 and 10.

8. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

9. Set gas chromatograph to conditions given on page 5014-1 and optimize detector performance per manufacturer's instructions. Using given conditions, retention time of largest and most distinct peak in cluster was about 6.1 min.
10. Inject sample aliquot and measure detector response, e.g., height from base of cluster to top of most prominent peak.

CALCULATIONS:

11. Read the mass, μg, of chlorinated terphenyl found in each sample (W) and average media blank (B) from calibration graph.
12. Calculate concentration, C (mg/m^3), of chlorinated terphenyl in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Measurement precision was determined by analyzing spiked sampling media [1]. The average recovery was 1.006. There appeared to be no effect on recovery when up to 2700 L of charcoal-filtered air (40 °C and 40% relative humidity) was passed through filters spiked at the 1-μg level. Recoveries from 100-L samples collected from generated aerosol were 1.05 ($\bar{S}_r$ = 0.162) after seven days storage, and 0.875 ($\bar{S}_r$ = 0.206) after 14 days storage, relative to the amount found after one day. Generated concentrations were not reproducible, and independent methods for determining the true concentration appeared to provide lower and more imprecise results than this method. Because of the difficulty in determining the true concentration, overall precision and bias were not determined. References [1] and [2] provide additional information.

REFERENCES:

[1] Graham, M. M., and H. K. Dillon. Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene, 1,2,4,5-Tetrachlorobenzene, Pentachlorobenzene, and Polychlorinated Terphenyls: Research Report for Polychlorinated Terphenyls, NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL, available from NTIS (1982) as PB-83-140-087.

[2] Kimbrough, R. D., ed. "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products," Topics in Environmental Health, V. 4, Elsevier/North-Holland Biomedical Press, Amsterdam, 20-21 (1980).

METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0102.

CHLORINE

Cl_2 MW: 70.91 CAS: 7782-50-5 RTECS: FO2100000

METHOD: 6011, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 1 ppm
NIOSH: 0.5 ppm; STEL 1 ppm
ACGIH: 0.5 ppm; STEL 1 ppm
(1 ppm = 2.90 mg/m^3 @ NTP)

PROPERTIES: gas; d 3.214 g/L at 0 °C; BP −34.6 °C; vapor density (air = 1) 2.5

SYNONYMS: None.

SAMPLING

SAMPLER: PREFILTER + FILTER (PTFE, 0.5-μm + silver membrane, 25-mm, 0.45-μm)

FLOW RATE: 0.3 to 1 L/min

VOL-MIN: 2 L @ 0.5 ppm
-MAX: 90 L

SHIPMENT: routine, protect from light

SAMPLE STABILITY: ≥30 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.35 to 6.77 mg/m^3 (15-L samples)

BIAS: − 1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.075 [1]

ACCURACY: ± 14.8%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY

ANALYTE: chloride ion (Cl^-) or bromide ion (Br^-)

EXTRACTION: 3 mL 6 mM $Na_2S_2O_3$, 10 min

INJECTION VOLUME: 50 μL

COLUMN: Dionex HPIC-AG4A guard, HPIC-AS4A separator MFC-1 precolumn, AMMS anion suppressor

DETECTOR SETTING: 10 μS full scale

ELUENT: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol, 2 mL/min

CALIBRATION: standard solutions of Cl^- in deionized water

RANGE: 2 to 50 μg Cl^- per sample [1]

ESTIMATED LOD: 0.6 μg Cl^- per sample [1]

PRECISION ($\bar{S}_r$): 0.067 @ 5.3 to 100 μg per sample [1]

APPLICABILITY: The working ranges for Br_2 and Cl_2 are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m^3) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m^3) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference up to a maximum of 15 μg per sample. HBr gives a positive interference as it is sampled continuously [1].

OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

REAGENTS:

1. Sodium thiosulfate, reagent grade.
2. Water, deionized.
3. Extraction solution: 6 mM $Na_2S_2O_3$. Dissolve 0.474 g $Na_2S_2O_3$ in 500 mL deionized water.
4. Eluent: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol. Dissolve 0.041 g $NaHCO_3$, 0.848 g Na_2CO_3 and 0.186 g p-cyanophenol in 2 L filtered deionized water.
5. Suppressor regenerant, 0.025 N H_2SO_4. Dilute 2.8 mL conc. H_2SO_4 to 4 L with deionized water.*
6. Calibration stock solutions, 1 mg/mL (as anion).
   (1) Dissolve 0.149 g KBr in 100 mL deionized water
   (2) Dissolve 0.21 g KCl in 100 mL deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Silver membrane filter,* 25-mm, 0.45-μm, (Costar/Nuclepore, Poretics, or equivalent) with porous plastic support pad (Costar/Nuclepore); prefilter, PTFE with PTFE support, 0.5-μm (Gelman Zefluor, SKC, or equivalent), or polyester, 0.4-μm (Costar/Nuclepore) with porous plastic support pad; three-piece, 25-mm carbon-filled polypropylene cassette (opaque) with 50-mm extension (Costar/Nuclepore or Gelman) (Fig. 1).
   a. In the outlet piece of cassette, place porous plastic support pad and cleaned silver filter. Insert 50-mm extension (cowl) securely.
   b. At the inlet (top) of the extension, place porous plastic support pad and prefilter. Insert inlet cassette piece securely.
   c. Seal each connection with shrinkable bands or tape.
2. Personal sampling pump, 0.3 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph with Dionex MFC-1, HPIC-AG4A, HPIC-AS4A columns, AMMS anion micromembrane suppressor, conductivity detector and integrator (page 6011-1).
4. Bottles, 30-mL, wide mouth with screw caps, amber or opaque polyethylene.
5. Micropipettes, with disposable tips.
6. Volumetric flasks, 10- and 100-mL.
7. Repipet reagent dispensers, 0 to 10-mL.
8. Syringes, 10-mL, polyethylene, luer-tip.
9. Forceps.

* Silver membrane filters must be cleaned prior to use (see Appendix).

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive to skin, eyes, and mucous membranes. Wear protective clothing. Handle in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.3 and 1 L/min for a total sample size of 8 to 360 L for bromine or 2 to 90 L for chlorine.
4. Seal ends of sampler with plugs. Pack securely for shipping.

SAMPLE PREPARATION:

NOTE: Silver halides are photosensitive. Protect from light during transfer and desorption.

5. Under very dim or red light, open cassette and transfer the silver filter with forceps to amber bottle. Add 3 mL 6 mM $Na_2S_2O_3$ and cap.
   NOTE: Prefilter may be analyzed for particulate halides, or discarded.
6. Allow samples to stand a minimum of 10 min with occasional swirling.
   NOTE: Once desorbed, samples are no longer photosensitive.
7. Uncap the sample bottles and add 7 mL deionized water for a total solution volume of 10 mL.
8. Pour sample into 10-mL plastic syringe for manual injection or into autosampler vials.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of 0.2 to 15 μg bromide and/or 0.05 to 5 μg chloride per mL of sample.
   a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark with deionized water.
   b. Prepare fresh working standards biweekly.
   c. Analyze working standards together with samples and blanks (steps 11 through 13).
   d. Prepare a calibration graph (peak height vs. μg of anion per sample).
10. Analyze three quality control spikes, three analyst spikes and media blanks to ensure that calibration graph is in control.

MEASUREMENT:

11. Set ion chromatograph according to manufacturer's instructions and to conditions given on page 6011-1.
    NOTE: The use of an inline filter (5-μm) in the eluent stream prior to the chromatographic columns is recommended.
12. Inject 50-μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from syringe to ensure complete rinse of the sample loop.
13. Measure peak height. If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. From the calibration graph, determine the mass of Br^- or Cl^- in each sample, W (μg), and in the average blank, B (μg).
15. Calculate the concentration, C (mg/m^3), of Br_2 or Cl_2 in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of Br_2 and Cl_2 at both high (80%) and low (20%) relative humidities [1]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m^3 for Br_2 and 0.354 to 6.77 mg/m^3 for Cl_2. Overall recovery for Br_2 was 98.8% with total overall precision, $\hat{S}_{rT}$, of 6.8%. Overall recovery for Cl_2 was 98.6% with total overall precision, $\hat{S}_{rT}$, of 6.7%. Samples for Cl_2 were stable at least 30 days at 25 °C (103 ± 4% Recovery) and up to 60 days at 5 °C (101 ± 3% Recovery). The Br_2 samples were stable up to 60 days at 25 °C (99.2 ± 10.1% Recovery).

REFERENCES:

[1] Cassinelli, M.E. Development of Solid Sorbent Monitoring Method for Chlorine and Bromine with Determination by Ion Chromatography, Appl. Occup. Environ. Hyg., 6:215-226 (1991).

[2] NIOSH Manual of Analytical Methods, 2nd ed.; Taylor, D.G., Ed.; V. 1, P&CAM 209; U.S. Department of Health Education and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 77-157, 1977.

[3] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, Method No. ID-101). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

[4] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-108). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE

APPENDIX: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 mM $Na_2S_2O_3$.
2. Allow to stand for a minimum of 10 min with occasional swirling.
3. Discard solution and rinse thoroughly with deionized water. Allow the filters to stand in last rinse for a few minutes.
4. Remove filters from bottles and dry between layers of absorbent laboratory towels.
5. Store cleaned filters between paper disks in manufacturer's container. Filters are stable for at least 8 months.

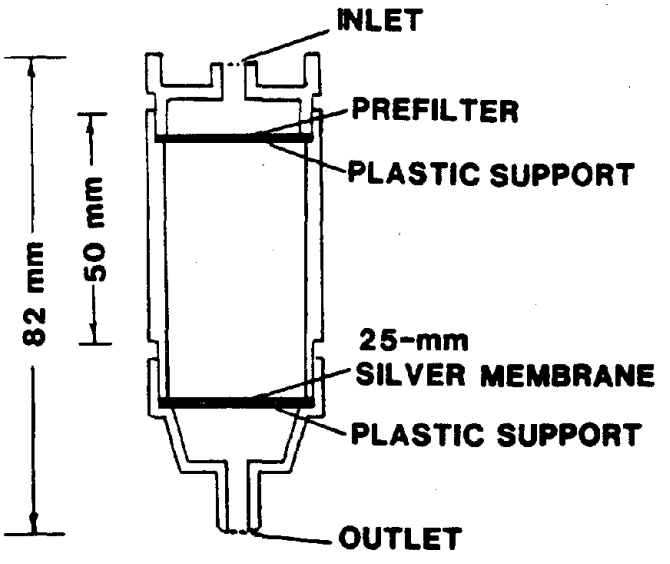


Figure 1. Silver Filter Sampler

CHLOROACETALDEHYDE

CH_2ClCHO MW: 78.50 CAS: 107-20-0 RTECS: AB2450000

METHOD: 2015, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 1 ppm
NIOSH: C 1 ppm
ACGIH: C 1 ppm
(1 ppm = 3.21 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.236 g/mL @ 20 °C; sp. gr. (40% aq. soln.) 1.19; BP 85 °C; MP −16.3 °C; VP 13.3 kPa (100 mm Hg)

SYNONYMS: 2-chloroacetaldehyde; 2-chloroethanal

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 520 mg/260 mg)

FLOW RATE: 0.05 to 0.2 L/min (0.2 L/min for 15-min ceiling sample)

VOL-MIN: 0.3 L @ 1 ppm
-MAX: 16 L

SHIPMENT: routine; submit separate bulk sample

SAMPLE STABILITY: at least 7 days @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.8 to 6.4 mg/m^3 (3-L samples)

BIAS: −0.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.060 [1]

ACCURACY: ±12.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: chloroacetaldehyde

DESORPTION: 25 mL 50% aqueous methanol, 30 min

INJECTION VOLUME: 2 μL with 3 μL water as flush

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 150 °C

CARRIER GAS: 5% argon in methane, 50 mL/min

COLUMN: glass, 1.8 m x 6 mm OD, packed with 60/80 mesh Chromosorb 101

CALIBRATION: standard solutions of chloroacetaldehyde in 50% aqueous methanol

RANGE: 1 to 19 μg per sample [1]

ESTIMATED LOD: 0.1 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.036 [1]

APPLICABILITY: The working range is 0.1 to 2 ppm (0.33 to 6.3 mg/m^3) for a 3-L air sample. The method is not able to distinguish between chloroacetaldehyde and the monomer or dimer hydrate forms of chloroacetaldehyde.

INTERFERENCES: None identified.

OTHER METHODS: This is method S11 [2] in a revised format. Chloroacetaldehyde in air has also been determined by differential pulse polarography [3].

REAGENTS:

1. Chloroacetaldehyde*, ~50% (w/w) solution in water.
2. Water, deionized, distilled.
3. 50% Aqueous methanol.
4. 5% Hydrazine sulfate solution. Dissolve 12.5 g hydrazine sulfate in 250 mL deionized distilled water.
5. Ferric ammonium sulfate solution, saturated, in 1 M HNO_3.
6. Ammonium thiocyanate, 0.100 N. Accurately weigh 7.6139 ammonium thiocyanate and dilute to 1 L with deionized distilled water.
7. Silver nitrate solution, 0.100 N. Accurately weigh 16.987g silver nitrate and dilute to 1 L with deionized distilled water.
8. Nitric acid solution. Add 25 mL conc. nitric acid to 25 mL water. Boil until colorless to remove nitrous acid.
9. Nitrobenzene.
10. 5% Argon/methane.
11. Calibration stock solution. Dilute 1 mL 50 % chloroacetaldehyde solution to 250 mL with deionized distilled water. See APPENDIX for standardization method.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass, 8 cm long, 6-mm ID, containing two sections of 20/40 mesh silica gel (front = 520 mg; back = 260 mg), separated by 2 mm of urethane foam. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.05 to 0.2 L/min with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron-capture detector, integrator and column (page 2015-1).
4. Volumetric flasks, 25-mL, 1-L and other convenient sizes for preparing standards.
5. Erlenmeyer flasks, 50-mL, 250-mL.
6. Buret, 10-mL.
7. Pipets, glass, 25-mL and other convenient sizes for making dilutions.
8. Syringes, 10-, 50-, and 100-μL.

SPECIAL PRECAUTIONS: Chloroacetaldehyde is corrosive to the skin and an eye irritant in low vapor concentrations. In storage, chloroacetaldehyde forms a water-insoluble polymer [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 3 to 16 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the glass wool plug and front section of silica gel to a 50-mL Erlenmeyer flask. Transfer the backup sorbent section to another flask.
6. Pipet 25 mL 50% aqueous methanol into each flask.
7. Shake each flask occasionally over a 30-min period. Analyze samples within 1 day.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 19 μg chloroacetaldehyde per sample.

a. Add known amounts of calibration stock solution to 25-mL volumetric flasks and dilute to the marks with 50% aqueous methanol. Use serial dilution as necessary to prepare lower concentrations.
b. Analyze together with samples and blanks (steps 11 through 13).
c. Prepare calibration graph of μg chloroacetaldehyde/25 mL vs. peak area.

9. Determine desorption efficiency (DE) at least once for each batch of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard the back sorbent section of a media blank sampler.
   b. Inject a known amount of standard ($\leq$ 100 μL) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 through 13).
   e. Prepare a graph of DE vs. μg chloroacetaldehyde recovered.
10. Analyze three quality control blind spikes and five analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacture's recommendations and to conditions given on page 2015-1.
12. Inject 2-μL sample aliquot along with 3 μL of water as solvent flush.
13. Measure peak area.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE), of chloroacetaldehyde found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of chloroacetaldehyde in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 1.8 to 6.4 mg/m^3 at 20 °C and 761 mm Hg using 3-L samples [1]. The concentration of chloroacetaldehyde in the test atmospheres was independently monitored using bubblers containing 15 mL deionized distilled water. Breakthrough from front sorbent sections occurred after sampling for 92 min at 0.2 L/min in an atmosphere containing 5.16 mg/m^3. The relative humidity was 80%. Samples collected at 1X the OSHA standard and stored at room temperature for 1 week lost 8.3% and 5.3% when the relative humidity was 20% and 80%, respectively. No correction for desorption efficiency was needed for loadings at 0.5-, 1-, and 2X the OSHA standard.

Recoveries of samples collected at 80% RH had a positive bias of 3.4%, and samples collected at 20% RH had a negative bias of -4.2%. The overall mean bias was −0.4%.

REFERENCES:

[1] Backup Data Report No. S11 for Chloroacetaldehyde, prepared under NIOSH Contract No. 210-76-0123.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S11, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Williams, R.G., Determination of Chloroacetaldehyde in Air by Differential Pulse Polarography, Anal. Chem., 54(12), 2121-2 (1982).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S11 originally developed under NIOSH Contract 210-76-0123.

APPENDIX: STANDARDIZATION OF CALIBRATION STOCK SOLUTION.

Pipet 10-mL aliquots of the stock solution into two separate 250-mL Erlenmeyer flasks. Add 10 mL 2.5% hydrazine sulfate to one of the flasks and allow to stand 10 minutes with occasional swirling. The other flask serves as a blank and determines any free halide ion already present.

Add 10 mL 0.100 N silver nitrate solution, 5 mL nitric acid solution, and 2 mL ferric ammonium sulfate solution to each flask. Swirl and add 2 mL nitrobenzene. The nitrobenzene forms an oily coating on the particles of precipitated silver chloride and prevents their undesired reaction with the thiocyanate ion.

Titrate contents of each flask with 0.1 N ammonium thiocyanate to a faint orange-brown color that is permanent on shaking. The endpoint color is due to the formation of the $Fe(SCN)_6^{-3}$ ion.

Compute the volumes, V_S, of standard silver solution in excess of that used by the chloride in each flask.

$$V_S = V_T \times \frac{N_T}{N_S}, \text{ mL.}$$

where: V_T = volume, mL, of standard thiocyanate solution titrated
N_T = normality of NH_4SCN solution
N_S = normality of $AgNO_3$ solution

Compute the net volume, V_N, of silver solution required for the precipitation of the chloride liberated from chloroacetaldehyde.

$$V_N = V_S \text{ (blank)} - V_S \text{ (stock)}, \text{ mL}$$

Calculate the concentration, C, of chloroacetaldehyde in calibration stock solution.

$$C = V_N \times N_S \times 7.85, \text{ mg/mL}$$

CHLOROACETIC ACID 2008

$ClCH_2COOH$ MW: 94.50 CAS: 79-11-8 RTECS: AF8575000

METHOD: 2008, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm = 3.87 mg/m^3 @ NTP)

PROPERTIES: solid; MP 61 to 63 °C; BP 189 °C; VP 0.1 kPa (0.75 mm Hg) @ 20 °C; flash point 126 °C; lower explosive limit in air 8% v/v

SYNONYMS: chloroethanoic acid; monochloroacetic acid

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (silica gel, 100 mg/50 mg)	**TECHNIQUE:**	ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION
FLOW RATE:	0.05 to 0.2 L/min	**ANALYTE:**	chloroacetate ion
VOL-MIN:	1 L @ 0.25 ppm	**DESORPTION:**	2 mL deionized water
-MAX:	100 L	**INJECTION LOOP VOLUME:**	500 µL
SHIPMENT:	routine	**ELUENT:**	1.5 mM $NaHCO_3$; 1.0 mL/min
SAMPLE STABILITY:	at least 7 days @ 25 °C; 32 days refrigerated [1]	**COLUMNS:**	Ion Pac AS4A Separator, AG4A Guard, micromembrane suppressor (see OTHER METHODS)
BLANKS:	2 to 10 field blanks per set	**CALIBRATION:**	standard solutions of chloroacetic acid in deionized water
ACCURACY		**RANGE:**	1 to 80 µg per sample [1]
RANGE STUDIED:	0.35 to 29 mg/m^3 [1,2] (3-L samples)	**ESTIMATED LOD:**	0.04 µg per sample [2]
BIAS:	− 2.0%	**PRECISION ($\hat{S}_r$):**	0.016 [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.08 [1]		
ACCURACY:	± 17.7%		

APPLICABILITY: The working range is 0.09 to >85 ppm (0.3 to 30 mg/m^3) for a 3-L air sample.

INTERFERENCES: Chloroacetyl chloride is a positive interferent since it is hydrolyzed to monochloroacetic acid by the measurement procedure and is efficiently collected by silica gel [3]. Particulate salts of the acid are positive interferents. The chromatographic conditions given will separate acetate, chloride, dichloroacetate, fluoride, glycolate, and trichloroacetate ions from chloroacetate ion.

OTHER METHODS: This revises P&CAM 332 [2]. The columns used in P&CAM 332 are no longer available. The newer columns indicated here show improvements in the analytical range and sensitivity.

REAGENTS:

1. Water, filtered, deionized. Specific conductance ≤ 10 μS/cm.
2. Sodium bicarbonate ($NaHCO_3$), reagent grade.
3. Chloroacetic acid, $\geq 99\%$.*
4. Eluent: 1.5 mM $NaHCO_3$. Dissolve 0.504 g $NaHCO_3$ in 4 L filtered, deionized water.
5. Calibration stock solution, 1000 μg/mL. Dissolve 100 mg chloroacetic acid in 100 mL filtered, deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, with plastic caps, containing two sections of 20/40 mesh silica gel (front = 100 mg; back = 50 mg) contained and separated by three silanized glass wool plugs. Pressure drop across the tube at 0.2 L/min is ca. 0.6 kPa (2.6 in. H_2O). Tubes are commercially available (SKC, Inc. 226-47-01, or equivalent).
   NOTE: Chloroacetic acid is irreversibly adsorbed on urethane plugs. Use sorbent tubes with glass wool plugs.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separator and guard column, anion suppressor (page 2008-1), conductivity detector, integrator, and strip chart recorder.
4. Ultrasonic bath.
5. Vials, 20-mL, glass, with aluminum-lined plastic screw caps.
6. Syringes, 3-mL, polyethylene with luer tip.
7. Filter holder, luer tip, 13-mm, with PTFE filter, 5-μm pore size, or PTFE syringe filter.
8. Pipets, 10-μL to 2-mL.
9. Flasks, volumetric, 10- and 100-mL.

SPECIAL PRECAUTIONS: Chloroacetic acid is irritating to skin and mucous membranes [4]. Work with the concentrated material only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 to 0.2 L/min for a total sample size of 1 to 100 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Store samples in the dark. Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate to room temperature.
6. Transfer front sorbent section with front glass wool plug to vial. Place back sorbent section and other two glass wool plugs in separate vial.
7. Add 2.0 mL deionized water to each vial. Cap immediately.
8. Agitate vials in ultrasonic bath for 30 min at room temperature.
9. Draw sample extract through 13-mm PTFE filter with 3-mL syringe.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain chloroacetic acid concentrations in the range 0.02 to 40 μg/mL.
    b. Analyze together with samples and blanks (steps 13 through 15).
    c. Prepare calibration graph [peak height (mm or μS) vs. μg chloroacetic acid per sample].
11. Determine desorption efficiency (DE) for each batch of silica gel used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place silica gel from unused front section in vial.
    b. Inject a known amount (2 to 20 μL) of calibration stock solution, or a serial dilution thereof, onto front sorbent section with a microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 7 through 9) and analyze together with working standards (steps 13 through 15).
    e. Prepare graph of DE vs. μg chloroacetic acid recovered.
12. Analyze three quality control spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 2008-1.
14. Inject sample aliquot manually or use autosampler.
    a. Flush sample loop with 0.5 mL sample extract, then inject 0.5 mL sample.
    b. Rinse sample loop with 1 to 2 mL deionized water between determinations of separate samples.
    NOTE: All samples, eluents, and water flowing through the IC must be filtered to avoid plugging the system valves or columns.
15. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply appropriate dilution factor.

CALCULATIONS:

16. Determine mass, μg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
17. Calculate concentration, C, of chloroacetic acid in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was developed and evaluated by Southern Research Institute [1] using dynamically-generated atmospheres of chloroacetic acid over the concentration range of 0.35 to 29 mg/m^3 at 25 to 27 °C and at relative humidity ≥80%. Average recovery based on 18 samples, six at each of three levels, was 98% representing a negligible bias. Precision at 0.35 mg/m^3 was inhomogeneous with those of higher levels; therefore, precisions were not pooled. Using this poorest precision (S_r = 0.064), the overall precision ($\hat{S}_{rT}$) was estimated to be ≤0.081.

The breakthrough volume of the 100-mg sorbent section was found to be >100 L at 0.2 L/min when sampling chloroacetic acid concentrations of 60 mg/m^3 at 42 °C and RH of 10 and 80% and 35 mg/m^3 at 27 °C and 10 and 90% RH. Samples stored at ambient temperature for 7 days had a mean recovery of 91% and a precision, S_r, of 0.047. Samples refrigerated after day 7, and stored for 32 days exhibited a mean recovery of 100% with a precision, S_r, of 0.085 based on samples analyzed on day 1.

REFERENCES:

[1] Dillon, H. K., D. W. Mason, and K. W. Boyd. Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for Monochloroacetic Acid, NIOSH Contract 210-78-0012, Southern Research Institute, Birmingham, AL (1980).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 322, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] McCullough, P. R. and J. W. Worley. "Sampling of Chloroacetyl Chloride in Air on Solid Support and Determination by Ion Chromatography," Anal. Chem., 51, 1120-1122 (1979).

[4] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

CHLOROBENZENE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

CHLOROBROMOMETHANE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

CHLORODIFLUOROMETHANE
See DICHLORODIFLUOROMETHANE (Method 1018) for procedure

$CHClF_2$ MW: 86.47 CAS: 75-45-6 RTECS: PA6390000

METHOD: 1018, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : no PEL
NIOSH: 1000 ppm; STEL 1250 ppm
ACGIH: 1000 ppm
(1 ppm = 3.54 mg/m^3 @ NTP)

PROPERTIES: gas; BP −40.8 °C; MP −160 °C; nonflammable

SYNONYMS: difluorochloromethane; Refrigerant 22.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400/200 mg and 100/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 1000 ppm
-MAX: 4 L

SHIPMENT: refrigerated

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1800 to 6970 mg/m^3 [3]

BIAS: 0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.074 [3]

ACCURACY: ±14.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: chlorodifluoromethane

DESORPTION: 20 mL methylene chloride

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 260 °C
-COLUMN: 35 °C for 3 min, 15 °C/min to 75 °C, hold 6 min

CARRIER GAS: He, 1.5 mL/min

COLUMN: DB-1 fused silica capillary, 30 m x 0.32-mm ID, 1-µm film thickness or equivalent

CALIBRATION: standard solutions of analyte in methylene chloride

RANGE: 0.1 to 14 mg per sample [3]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION ($\bar{S}_r$): 0.051 @ 0.53-10 mg per sample [3]

APPLICABILITY: The working range is 280 to 4000 ppm chlorodifluoromethane (1000 to 14,000 mg/m^3) for a 1-L air sample. This method was first evaluated for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane with packed column gas chromatography [1]. The method was recently evaluated specifically for chlorodifluoromethane using capillary chromatography [3].

INTERFERENCES: None identified.

OTHER METHODS: This combines and revises Methods S111 and S108 [2].

CHLOROFORM

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

4-CHLORONITROBENZENE

See NITROBENZENES (Method 2005) for procedure

p-CHLOROPHENOL 2014

C_6H_4ClOH MW: 128.56 CAS: 106-48-9 RTECS: SK2800000

METHOD: 2014, Issue 2 **EVALUATION: FULL** **Issue 1: 19 September 1980**
Issue 2: 15 August 1994

OSHA: no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm = 5.26 mg/m^3 @ NTP)

PROPERTIES: crystals; d 1.224 g/mL @ 20 °C; MP 43.2-43.7 °C; BP 220 °C; VP 0.013 kPa (0.1 mm Hg) @ 20 °C; flash point 121 °C (closed cup)

SYNONYMS: 4-chlorophenol; 4-chloro-1-hydroxybenzene

SAMPLING

SAMPLER: SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.05 - 0.2 L/min

VOL-MIN: 1.5 L @ 1 ppm
-MAX: 40 L

SHIPMENT: Routine

SAMPLE STABILITY: 7 days @ 25 °C
at least 29 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.910 to 23.4 mg/m^3 [1] (3-L samples)

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): 0.061 for range studied [1]

ACCURACY: ± 15% (12-28%)

MEASUREMENT

TECHNIQUE: HPLC/UV

ANALYTE: p-chlorophenol

EXTRACTION: 1 mL acetonitrile

INJECTION VOLUME: 100 µL

MOBILE PHASE: 30% acetonitrile, 70% water to 80% acetonitrile/20% water in 20 minutes, 1 mL/min

COLUMN: C18. (5 µm particle size, 4-mm ID by 30-cm long stainless steel)

DETECTOR: UV, 280 nm

CALIBRATION: p-chlorophenol in 30% (v/v) acetonitrile in water

RANGE: 8 to 64 µg/sample [1]

ESTIMATED LOD: 2.5 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 0.15 to 53 ppm (0.8 to 280 mg/m^3) for a 10-L air sample.

INTERFERENCES: None identified. The chromatographic conditions described will separate phenol ; o-chlorophenol; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5- dichlorophenol; o- and p-nitrophenol; 2,4-dimethylphenol; 2,4,5-trichlorophenol; 4-chloro-o-methylphenol; 2,4-dinitrophenol; 4,6-dinitro-2-methylphenol; and pentachlorophenol.

OTHER METHODS: This method replaces P&CAM 337 [2]. The other columns for the analysis of p-chlorophenol have been reported in the literature [3-5].

REAGENTS:

1 p-Chlorophenol 99%.*
2. Acetonitrile, distilled in glass.
3. Hexane, distilled in glass.
4. Water, HPLC quality.
5. p-Chlorophenol stock solution, 20 mg/mL. Dissolve 500 mg p-chlorophenol in 30% (v/v) acetonitrile in water to make 25 mL solution. Stable at least 3 months in airtight container.
6. DE stock solution, 5 mg/mL. Dissolve 125 mg p-chlorophenol in hexane to make 25 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Pyrex tubes, 7 cm long with a 6-mm OD and a 4-mm ID, flame sealed at both ends. Each tube contains two sections of 20/40 mesh silica gel (a 150-mg sorbing section and a 75-mg backup section separated and held in place with glass wool plugs). Tubes are commercially available (SAC, Inc. 226-10 or equivalent.)
2. Personal sampling pump, calibrated, capable of operating 8 hours at 0.05 to 0.2 L/min with flexible connecting tubing.
3. HPLC with UV detector (280 nm), C18 column (Variant MicroPak MCH-5 or equivalent), injector, and electronic integrator.
4. Microliter syringes, various sizes.
5. Volumetric flasks, various sizes.
6. Centrifuge tubes, 12-mL, glass with screw caps.
7. Pipette, 1- and 2-mL, and convenient sizes for making dilutions.
8. Vials, 1-mL, with caps containing PTFE-lined silicone septa.
9. Ultrasonic bath.

SPECIAL PRECAUTIONS: p-Chlorophenol is toxic by skin absorption, inhalation, or ingestion. It also is a strong irritant to tissue and is combustible with a flash point of 121 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break open the ends of the tube to provide openings that are at least 2-mm in diameter. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flowrate between 0.05 and 0.2 L/min for a total sample size of 1 to 40 liters.
4. Cap the tubes, record sample identity and all relevant sample data (duration, ambient temperature and pressure). Pack securely for shipment.
   NOTE: Refrigerate all samples at 0 °C when stored longer than 7 days.

SAMPLE PREPARATION:

5. If refrigerated, allow tube to equilibrate to room temperature.
6. Transfer each section of silica gel in a sorbent tube to a separate 12-mL centrifuge tube. Combine the glass wool plug near the inlet with the front sorbent section. Combine the two urethane foam plugs with the back section.
7. Add 1 mL of acetonitrile, cap, and desorb in an ultrasonic bath for 30 minutes.
8. Add 2 mL of distilled, deionized water to each tube, cap, and mix the solutions.
9. Centrifuge the samples and transfer about 1 mL of the supernatant in each tube to a separate vial and seal with a PTFE-lined septum.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards in the range 2.5 to 64 μg per sample.
    a. Dilute aliquots of p-chlorophenol stock solution with 30% (v/v) acetonitrile in water in volumetric flasks to encompass the range of interest. Prepare fresh daily.
    b. Analyze working standards with samples and blanks steps.
    c. Prepare calibration graph (peak area or peak height vs. μg of p-chlorophenol per sample.
11. Determine desorption efficiency (DE) for each lot of silica gel used for sampling in the calibration range. Prepare three tubes at each of five levels.
    a. Remove backup section. Inject known amounts of DE stock solution (2 to 10 μL) onto the silica gel with a microliter syringe.
    b. Cap the tubes and allow to stand overnight.
    c. Desorb (steps 7 through 9) and analyze together with standards and blanks (steps 13 and 14).
    d. Prepare a graph DE vs. μg p-chlorophenol recovered.
12. Analyze three quality control spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set HPLC according to manufacturer's recommendations and to conditions on page 2014-1. Inject sample aliquot manually or with autosampler.
    NOTE: If peak is above the linear range of the working standards, dilute with 30% (v/v) acetonitrile in water, reanalyze, and apply the appropriate dilution factor.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, μg (corrected for DE), of analyte found on the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
16. Calculate concentration of p-chlorophenol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The overall method was evaluated by collecting 3-L samples of test atmospheres containing p-chlorophenol in the range of 0.91 - 23.4 mg/m^3 at 29 °C and a relative humidity of greater than 80%. The amounts collected ranged from 2.6 - 64 μg per 150-mg bed of silica gel. The breakthrough volume of the sorbent tube was found to be approximately 60 L with a sampling rate of 0.2 L/min at a p-chlorophenol concentration of about 70 mg/m^3, a sampling temperature of 43 °C, and a relative humidity of greater than 80%. Samples of p-chlorophenol on silica gel were found to be stable at 25 °C for 7 days and for 29 days if stored at 0 °C after the seventh day. Silica gel gave an average desorption efficiency of 96% with a $\bar{S}_r$ 2.4% for loadings of 2.54 - 48.0 μg of p-chlorophenol on 150-mg beds of sorbent material.

REFERENCES:

[1] Dillon, H.K., Emory, M.B. Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for p-Chlorophenol. NIOSH Contract 210-78-0012, Southern Research Institute, Birmingham, Alabama (1980).

[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 337, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
[3] Korhonen, I.O. "Separation of Chlorophenol Isomers on Quartz Columns." J. Chromatogr., 303 (1), 197-205 (1980).
[4] Buisson et al., "Determination of Chlorinated Phenols by Capillary GC/ECD." J. Chromatogr. Sci., 22 (8), 399-42 (1984).
[5] Lee, H.B. et al, "Determination of Chlorinated Phenolics in Pulp and Paper Effluents." J. Assoc. of Anal. Chem., 72 (6), 979-984 (1989).

METHOD REVISED BY:

Charles Neumeister, NIOSH/DPSE.

β-CHLOROPRENE 1002

$CH_2=CCICH=CH_2$ MW: 88.54 CAS: 126-99-8 RTECS: EI9625000

METHOD: 1002, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 25 ppm (skin)
NIOSH: C 1 ppm/15 min; carcinogen
ACGIH: 10 ppm (skin)
(1 ppm = 3.62 mg/m^3 @ NTP)

PROPERTIES: liquid; d = 0.958 g/mL @ 20 °C; BP 59.4 °C; MP −130 °C; VP 25 kPa (188 mm Hg; 25% v/v) @ 20 °C; explosive range 4 to 20% v/v in air

SYNONYMS: chloroprene; 2-chloro-1,3-butadiene; chlorobutadiene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 1.5 L @ 25 ppm
-MAX: 8 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 44 to 174 mg/m^3 [2] (3-L samples)

BIAS: − 1.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [2]

ACCURACY: ± 13.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: chloroprene

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 to 2 μL, splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 35 °C, 2 min; 15 °C/min to 300 °C, hold 5 min

CARRIER GAS: N_2 or He, 1-3 mL/min

MAKEUP GAS: nitrogen, 30 ml/min

COLUMN: DB-1 fused capillary, 30 m x 0.25-mm ID, 1.0-μm film [3]

CALIBRATION: solutions of distilled chloroprene in CS_2; hexane reference standard

RANGE: 0.1 to 0.6 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample [2,3]

PRECISION ($\bar{S}_r$): 0.021 [2]

APPLICABILITY: The working range is 10 to 60 ppm (40 to 200 mg/m^3) for a 3-L air sample. The method is sensitive enough to determine concentrations as low as 12 ppm in 15-min samples taken at 0.2 L/min. NIOSH has sampled for chloroprene at two polychloroprene processing plants.

INTERFERENCES: None known.

OTHER METHODS: This is Method S112 with improved GC column in a new format [4]. A similar method appears in the chloroprene criteria document [1].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Chloroprene*, freshly distilled from xylene solution at reduced pressure; BP = 31 °C at 354 mm Hg (47 kPa).
3. n-Pentane, reagent grade.
4. n-Hexane, reagent grade.
5. Calibration stock solution, 47.9 mg/mL. Deliver 0.500 mL (0.479 g at 20 °C) freshly distilled chloroprene from a delivery pipet under the surface of pentane in a partially filled 10-mL volumetric flask. Dilute to the mark with pentane. Stable one day at −15 °C.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1002-1).
4. Micro-distillation apparatus for vacuum distillation of chloroprene.
5. Vials, 2-mL, glass with PTFE-lined septa and crimp seals.
6. Syringe, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, graduated in 0.1 mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable. Work with it only in a hood.

Chloroprene incompatibilities by contact with oxidizers (e.g., peroxides) may cause polymerization with evolution of heat and rupture of containers. Chloroprene attacks some plastics, rubber, and coatings. It will autoxidize very rapidly, even at 0 °C, producing an unstable peroxide (mixed 1,2- and 1,4-addition copolymer with oxygen) which catalyzes exothermic polymerization. Therefore, immediately after distilling, store at −15 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 1.5 to 8 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation. Decant the liquid into a clean vial.

NOTE 1: Desorbed samples are unstable in the presence of charcoal, losing significant amounts over several hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.03 to 0.5 mg chloroprene per sample.
   a. Add known amounts of calibration stock solution below the surface of CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg chloroprene).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg chloroprene recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1002-1. Inject sample aliquot either with autosampler or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of chloroprene found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of chloroprene in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S112 was issued on October 29, 1976, and validated over the range 44 to 175 mg/m^3 with eighteen 3-L samples from dynamically-generated test atmospheres, as well as a set of six samples at one times the OSHA standard concentration stored at room temperature for eight days to establish stability [2,5]. Eighteen more samples were spiked (six each at one-half, one and two times the OSHA standard, 0.14 to 0.54 mg) directly. The pooled precision ($\bar{S}_r$) for these three sets of analytical samples was 0.021. The average recovery for all three concentrations was 98.8%, representing a non-significant bias. The value for the taken concentration was obtained by monitoring during generation with a gas chromatograph with a 2-mL sampling loop. Bag standards were used to calibrate the gas chromatograph. The stored samples results were within 1% of samples analyzed after one day, indicating adequate storage stability for eight days. Six parallel breakthrough tubes were run at a time. The generated atmosphere was pulled through the charcoal tubes (critical orifices to control flow).

Several breakthrough studies were done. With 94% relative humidity, breakthrough occurred at 30 min when sampling 0.194 L/min of 195 mg/m^3 (5.8 L). With 91% relative humidity, no breakthrough occurred after 240 min when sampling 0.045 L/min of 197 mg/m^3 (10.8 L).

REFERENCES:

[1] Criteria for a Recommended Standard-Occupational Exposure to Chloroprene, Appendices I and III, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-210 (1977).
[2] NIOSH Backup Data Report, S112, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712 from NTIS, Springfield, VA 22161.
[3] Grote, A. Sequence 7239 and 7316 Reports, DPSE/MRSB internal reports (unpublished) (1991).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S112, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Y. T. Gagnon, NIOSH/DPSE; S112 originally validated in NIOSH Contract 210-76-0123.

CHROMIUM and compounds, as Cr 7024

Cr MW: 52.00 (Cr) CAS: 7440-47-3 (Cr metal)
22541-79-3 [Cr(II)]
16065-83-1 [Cr(III)]
RTECS: (Cr) GB4200000
Cr(II) GB6260000
Cr(III) GB6261000

METHOD: 7024, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1.0 mg/m^3 (metal);
0.5 mg/m^3 [Cr(II), Cr(III)]
NIOSH: 0.5 mg/m^3 [Cr metal, Cr(II), Cr(III)]
ACGIH: 0.5 mg/m^3 [Cr metal, Cr(II), and Cr(III)]; see Method 7600 for Cr(VI)

PROPERTIES: metal; d 7.14 g/cm^3; MP 1890 °C; valences +1 to +6 in salts

SYNONYMS: vary depending on the compound

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 0.5 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.4 to 1.8 mg/m^3 (insoluble)
0.3 to 1 mg/m^3 (soluble) [1]
(90-L samples)

BIAS: -- 0.64%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 (insoluble) [1]
0.085 (soluble [1]

ACCURACY: ± 20.91%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: chromium

ASHING: conc. HCl, 9 mL; 140 °C
conc. HNO_3, 9 mL; 400 °C

FINAL SOLUTION: 5% HNO_3, 20 mL

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 357.9 nm

CALIBRATION: standard solutions of Cr in 5% HNO_3

RANGE: 5 to 250 μg per sample [2,3]

ESTIMATED LOD: 0.06 μg per sample [4]

PRECISION ($\hat{S}_r$): 0.04 to 0.06 [5]

APPLICABILITY: The working range is 0.05 to 2.5 mg/m^3 for a 100-L air sample. This is an elemental analysis for total Cr, not compound specific. Some compounds of Cr may not be dissolved by this method. Aliquots can be analyzed separately for approximately four additional metals.

INTERFERENCES: Interferences from iron and nickel are minimized by using a high temperature flame (reducing nitrous oxide-acetylene or oxidizing air-acetylene).

OTHER METHODS: This method combines and replaces P&CAM 173 [4], P&CAM 152 [5], S323 [2], and S352 [3]. Method 7300 (Elements by ICP-AES) is an alternate analytical method. Hexavalent chromium, sampled on PVC filters, may be determined colorimetrically by Method 7600 or Method 7604.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Nitric acid, 5%. Add 50 mL conc. HNO_3 to water; dilute to 1 L.
4. Calibration stock solution, 1000 μg/mL Cr. Dissolve 3.735 g K_2CrO_4 or 2.829 g $K_2Cr_2O_7$ in distilled or deionized water to make 1 L solution.
5. Distilled or deionized water.
6. Nitrous oxide.
7. Acetylene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and chromium hollow cathode lamp.
4. Regulators, two-stage, for nitrous oxide and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Graduated centrifuge tubes, 15-mL.*
8. Assorted volumetric pipets, as needed.*
9. Hotplate, surface temperature to 140 °C.

* Clean all glassware with nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 10 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [2,3]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be necessary for some samples, especially if several metals are to be determined on a single filter.

3. Open the cassettes and filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HCl, cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HCl.
   NOTE: Start reagent blanks at this step.
5. Add 3 mL conc. HNO_3, cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HNO_3.
6. Cool solution and dissolve the residues in 1 mL conc. HNO_3.
7. Transfer the solution quantitatively to a 15-mL graduated centrifuge tube.
8. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate with at least six working standards. Add known amounts of calibration stock solution, covering the range 0 to 1000 μg Cr (0 to 200 μg Cr per sample) to 100-mL volumetric flasks and dilute to volume with 5% HNO_3.
10. Analyze the working standards together with the blanks and samples (steps 15 and 16).
11. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
12. Aspirate a standard for every 10 samples to check instrument drift.
13. Check analytical recoveries with at least one spiked media blank per 10 samples.
14. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

15. Set spectrophotometer as recommended by the manufacturer and to conditions on page 7024-1.
    NOTE: Air-acetylene flame may also be used. In a fuel-lean air-C_2H_2 or reducing (fuel-rich) N_2O-C_2H_2 flame, interference by Fe or Ni is minimized or eliminated, but sensitivity for Cr is reduced. A reducing air-C_2H_2 flame provides the best sensitivity, but the greatest susceptibility to interference [5].
16. Aspirate standards and samples. Record absorbance readings
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Using the measured absorbances, calculate the corresponding solution concentrations (μg/mL) of chromium in the sample, C_s, and average media blank, C_b, from the calibration graph.
18. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of chromium, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Lab testing with spiked filters and generated atmospheres of soluble chromium (potassium dichromate) was done at one-half, one and two times the OSHA standard for chromium compounds other than Cr(VI) of 0.5 mg/m^3. The range studied was 0.28 to 0.95 mg/m^3. The precision was 0.082 and a bias was not observed [1,2].

Lab testing with spiked filters and generated atmospheres of insoluble chromium, (produced from thermal decomposition of chromium hexacarbonyl) was done at one-half, one and two times the OSHA standard for chromium metal of 1.0 mg/m^3 [1,3]. Collection efficiency was 1.00 and analytical recoveries averaged 98% in the range 45 to 190 μg Cr per sample.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S323, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[3] Ibid, S352.
[4] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[5] Analytical Methods for Atomic Aborption Spectrophotometry, Perkin-Elmer (1976).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; Methods S323 and S352 developed under NIOSH Contract CDC-99-74-45.

CHROMIUM, HEXAVALENT

Cr(VI) MW: 52.00 (Cr); 99.99 (CrO_3) CAS: 18540-29-9 RTECS: GB6262000

METHOD: 7600, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3 (as CrO_3)
NIOSH: 0.001 mg/m^3/10 h; carcinogen
ACGIH: 0.050 mg/m^3 (as Cr, soluble); some insoluble chromates are human carcinogens

PROPERTIES: oxidizing agent

SYNONYMS: vary depending upon the compound

SAMPLING

SAMPLER:	FILTER (5.0-μm PVC membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	8 L @ 0.025 mg/m^3
-MAX:	400 L
SHIPMENT:	routine
SAMPLE STABILITY:	analyze within 2 weeks [1]
FIELD BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.05 to 0.2 mg/m^3 [2] (22-L samples)
BIAS:	− 5.48%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.084 [2]
ACCURACY:	± 18.58%

MEASUREMENT

TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
ANALYTE:	CrO_4^{2-}-diphenylcarbazide complex
EXTRACTION SOLUTION:	0.5 N H_2SO_4 or 2% NaOH-3% Na_2CO_3 (see steps 4 and 5)
WAVELENGTH:	540 nm; 5-cm path length
CALIBRATION:	standard solutions of K_2CrO_4 in 0.5 N H_2SO_4
RANGE:	0.2 to 7 μg per sample
ESTIMATED LOD:	0.05 μg per sample
PRECISION ($\bar{S}_r$):	0.029 @ 0.3 to 1.2 μg per sample [3]

APPLICABILITY: The working range is 0.001 to 5 mg/m^3 for a 200-L air sample. This method may be used for the determination of soluble Cr(VI) (using 0.5 N H_2SO_4 as extraction solution or insoluble Cr(VI) (using 2% NaOH - 3% Na_2CO_3) [3].

INTERFERENCES: Possible interferences are iron, copper, nickel, and vanadium; 10 μg of any of these causes an absorbance equivalent to about 0.02 μg Cr(VI) due to formation of colored complexes. Interference due to reducing agents (e.g., Fe, Fe^{++}) is minimized by alkaline extraction (step 5).

OTHER METHODS: This method combines and replaces P&CAM 169 [1], S317 [2] and P&CAM 319 [3]; the Cr(VI) criteria document [4] contains a method similar to P&CAM 169. Method 7604 is also specific for hexavalent chromium, using ion chromatography for measurement.

REAGENTS:

1. Sulfuric acid, conc. (98% w/w).
2. Sulfuric acid, 6 N. Add 167 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
3. Sulfuric acid, 0.5 N. Add 14.0 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
4. Sodium carbonate, anhydrous.
5. Sodium hydroxide.
6. Potassium chromate.
7. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 mL acetone and 100 mL water.
8. Cr(VI) standard, 1000 μg/mL. Dissolve 3.735 g K_2CrO_4 in deionized water to make 1 L, or use commercially available solution.*
9. Calibration stock solution, 10 μg/mL. Dilute 1000 μg/mL Cr(VI) standard 1:100 with deionized water.
10. Filter extraction solution, 2% NaOH-3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
11. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-μm pore size, 37-mm diameter in polystyrene cassette filter holder (FWSB [MSA] or VM-1 [Gelman] or equivalent).
   NOTE: Some PVC filters promote reduction of Cr(VI). Check each lot of filters for recovery of Cr(VI) standard.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Vials, scintillation, 20-mL glass, PTFE-lined screw cap.**
4. Forceps, plastic.
5. Spectrophotometer, UV-visible (540 nm), with cuvettes, 5-cm path length.
6. Filtration apparatus, vacuum.**
7. Beakers, borosilicate, 50-mL.**
8. Watchglass.**
9. Volumetric flasks, 25-, 100- and 1000-mL.**
10. Hotplate, 120 to 400 °C.
11. Micropipettes, 10-μL to 1-mL.
12. Centrifuge tubes, 40-mL, graduated, with plastic stoppers.**
13. Buchner funnel.**
14. Pipettes, TD 5 mL.**

** Clean all glassware with 1:1 HNO_3 and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [4]. All sample preparation should be performed in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 8 to 400 L. Do not exceed 1 mg total dust loading on the filter.
3. Remove the filter from the cassette within 1 h of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

NOTE: There are two sample preparation techniques outlined below. For soluble chromates or chromic acid, follow step 4; for insoluble chromate or Cr(VI) in the presence of Fe, Fe^{2+} or other reducing agents, follow step 5.

4. Sample preparation for soluble chromates and chromic acid.
   a. Remove the blank and sample filters from the vials, then fold and place them into centrifuge tubes.
   b. Add 6 to 7 mL 0.5 N H_2SO_4 to each tube, cap, and shake to wash all surfaces of the filter. Allow filter to remain in tube 5 to 10 min [6].
   c. Remove the filter from the tube with plastic forceps, carefully washing all surfaces with an

additional 1 to 2 mL 0.5 N H_2SO_4. Discard the filters. Start reagent blanks at this point.

d. Filter the solution through a moistened PVC filter in a Buchner funnel to remove interferences from suspended dust. Collect the filtrate in a clean centrifuge tube. Rinse the bottle, which contained the filter, with 2 to 3 mL 0.5 N H_2SO_4 and pour into the funnel. Rinse the funnel and filter with 5 to 8 mL 0.5 N H_2SO_4.

e. Add 0.5 mL diphenylcarbazide solution to each centrifuge tube. Bring the total volume in each centrifuge tube to 25 mL with 0.5 N H_2SO_4. Shake to mix and allow color to develop (at least 2 min but no longer than 40 min. [6]). Transfer the solution to a clean 5-cm cuvette and analyze within 40 min of mixing (steps 9 through 11).

5. Sample preparation for insoluble chromates and for Cr(VI) in the presence of iron or other reducing agents:

NOTE: If significant amounts of Cr(III) are expected to be present, degas the sample solution by bubbling nitrogen through it for 5 min. before proceeding and purge the headspace above the solution during step 5.a.

a. Remove the PVC filter from the bottle, place it in a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH/3% Na_2CO_3. Start reagent blanks at this point. Purge the headspace above the solution with nitrogen throughout the extraction process to avoid oxidation of any Cr(III). Cover the beaker with a watchglass and heat it to near the boiling point on a hotplate with occasional swirling for 30 to 45 min. Do not boil the solution or heat longer than 45 min. Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost owing to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

b. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask, keeping the total volume about 20 mL.

NOTE: If the solution is cloudy, filter it through a PVC filter in a vacuum filtration apparatus using distilled water rinses.

c. Add 1.90 mL 6 N sulfuric acid to the volumetric flask and swirl to mix.

CAUTION: CARBON DIOXIDE WILL BE EVOLVED CAUSING INCREASED PRESSURE IN THE FLASK. LET THE SOLUTION STAND FOR SEVERAL MINUTES UNTIL VIGOROUS GAS EVOLUTION CEASES.

d. Add 0.5 mL diphenylcarbazide solution, dilute to the mark with distilled water and invert several times to mix thoroughly. Pour out about one-half of the contents of the flask, stopper the flask and shake it vigorously several times, removing the stopper each time to relieve pressure.

NOTE: This step releases bubbles of carbon dioxide which otherwise would cause high and erratic readings.

e. Transfer an aliquot of the solution remaining in the flask to a 5-cm cuvette and analyze (steps 9 through 11).

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards. Transfer 6 to 7 mL 0.5 N H_2SO_4 to each of a series of 25-mL volumetric flasks. Pipet 0 to 0.7 mL of 10 μg/mL calibration stock solution into the volumetric flasks. Add 0.5 mL diphenylcarbazide solution to each and sufficient 0.5 N H_2SO_4 to bring the volume to 25 mL. These working standards contain 0 to 7 μg Cr(VI).
7. Analyze the working standards together with blanks and samples (steps 9 through 11).
8. Prepare a calibration graph [absorbance vs. μg Cr(VI)].

MEASUREMENT:

9. Set wavelength on the spectrophotometer to 540 nm.
10. Set to zero using a 0.5 N H_2SO_4 reagent blank.
11. Transfer sample solution to a cuvette and record the absorbance.

NOTE 1: A sample containing 1.5 μg Cr(VI)/25 mL gives ca. 0.2 absorbance.

NOTE 2: If the absorbance values for the samples are higher than the standards, dilute using 0.5 N H_2SO_4, repeat this step, and multiply the resulting absorbance by the appropriate dilution factor.

CALCULATIONS:

12. From the calibration graph, determine the mass of Cr(VI) in each sample, W (μg), and in the average blank, B (μg).
13. Calculate the concentration, C (mg/m^3), of Cr(VI) in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 169 and S317 are essentially the same method and are suitable for soluble chromate and chromic acid. Method S317 was validated with generated samples of chromic acid mist [2,6], and P&CAM 169 was tested with field samples [1,7]. P&CAM 319 was developed because a method was needed to analyze for insoluble chromates [3]. This method was tested with insoluble chromates in matrices such as paints, primer and ceramic powders [3].

Precision, analytical range, recovery data, etc., for the three methods pooled are as follows:

Total $\hat{S}_{rT}$:	0.084
Measurement $\bar{S}_r$ [1-3]:	0.02 to 0.04
Range [3]:	0.5 to 10 μg/m^3
Collection Efficiency [5]:	94.5%
Sampling Rate [1,3]:	1.5 to 2.5 L/min
Stability (two weeks) [1]:	96% recovery
Acceptable Filters [3]:	FWSB (MSA); VM-1 (Gelman).

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Ibid, V. 3, S317, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Ibid, V. 6, P&CAM 319, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH (1975) Criteria for a Recommended Standard: Occupational Exposure to Chromium (VI). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 76-129.
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. Occupational Health Guidelines for Chromic Acid and Chromates. U.S. Department of Health and Human Services (NIOSH) Publication No. 81-123 (1981).
[6] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[7] Abell, M. T. and J. R. Carlberg. A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium, Am. Ind. Hyg. Assoc. J., 35, 229 (1974).

METHOD REVISED BY:

Martin T. Abell, NIOSH/DPSE; Method S317 validated under NIOSH Contract CDC-99-74-45.

CHROMIUM, HEXAVALENT 7604

Cr (VI) MW: 52.00 (Cr); 99.99 (CrO_3) CAS: 18540-29-9 RTECS: GB6262000

METHOD: 7604, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3 (as CrO_3)
NIOSH: 0.001 mg/m^3/10 h; carcinogen
ACGIH: 0.050 mg/m^3 (as Cr, soluble); some insoluble chromates are human carcinogens

PROPERTIES: oxidizing agent

SYNONYMS: vary according to the compound.

SAMPLING

SAMPLER:	FILTER (5.0-μm PVC membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	100 L @ 0.1 mg/m^3
-MAX:	1000 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 2 weeks at 25 °C
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.05 to 0.15 μg/m^3 (400-L samples)
BIAS:	+ 0.08%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.066 [1]
ACCURACY:	± 13.0%

MEASUREMENT

TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION
ANALYTE:	chromate ion
EXTRACTION:	5 mL 2% NaOH/3% Na_2CO_3
INJECTION VOLUME:	50 μL
ELUENT:	7.0 mM Na_2CO_3/0.5 mM NaOH, 2.0 mL/min
COLUMN:	Dionex HPIC-AG5 guard, HPIC-AS5 separator, and anion suppressor, or equivalent
DETECTOR:	1 μS full scale
CALIBRATION:	standard solutions of Cr(VI) in 0.4% NaOH/0.6% Na_2CO_3
RANGE:	10 to 250 μg per sample [1]
ESTIMATED LOD:	3.5 μg per sample [1]
PRECISION ($\hat{S}_r$):	0.043 @ 22 to 62 μg per sample [1]

APPLICABILITY: The working range is 0.01 to 4 mg/m^3 for a 500-L air sample. This method is less sensitive than method 7600 (colorimetric), but it contains fewer sample preparation steps and was found free from interferences when used for samples of five chromate-containing paints. This method may be used for the determination of insoluble or soluble Cr(VI).

INTERFERENCES: Interferences from reducing agents (e.g., Fe, Fe^{++}) are eliminated by alkaline extraction. Cations of metals, interfering with the colorimetric method, do not interfere with this method. Inadequately-cleaned glassware may create a negative bias.

OTHER METHODS: This method is an alternative to NIOSH Method 7600 (colorimetric).

REAGENTS:

1. Sodium carbonate, anhydrous.
2. Sodium hydroxide, reagent grade.
3. Extraction solution, 2% NaOH/3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
4. Eluent, 7.0 mM Na_2CO_3-0.5 mM NaOH. Dissolve 2.97 g Na_2CO_3 in 4 L deionized water. Add 20 mL of 0.1 M NaOH (8 g/L).
5. Suppressor regenerant, 0.025 N H_2SO_4. Dilute 2.8 mL of conc. H_2SO_4 in deionized water to 4 L.
6. Cr(VI) standard, 1000 μg/mL.
7. Calibration stock solution, 100 μg/mL. Dilute 1000 μg/mL Cr(VI) standard 1:100 with distilled or deionized water.
8. Nitrogen, purified.
9. Water, distilled or deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-μm pore size, 37-mm diameter (FWSB [MSA] or VM-1 [Gelman], or equivalent) with backup pad in polystyrene cassette filter holder.
   NOTE: Some PVC filters promote reduction of Cr(VI). Check each lot of filters for recovery of Cr(VI) standard.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ion chromatograph, with conductivity detector, columns, suppressor (p. 7604-1).
4. Vials, scintillation 20-mL glass, PTFE-lined screw cap.
5. Forceps, plastic.
6. Syringe, 10-mL, with in-line membrane filter 0.45-μm pore size.
7. Beakers, borosilicate, 50-mL.
8. Watchglasses.
9. Volumetric, flasks, 25-, 100-, and 1000-mL.
10. Hotplate, 120 to 400 °C.
11. Micropipette, 20-μL, and other sizes.
12. Centrifuge tubes, 40-mL, graduated, with plastic, screw caps.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [2]. All sample preparation should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 100 to 1000 L. Do not exceed 2 mg of particulate loading on the filter.
3. Remove the filter from the cassette within 1 hour of completion of sampling, and place it in a vial to be shipped to the laboratory. Handle the filters only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

4. Place the filter face down in a 50-mL beaker, and add 5.0 mL extraction solution. Start reagent blanks at this point.
   NOTE 1: If significant amounts of Cr(III) are expected to be present, degas the extraction solution by bubbling a slow stream of nitrogen through it for 5 min before proceeding and purge the headspace above the solution with nitrogen during this step.
   NOTE 2: If only soluble chromates are of interest use distilled water in place of extraction solution.
5. Cover the beaker with a watchglass and place on a hotplate preheated to 135 °C. Heat the samples for 45 min with occasional swirling.
   NOTE 1: Do not allow the solution to boil or evaporate to dryness. Hexavalent chromium may be lost by reaction with the PVC filter, as indicated by a brown coloring in the filter.
   NOTE 2: Longer heating times, up to 90 min. may be necessary for some samples (e.g., paint spray [1]).

6. Cool the solution and transfer it quantitatively with distilled water rinses to a graduated centrifuge tube. Adjust the final volume to 25 mL with distilled water.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range of 0 to 250 μg Cr (VI) per sample.
   a. Pipet 0 to 2.5 mL calibration stock solution into each of a series of 25-mL volumetric flasks. Add 5 mL extraction solution to each flask and dilute to the mark with deionized water.
   b. Analyze the working standards (steps 8 through 10).
   c. Prepare a calibration graph [peak height vs. μg Cr(VI) per sample].

MEASUREMENT:

8. Set ion chromatograph according to manufacturer's recommendations and to conditions on page 7604-1. Set regenerant flow to 3 mL/min.
9. Inject 50 μL sample aliquot manually or with autosampler.
   NOTE: All samples and standards must be filtered before injection to avoid plugging columns and lines.
10. Measure peak height. (Retention time for Cr(VI) peak is approximately 12 min under these conditions.)

CALCULATIONS:

11. From the calibration graph, determine the mass of Cr(VI) in each sample, W (μg), and in the average blank, B (μg).
12. Calculate the concentration, C (mg/m^3), of Cr(VI) in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated with three sets of 16 filter samples which were collected from a chromate-containing paint aerosol [2]. The average amount of Cr(VI) on the filter ranged from 24 to 62 micrograms. Half of the samples were analyzed by this method while the other half were analyzed by Method 7300 (ICP). The results were not significantly different at the 95% confidence level. To examine sample stability, selected members of a fourth set of filters were analyzed and the remainder were stored for two weeks under cover in a constant temperature and constant humidity environment. Comparison of the results of analysis before and after storage indicated that the amount of Cr(VI) did not change during this period.

REFERENCES:

[1] Molina, D. and M. T. Abell. An Ion Chromatographic Method for Insoluble Chromium in Paint Aerosol. Am. Ind. Hyg. Assoc. J. 48:830-835 (1987).
[2] NIOSH Testimony on the OSHA Proposal Rules on Air Contaminants, Docket #H-020, August 1, 1988.

METHOD REVISED BY:

Martin T. Abell, NIOSH/DPSE.

COBALT and compounds, as Co 7027

Co MW: 58.93 (Co) CAS: 7440-48-4 (Co) RTECS: GF8750000

METHOD: 7027, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.01 mg/m^3
NIOSH: 0.05 mg/m^3
ACGIH: 0.05 mg/m^3 (fume, dust)

PROPERTIES: magnetic, hard metal; valence +2, +3; MP 1495 °C; VP not significant

SYNONYMS: vary depending upon the compound

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.1 mg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.03 to 0.26 mg/m^3 [1] (270-L samples)

BIAS: 5.59%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.070 [1]

ACCURACY: ± 18.05%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: cobalt

ASHING: aqua regia, 3 mL, 140 °C; conc. HNO_3, 6 mL, 140 °C; room temperature, 30 min; 140 °C to near dryness

FINAL SOLUTION: 5% HNO_3, 10 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 240.7 nm

BACKGROUND CORRECTION: D_2 or H_2 lamp

CALIBRATION: Co^{2+} in 5% HNO_3

RANGE: 3 to 90 μg per sample [2]

ESTIMATED LOD: 0.6 μg per sample [3]

PRECISION ($\bar{S}_r$): 0.03 [1]; 0.02 [3]

APPLICABILITY: The working range is 0.01 to 0.3 mg/m^3 for a 300-L sample. This is an elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure. Aliquots of the samples can be analyzed separately for approximately four additional metals.

INTERFERENCES: The use of D_2 or H_2 continuum background correction is required to control molecular or flame absorption. There are no known spectral line interferences.

OTHER METHODS: This method combines and replaces P&CAM 173 [4] and S203 [2] for cobalt. Method 7300 (Elements by ICP-AES) is an alternate analytical technique.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Aqua regia: mix 3 volumes conc. HCl with 1 volume conc. HNO_3.
4. Nitric acid, 5% (w/v). Add 50 mL conc. HNO_3 to water; dilute to 1 L.
5. Calibration stock solution, 1000 μg/mL Co. Commercially available or dissolve 1.000 g Co metal in minimum volume of aqua regia. Dilute to 1 L with 5% HNO_3.
6. Distilled or deionized water.
7. Air, filtered.
8. Acetylene.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and cobalt hollow cathode lamp.
4. Regulators, two-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Micropipets, 5 to 60 μL.*
8. Hotplate, surface temperature 140 °C.

* Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 30 to 1500 L. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be necessary for some samples, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL aqua regia, cover with a watchglass, let stand at room temperature 30 min. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until most of the acid has evaporated (ca. 0.5 mL remains).
6. Repeat 2 more times using 3 mL conc. HNO_3 each time. Leave about 1 mL solution after the last digestion.
7. Cool each beaker, remove watchglass, and rinse into the beaker with 5% HNO_3.
8. Dissolve the residues in 2 to 3 mL 5% HNO_3.
9. Transfer the solution quantitatively to a 10-mL volumetric flask.
10. Dilute to volume with 5% HNO_3.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards. Add known amounts, covering the expected range of samples (0 to 60 μg Co per sample), of calibration stock solution to 10-mL volumetric flasks and dilute to volume with 5% HNO_3.

12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (mg/mL).
14. Aspirate a standard for every 10 samples to check instrument drift.
15. Check recoveries with at least one spiked media blank per 10 samples.
16. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to the manufacturer's recommendations and to the conditions on page 7027-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of cobalt in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of cobalt in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S203 [2] was issued on February 18, 1977, and validated over the range 0.03 to 0.22 mg/m^3 Co fume and 0.04 to 0.26 mg/m^3 Co dust using spiked filters and generated atmospheres of cobalt dust and fume (Co_2O_3) [1]. Precision and accuracy data are given on page 7027-1. A separate check on this method showed 98% recovery from filters spiked with 12 or 96 μg soluble Co [3].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, Method S203, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] User check, UBTL, NIOSH Seq. #3990-N (unpublished, November 29, 1983).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S203 originally validated under NIOSH Contract CDC-99-74-45.

COPPER (dust and fume) 7029

Cu MW: 63.54 CAS: 7440-50-8 (Cu) RTECS: GL5325000

METHOD: 7029, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 0.1 mg/m^3 (fume); 1 mg/m^3 (dust)
NIOSH: 0.1 mg/m^3 (fume); 1 mg/m^3 (dust)
ACGIH: 0.2 mg/m^3 (fume); 1 mg/m^3 (dust, mist)

PROPERTIES: soft metal; valence +1, +2 in salts; MP 1083 °C

SYNONYMS: vary depending upon the compound; CAS #1317-39-1 (Cu_2O), CAS #1317-38-0 (CuO)

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L @ 0.1 mg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.05 to 0.59 mg/m^3 (fume) [1,2]
0.47 to 1.8 mg/m^3 (dust) [3]

BIAS: − 0.44%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.044 (fume) [1,2]
0.051 (dust)[3]

ACCURACY: ± 11.0%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: copper

ASHING: conc. HNO_3, 6 mL, 140 °C;
conc. HCl, 6 mL, 400 °C

FINAL SOLUTION: 0.5 N HCl; 25 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 324.7 nm

BACKGROUND CORRECTION: not required

CALIBRATION: standard solutions of Cu^{2+} in 0.5 N HCl

RANGE: 5 to 125 μg per sample [4]

ESTIMATED LOD: 0.05 μg per sample [5]

PRECISION ($\bar{S}_r$): 0.03 [1,3,5]

APPLICABILITY: The working range is 0.05 to 1.3 mg/m^3 for a 100-L air sample. This is an elemental analysis, applicable to either dust or fume, with an additional separation step to quantitate soluble copper dust (e.g., $CuSO_4$) in the presence of copper fume. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is not required. Interferences to the fume/soluble dust separation step include insoluble copper compounds and copper compounds such as copper acetate which form insoluble hydroxides when dissolved in water.

OTHER METHODS: This method combines and replaces P&CAM 173 [5], S354 [4], and S186 [6]. Method 7300, plasma emission (ICP-AES), is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water, dilute to 1 L.
4. Calibration stock solution, 1000 μg/mL. Commercially available, or dissolve 1.000 g Cu metal in minimum volume of (1:1) HNO_3. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37 mm-diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and copper hollow cathode lamp and two-stage regulators for air and acetylene.
4. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
5. Volumetric flasks, 25-mL.*
6. Assorted volumetric pipets, as needed.*
7. Hotplate, surface temperature 140 °C and 400 °C.
8. Equipment for fume/dust separation step:
   a. cellulose ester membrane filters, 47-mm, 0.3-μm pore size (Millipore PHWP or equivalent);
   b. cellulose ester membrane filter, 47-mm, 5-μm pore size (Millipore SMWP or equivalent);
   c. filtration apparatus (Gelman No. 1107 or equivalent).

* Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 50 to 1500 L. Do not exceed a total filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Other quantitative ashing techniques (e.g., HNO_3-$HClO_4$ [Method 7300]) may be useful alternatives, especially if several metals are to be determined on a single filter.

3. Proceed to step 4 if fume/dust separation is not desired. For fume/dust separation:
   a. Using forceps, prewet a 47-mm, 0.3-μm pore size cellulose ester membrane filter by placing it on the surface of distilled water. Remove the filter, tap off excess water, and mount it on the filtration unit.
   b. Transfer the sample filter from the cassette filter holder to the filtration unit, placing it concentrically on top of the 47-mm filter with the fume deposit up.

c. Apply and release the vacuum so that the 37-mm filter is gently wetted from the moisture retained on the 47-mm filter. This also insures the removal of any air bubbles between the filters.
d. When the fume sample is visually clear of air bubbles and wet throughout, apply a vacuum of 10 to 15 PSIG (69 to 103 kPa). Release the vacuum.
e. Place a 47-mm, 5-μm cellulose ester membrane filter on the surface of water to wet it, remove excess water by blotting with tissue, and place it concentrically on top of the 37-mm filter. Press the surface of the top filter with a clean tissue to insure that no air bubbles remain between any of the filters.
f. Mount the upper part of the filtration unit, add 5 mL of distilled water, and allow vacuum to draw water through the filters. Repeat with 5 mL more water. Combine the filtrates which contain soluble copper compounds in a clean beaker. Start reagent blanks at this point.
g. Transfer all filters to a clean beaker. Proceed to step 5.
NOTE: Each sample blank is a combination of three filters.

4. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
5. Add 6 mL conc. HNO_3. Cover with a watchglass and heat on hotplate (140 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HNO_3 each time.
NOTE: Start reagent blanks at this point if step 3 was omitted.
6. Add 2 mL conc. HCl, cover with a watchglass, heat on hotplate (400 °C) until the volume is reduced to approximately 0.5 mL. Repeat two more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
7. Cool solution and add 10 mL distilled water.
8. Transfer the solution quantitatively to a 25-mL volumetric flask. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards. Add known amounts, covering the range 0 to 125 μg Cu per sample, of calibration stock solution to 25-mL volumetric flasks and dilute to volume with 0.5 N HCl.
10. Analyze the working standards together with the blanks and samples (steps 15 and 16).
11. Prepare a calibration graph by plotting absorbance versus solution concentration (μg/mL).
12. Aspirate a standard for every 10 samples to check instrument drift.
13. Check analytical recoveries with at least one spiked media blank per 10 samples.
14. Use method of additions occasionally to check for interferences.

MEASUREMENT:

15. Set spectrophotometer as specified by the manufacturer and to conditions on page 7029-1.
16. Aspirate standards, samples, and blanks. Record absorbance readings.
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the sample solutions with 0.5 N HCl, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of copper in the sample, C_s, and average media blank, C_b, from the calibration graph.
18. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of copper in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S186 was validated on August 29, 1975, with overall sampling and analytical precision, $\hat{S}_{rT}$ = 0.051, over the range 0.47 to 1.8 mg/m^3 for a 90-L sample of CuO dust [3,6] and Method S354 was validated on September 30, 1977, with overall sampling and analytical precision, $\hat{S}_{rT}$ = 0.058, over the range 0.05 to 0.37 mg/m^3 for a 480-L sample of Cu fume [1,4]. Copper fume atmospheres were generated by thermal decomposition and subsequent oxidation of cupric acetate aerosol. The size of the copper fume was 0.04 to 0.14 μm by electron microscopy and the collection efficiency of the sampler for this fume was 1.00 [1,4,9].

The dust-fume separation step was evaluated with samples laden with copper fume generated from copper welding; the samples were then placed into a dust generation system and overlaid with a known deposition of copper sulfate dust. With a dust loading of about 600 μg $CuSO_4$ and fume concentrations of 0.13 to 0.59 mg/m^3, an average of 96.5% of the dust was removed. The analysis of the copper fume had a pooled $\bar{S}_r$ of 4.4% with an average bias of 5.3% [2].

Efficiencies of removal of Cu dust and fume were determined from samples containing only dust or only fume. Measured efficiencies were: (1) from filters containing 213 to 265 μg $CuSO_4$, an average of 97.8% was removed using 10 to 50 mL water; (2) filters laden with ca. 200 μg Cu/filter lost 11.5% Cu after washing with 10 mL H_2O. Because the non-equilibrium nature of the washing process does not lend itself to accurate prediction of the amount of copper fume removed by the wash water, no correction factor for the amount of fume removed was determined or employed. The elemental analysis used in the evaluation did not distinguish between copper from the fume and from the dust [2].

REFERENCES:

[1] Backup Data Report for Copper Fume, S354, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 5," Order No. PB 287-499 from NTIS, Springfield, VA 22101.
[2] Carsey, T. Development of a Sampling and Analytical Method for Copper Fume, final report, NIOSH (DPSE) (unpublished, September, 1982).
[3] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[4] Ibid, V. 4, Method S354, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[6] Ibid, V. 3, Method S186, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[7] Winefordner, J. D., Ed. Spectrochemical Methods of Analysis, John Wiley & Sons (1971).
[8] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).
[9] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Mark Millson, NIOSH/DPSE, and R. DeLon Hull, Ph.D., NIOSH/DBBS; originally validated under NIOSH Contracts CDC-94-74-45 and 210-76-0123.

CRESOL (all isomers) and PHENOL

$CH_3C_6H_4OH$	MW: 108.14	CAS: 1319-77-3	RTECS: GO5950000
C_6H_5OH	94.11	108-95-2	SJ3325000

METHOD: 2546, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : Table 1
NIOSH:
ACGIH:

PROPERTIES: Table 1

SYNONYMS: o-cresol: 2-methylphenol; CAS #95-48-7; m-cresol: 3-methylphenol; CAS #108-39-4; p-cresol: 4-methylphenol; CAS #106-44-5.
phenol: carbolic acid; hydroxybenzene

SAMPLING

SAMPLER:	SOLID SORBENT TUBE (XAD-7, 100 mg/50 mg)
FLOW RATE:	0.01 to 0.1 L/min
VOL-MIN:	1 L @ 5 ppm
-MAX:	24 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 1 week @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	GAS CHROMATOGRAPHY, FID
ANALYTE:	cresol isomers/phenol
DESORPTION:	2 mL methanol; sonicate
INJECTION VOLUME:	1 µL (split 20:1)
TEMPERATURE-INJECTION:	250 °C
-DETECTOR:	300 °C
-COLUMN:	160 - 225 °C (3 °C/min)
CARRIER GAS:	He, 1 mL/min
COLUMN:	Stabilwax DA fused silica capillary, 30 m, 0.32-mm ID, 0.25-mm film or equivalent
CALIBRATION:	standard solutions of analytes in methanol
RANGE:	20 to 800 µg per sample
ESTIMATED LOD:	1 to 3 µg per sample
PRECISION ($\bar{S}_r$):	0.028 [1]

APPLICABILITY: The working range is 0.25 to 15 ppm (1 to 60 mg/m^3) for cresols and phenol in a 20-L air sample.

INTERFERENCES: None identified. A DB-wax fused silica capillary column is an alternate column.

OTHER METHODS: This method uses a sampler similar to that of OSHA 32 [1] and replaces methods 2001 (Cresols) [2] and 3502 (Phenol) [3]. Analysis of the sample extracts can also be done by HPLC/UV [1,4].

REAGENTS:

1. Methanol, chromatographic quality.
2. n-Hexane.
3. Cresol (all isomers).* Dissolve 2 g o-cresol (solid), 3 g p-cresol (solid) in 4 g (4.13 mL) of m-cresol and mix.
4. Calibration stock solution, 10.4 mg/mL. Dilute 104 mg cresol isomer mixture (1.0 mL at 20 °C) to 10 mL with n-hexane.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 6-mm OD, 4- mm ID;two sections of 20/40 mesh XAD-7 separated by a 2-mm portion of silanized glass wool (front = 100 mg, back = 50 mg).
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2001-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Cresol and phenol cause severe burns [5]. They are toxic if absorbed through skin, inhaled or ingested. All work with them should be performed in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 5 to 24 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section (together with the front glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard the other plugs.
6. Add 2.0 mL methanol to each vial. Attach crimp cap to each vial.
7. Ultrasonicate 30 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 800 µg cresol and phenol per sample.
   a. Add known amounts of calibration stock solution to methanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (total peak area vs. µg analyte).
9. Determine desorption efficiency (DE) at least once per year for each lot of sorbent used for sampling in the calibration range. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject 1-μL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure total peak area of the two analyte peaks.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of cresols and phenol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of cresols in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This is a modification of OSHA Method 32 (Phenol and Cresol) which uses the same sampling procedure [1]. Phenol and all cresol isomers were easily resolved by capillary GC using a split injection ratio of 20:1. The desorption efficiency (DE) results for all analytes were > 0.90. Analytes were stable for 30 days when refrigerated.

REFERENCES:

[1] Phenol and Cresol, Occupational Safety and Health Administration, OSHA Method 32, OSHA Analytical Laboratory, 1981.
[2] NIOSH Manual of Analytical Methods, 3rd ed., Vol. 2, Method 3502, U.S. Dept. of Health, Education, and Welfare, Publication #84-100 (NIOSH), 1984.
[3] Ibid, Method 2001.
[4] DataChem Laboratories Report, Seq. #7478-L (NIOSH, unpublished, May 8, 1992).
[5] NIOSH/OSHA, Occupational Health Guidelines for Chemical Hazards, USDHHS (NIOSH), Publ. 81-123 (1981).
[6] Pendergrass, S.M., An Improved Method for the Sampling and Analysis of Phenol and o-, m-, and p-Cresol by Capillary GC/FID, Amer. Ind. Hyg. Assoc. J. (accepted for publication, 1994).
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METHOD REVISED BY:

Stephanie M. Pendergrass, NIOSH/DPSE.

TABLE 1. PHYSICAL PROPERTIES [6].

Compound	BP (°C)	MP (°C)	Density @ 20 °C	Vapor Presssure 25 °C (Pa)	(mm Hg)	NIOSH REL*
o-cresol	190.95	30.9	1.047 g/mL	33	0.25	2.3 ppm
m-cresol	202.2	12.0	1.034	20	0.15	2.3 ppm
p-cresol	201.9	35.3	1.034	15	0.11	2.3 ppm
phenol	182.0	41.0	1.071 (25 °C)	47	0.35	5 ppm; C 15.6 ppm/15 min (skin)

* OSHA PEL and ACGIH TLV are 5 ppm (skin) for all the above compounds.
1 ppm = 4.42 mg/m^3 @ NTP for the cresols; 1 ppm = 3.85 mg/m^3 @ NTP for phenol.

CROTONALDEHYDE 3516

$CH_3CH=CHCHO$ MW: 70.09 CAS: 4170-30-3 RTECS: GP9499000

METHOD: 3516, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 2 ppm
NIOSH: 2 ppm
ACGIH: 2 ppm; suspect carcinogen
(1 ppm = 2.87 mg/m^3 @ NTP)

PROPERTIES: liquid; pungent odor; BP 104 °C; d 0.85 g/mL @ 20 °C; VP 2.7 kPa (20 mm Hg, 2.6% v/v) @ 20 °C; explosive range 2.1 to 15.5% v/v in air

SYNONYMS: crotonic aldehyde; trans-2-butenal, crotonal

SAMPLING

SAMPLER: MIDGET BUBBLER (hydroxylamine/formate buffer solution)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 1 L @ 2 ppm
-MAX: 49 L

SHIPMENT: refrigerate bubblers at 8 °C during shipment if samples cannot be analyzed within 4 h

SAMPLE STABILITY: 4 h maximum @ 25 °C, 7 days minimum at 8 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.9 to 23.4 mg/m^3 (12-L samples)

BIAS: −2.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.061 (2.9 to 11.6 mg/m^3) [1]

ACCURACY: ±14.8%

MEASUREMENT

TECHNIQUE: DIFFERENTIAL PULSE POLAROGRAPHY

ANALYTE: crotonaldehyde oxime

DROP TIME: 1 s

SCAN RATE: 5 mV/s

SCAN RANGE: −0.6 to −1.2 V (vs. SCE)

CALIBRATION: standard solutions of crotonaldehyde in hydroxylamine/formate buffer solution

RANGE: 35 to 139 μg per sample

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 1 to 10 ppm (2.9 to 29 mg/m^3) for a 12-L air sample. The upper limit of the method is dependent on the concentration of hydroxylamine, which should be maintained at 50-fold molar excess over total amount of crotonaldehyde sampled. Collection efficiency outside the method range has not been evaluated.

INTERFERENCES: Other volatile aldehydes (e.g., acrolein, formaldehyde, benzaldehyde).

OTHER METHODS: This is Method P&CAM 285 [2] in a revised format. An aldehyde screening method [3] and a method for priority pollutants [4], both of which include crotonaldehyde, have been described.

REAGENTS:

1. Hydroxylamine hydrochloride, reagent grade.
2. Sodium hydroxide, 0.1 M, reagent grade.
3. Formic acid, reagent grade.
4. Sodium formate, reagent grade.
5. Hydroxylamine collection solution. Dissolve 0.68 g of hydroxylamine hydrochloride in 1 L deionized water. Adjust to pH 5 with 0.1 M sodium hydroxide.
6. Formic acid/sodium formate buffer. Add 3.4 g sodium formate and 2 mL formic acid to 500-mL volumetric flask. Bring to volume with deionized water.
7. Crotonaldehyde,* 85%.
8. Crotonaldehyde stock solution. Prepare solutions containing 17.19 and 1.179 mg/mL of crotonaldehyde in deionized water.
9. Nitrogen, prepurified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Glass midget bubblers.
2. Personal sampling pump, 0.1 to 0.2 L/min, and trap with flexible tubing. Trap is a midget bubbler or impinger with stem broke off.
3. Volumetric flasks, 1-L, 500-mL, and convenient sizes for preparing stock standard solutions.
4. Pipets, 10-mL, 5-mL, and other convenient sizes.
5. Syringes for preparing spiked standard samples.
6. Potentiostat with differential pulse polarographic capability.
7. China marker.
8. PTFE tubing 15 cm x 7-mm ID or PTFE plugs for sealing the inlet and outlet of the bubbler stem before shipment.

NOTE: Wash all glassware with detergent, rinse with deionized water and dry. Midget bubblers should be heated in an oxidizing atmosphere at about 580 °C to remove organic contaminants.

SPECIAL PRECAUTIONS: Crotonaldehyde is highly toxic, flammable liquid [5]. Prevent contact with skin, eyes, and clothing. Do not breathe vapors; crotonaldehyde vapors irritate the mucous membranes, nose and respiratory tract. Vapors can severely irritate the eyes, causing lacrimation. Contact with eyes can cause corneal burns. Contact with skin causes irritation and may cause burns. Wash thoroughly after handling.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler and trap in line.
2. Rinse bubblers with 10 mL hydroxylamine solution. Pipet 10 mL of hydroxylamine solution buffered at pH 5 into each midget bubbler. Mark the liquid level on the bubbler with a china marker. Ensure that bubbler frit is covered.
3. Attach outlet of midget bubbler to inlet of trap used to protect pump during sampling. Attach trap to pump with metal holder. Connect outlet of trap to pump by flexible tubing.
4. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size of 1 to 49 L.
   NOTE: Sampled air should not pass through any tubing containing polyvinylchloride (PVC) before entering the bubbler; PVC tubing is known to give interferences in the method.
5. Discard any material collected by the trap. If more than 1 mL of material is collected in the trap, the sample should be considered invalid.
6. Seal the inlet and outlet of the bubbler stem by connecting a piece of PTFE tubing between them or by inserting PTFE plugs in the inlet and outlet. Pack securely for shipment. If samples cannot be analyzed within four hours, they must be refrigerated at 8 °C during shipping and until analysis time.
7. Collect a bulk sample (ca. 1 g) in a glass vial with a PTFE-lined cap and ship separately.

SAMPLE PREPARATION:

8. Remove bubbler stem and drain contents into bubbler flask. If necessary, bring to 10-mL mark with distilled water. Add 5 mL formate buffer solution and swirl bubbler to mix contents well.

CALIBRATION AND QUALITY CONTROL:

9. Prepare at least six working standards having concentrations to cover the range of 6 to 280 μg per sample (corresponding to 0.1 to 4 times the OSHA standard).
   a. Add appropriate aliquots ($\leq$ 100 μL) of stock solution to 10 mL of hydroxylamine solution, followed by addition of 5 mL of formate buffer solution.
   b. Analyze with samples and blanks (step 11).
   c. Prepare calibration graph of peak current vs. mass (μg) of crotonaldehyde per 15 mL of sample.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

11. Transfer sample to electrochemical cell and purge with oxygen-free nitrogen for 3 min at 200 mL/min. Analyze by differential pulse polarography: 1 second drop time, 5 mV/second scan rate, and -0.6 V to -1.2 V scan range vs. a saturated calomel electrode (SCE). Analysis should be conducted in a relatively stable temperature environment. Measure peak current due to reduction of crotonaldehyde oxime. The half wave potential, $E_{1/2}$, of crotonaldehyde oxime is -1.03 V vs. SCE. Rinse electrodes before analyzing next sample.

CALCULATIONS:

12. Determine the mass, μg, for each sample (W) and for the average media blank (B) from the standard calibration graph.
13. Calculate concentration, C, of crotonaldehyde in the air volume sampled, V (L), applying a correction for the collection efficiency, which was determined to be 96%:

$$C = \frac{(W - B)}{V \cdot 0.96}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The average concentrations obtained from analysis of samples collected from test atmospheres at 0.5X, 1X, 2X, and 4X the OSHA standard were 10.0% lower, 2.1% lower, 3.7% higher, and 3% higher, respectively, than the "true" concentrations. The difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no uncorrected bias. Storage stability studies on samples collected in a test atmosphere at a concentration of 5.80 mg/m^3 indicated that collected samples are stable for at least 7 days at 8 °C. Collection efficiency for the midget bubbler was determined to be 0.96 for an average of 24 samples and a correction must be applied. Statistical information [6] and details of the test procedures [1] can be found elsewhere.

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[1] Backup Data Report for Crotonaldehyde, prepared under NIOSH Contract No. 210-76-0123.
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[6] Documentation of the NIOSH Validation Test, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

METHOD REVISED BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-76-0123.

CUMENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

CYANIDES, aerosol and gas

HCN and salts	MW: 27.03 (HCN); 65.11 (KCN)	CAS: 74-90-8 (HCN); 151-50-8 (KCN)	RTECS: MW6825000 (HCN); TS8750000 (KCN)

METHOD: 7904, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 11 mg/m^3; skin (HCN)
5 mg/m^3; skin (cyanides, as CN^-)
NIOSH: C 5 mg/m^3/10 min (as CN^-)
ACGIH: C 11 mg/m^3; skin (HCN);
5 mg/m^3; skin (cyanides, as CN)

PROPERTIES: HCN: gas, BP 26 °C; VP 620 mm Hg 20 °C; vapor density 0.94 (air = 1); KCN: solid, d 1.52 g/mL, MP 634 °C

SYNONYMS: HCN: hydrocyanic acid, prussic acid, formonitrile, cyanides.

SAMPLING

SAMPLER:	FILTER + BUBBLER (0.8-μm PVC membrane + 15 mL 0.1 N KOH) [1]
FLOW RATE:	0.5 to 1 L/min
VOL-MIN:	10 L @ 0.5 mg/m^3 (as CN^-)
-MAX:	180 L @ 11 mg/m^3 (as CN^-)
SHIPMENT:	routine
SAMPLE STABILITY:	analyze within 5 days; particulate on filter may liberate HCN gas [2]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	5 to 21 mg/m^3 (HCN) [3]; 2.6 to 10 mg/m^3 (KCN) [2]
BIAS:	− 7.6%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.062 (HCN) [3]; 0.103 (KCN) [2]
ACCURACY:	± 20.0%

MEASUREMENT

TECHNIQUE:	ION-SPECIFIC ELECTRODE
ANALYTE:	cyanide ion (CN^-)
EXTRACT FILTER:	25 mL 0.1 N KOH; 30 min
RINSE BUBBLER:	2 mL 0.1 N KOH; dilute to 25 mL with 0.1 N KOH
MEASURE:	mV reading of cyanide ion electrode vs. reference electrode
CALIBRATION:	solutions of KCN in 0.1 N KOH
RANGE:	0.05 to 2 mg CN^-
ESTIMATED LOD:	2.5 μg CN^- [2]
PRECISION ($\bar{S}_r$):	0.043 (HCN) [3]; 0.038 (KCN) [2]

APPLICABILITY: The working range (as CN^-) is 0.5 to 15 mg/m^3 for a 90-L air sample or 5 to 20 mg/m^3 for a 10-L air sample.

INTERFERENCES: Sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron and mercury interfere. In humid atmospheres, some particulate cyanide collected on the filter will liberate hydrogen cyanide which will be trapped in the bubbler [2]. The method cannot distinguish between HCN formed in this manner and HCN originally present in air.

OTHER METHODS: This method combines and replaces Methods S288 [4], S250 [5], and P&CAM 116 [6]. Method 6010 (Hydrogen Cyanide) uses a soda lime tube as sampler, with colorimetric measurement.

REAGENTS:

1. Deionized water.
2. Potassium cyanide.*
3. Calibration stock solution, 1000 μg/mL CN^-. Dissolve 0.250 g KCN in 0.1 N KOH to make 100 mL solution. Stable for at least 1 week in polyethylene bottle.
4. Potassium hydroxide (KOH), 0.1 N. Dissolve 5.6 g KOH in deionized water; dilute to 1000 mL.
5. Lead acetate paper.
6. Cadmium carbonate (if sulfide present).
7. Hydrogen peroxide, 30% (if sulfide present).
8. Sodium sulfite, 1 M (if sulfide present).
9. Potassium hydroxide (KOH) pellets.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride membrane filter, 37-mm diameter, 0.8-μm pore size in 2-piece filter cassette holder, followed by a glass midget bubbler containing 15 mL 0.1 N KOH.
2. Personal sampling pump, 0.5 to 1 L/min, with splashover protection and flexible connecting tubing.
3. Vials, polyethylene, with screw caps, 20-mL, and plastic tape for sealing.
4. Cyanide ion electrode, (Orion 94-06 or equivalent).
5. Reference electrode.
6. pH meter, readable to 0.1 mV.
7. Magnetic stirrer and stirring bars.
8. Jars, ointment, 60-mL, squat-form with aluminum-lined screw caps.
9. Pipets, 0.05- to 2 and 25-mL, with pipet bulb.
10. Volumetric flasks, 25-mL.
11. Beakers, 50-mL.
12. Analytical balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hydrogen cyanide gas and the cyanide particulates may be fatal if swallowed, inhaled or absorbed through the skin. Work in a hood.

Amyl nitrite is the antidote for cyanide poisoning [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.5 to 1 L/min for a total sample size of 10 to 180 L.
   NOTE: Maintain bubblers in a vertical position during sampling. Do not allow the solution level to fall below 10 mL.
3. Remove the bubbler stem and tap it gently against the inside wall of the bubbler. Rinse the bubbler stem with 1 to 2 mL of unused 0.1 N KOH. Add the rinse to the bubbler.
4. Quantitatively transfer the contents of the bubbler to a 20-mL vial. Add 1 or 2 pellets of KOH to vial to keep pH in 13 to 14 range. Close cap tightly and wrap with plastic tape to avoid sample loss during transit. Label each vial.

SAMPLE PREPARATION:

5. Transfer the filter from the cassette filter holder to a 60-mL ointment jar.
6. Pipet 25.0 mL 0.1 N KOH into the jar. Cap and allow to stand for at least 30 min with occasional shaking to complete extraction. Analyze within 2 h after extraction.
7. Empty the contents of the vial into a 25-mL volumetric flask using 0.1 N KOH to rinse the vial. Add rinse to the volumetric flask. Dilute to the mark with 0.1 N KOH.
   NOTE: Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if present. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper; the paper will discolor in the presence of sulfide ion. If this test is positive, remove sulfide by one of the following methods:

a. Add 1 mL 1 M H_2O_2 and 1 mL 1 M Na_2SO_3 to sample solutions prior to diluting to volume.

b. Add a small amount (spatula tip) of powdered cadmium carbonate to the sample. Swirl to disperse the solid and recheck the liquid with lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution. When a drop of liquid no longer discolors a strip of lead acetate paper, filter the sample through a small plug of glass wool in a Pasteur pipette and proceed with the analysis.

CALIBRATION AND QUALITY CONTROL:

8. Prepare at least six working standards fresh daily to cover the range 50 to 2000 μg CN^- per sample by diluting aliquots of 1000 μg/mL calibration stock solution with 0.1 N KOH (e.g., 0.05 to 2.0 mL calibration stock solution diluted to 25 mL).
9. Analyze the working standards according to steps 11 and 12 together with the samples and blanks.
10. Prepare a calibration graph on semilog paper by plotting cyanide ion concentration on the logarithmic axis and mV on the linear axis.

MEASUREMENT:

11. Transfer the solution to be measured to a 50-mL beaker. Immerse the cyanide ion electrode and reference electrode in the sample and start the magnetic stirrer.
12. With the magnetic stirrer on, allow the potential reading to stabilize. Record the mV reading.

NOTE 1: Potential readings are a function of temperature. Measure samples and working standards at the same temperature (± 2 °C).

NOTE 2: The cyanide electrode will malfunction if chloride, iodide and bromide ions, which form insoluble silver salts, are present in sufficient quantity. Several metal ions are also known to complex with cyanide such as cadmium, zinc, silver, nickel, cuprous iron and mercury. Consult the electrode instruction manual for the procedure to use when such ions are present.

CALCULATIONS:

13. Read the mass, μg, of cyanide ion present in the sample filter (W_f), sample bubbler (W_b), average media blank filter (B_f) and media blank bubblers (B_b) from the calibration graph.
14. Calculate the concentration (mg/m^3) of particulate cyanide, C_p, and hydrogen cyanide, C_{HCN}, in the air volume sampled, V (L):

$$C_p = \frac{W_f - B_f}{V}, \text{ mg/m}^3 \qquad C_{HCN} = \frac{(W_b - B_b) \cdot 1.04}{V}, \text{ mg/m}^3.$$

where 1.04 is the stoichiometric conversion factor from CN^- to HCN.

NOTE: Particulate cyanides will be collected on the filter. In humid atmospheres, however, it has been observed that during the collection of particulate cyanide, HCN is gradually liberated [2]; therefore, particulate cyanide interference is not completely removed.

EVALUATION OF METHOD:

HCN: Method S288 was issued on September 2, 1977 [4]. Test atmospheres of HCN were generated by calibrated flow from a compressed mixture of HCN in nitrogen [3,8]. The range of HCN concentrations in air was 5 to 21 mg/m^3 for 12-L air samples. Eighteen HCN samples collected at 0.2 L/min for 60 min indicated overall precision of 6.2%, with a 96.7% recovery. An eight-day storage

stability study involving six samples at the OSHA standard concentration level indicated a 92.4% average recovery for the one-day old samples and a 92.6% for eight-day old samples. A collection efficiency study at twice the OSHA standard level, which included backup bubblers, indicated that an average of 99.8% of HCN was collected in the first bubbler. The HCN air generated concentrations were independently confirmed by a titration method [3].

KCN: Method S250 was issued on January 30, 1976 [5]. A set of six weighed KCN samples in the range of 1.8 to 2.5 mg KCN per filter indicated a 97% recovery and a 3.8% measurement precision [2]. Spiking with aqueous or basic solutions of KCN proved unsuccessful (low recovery) because of the cyanide instability in the presence of water and CO_2. Test atmospheres of KCN were generated by atomization of an aqueous solution (162 g/L) of KCN into a dry airstream. Eighteen KCN samples collected in 0.1 N NaOH at 1.5 L/min for 60 min indicated overall precision, $\hat{S}_{rT}$, of 0.103. Collection was accomplished with cellulose ester membrane filters followed with backup bubblers. The collection efficiency at twice the OSHA level was 100.0% on the filters. Cyanide salts are known to decompose in moist air with liberation of HCN. This instability was determined with two sets of six samples at the one and two times the OSHA level. Each of the samples which were twice the OSHA level were connected with two backup bubblers. Both sets indicated a loss of 16.5%.

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METHOD REVISED BY:

J. Palassis, NIOSH/DTMD; S250 and S288 originally validated under NIOSH Contracts CDC-99-74-45 and 210-76-0123, respectively.

CYANURIC ACID 5030

$C_3N_3(OH_3)$ MW: 129.08 CAS: 108-80-5 RTECS: XZ1800000

METHOD: 5030, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: no recommended exposure limit
ACGIH: no TLV

PROPERTIES: solid; d 2.50 g/mL @ 20 °C; MP >330 °C; (decomposes to cyanic acid); VP not significant

SYNONYMS: 2,4,6-trihydroxy-1,3,5-triazine; isocyanuric acid; 1,3,5-triazine-2,4,6(1H,3H,5H)trione.

SAMPLING

SAMPLER: Filter (5-μm PVC membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 69 days at 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: cyanuric acid

EXTRACTION: 3 mL 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water (pH = 7.0), 10 min ultrasonic

INJECTION VOLUME: 15 μL

MOBILE PHASE: 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water (pH = 7.0)

COLUMN: μ-Bondapak C_{18}, 10-μm particle, size; Radial PAK cartridge, 11 cm x 8-mm ID

DETECTOR: UV, 225 nm

CALIBRATION: standard solutions of cyanuric acid in mobile phase

RANGE: 1 to 750 μg per sample

ESTIMATED LOD: 0.3 μg per sample

PRECISION ($\bar{S}_r$): 0.020 @ 12 to 412 μg per sample [1]

APPLICABILITY: The working range is 0.01 to 10 mg/m^3 for a 100-L air sample.

INTERFERENCES: Trichloroisocyanuric acid interferes because it reacts with water (which is present in the eluent used for recovery) to form cyanuric acid.

OTHER METHODS: None identified for air analysis. HPLC method for measurement in solution is a variation of the method of Briggle et al. [2].

REAGENTS:

1. Cyanuric acid, ≥98% pure.*
2. Water, distilled.
3. Methanol, chromatographic quality.*
4. $Na_2HPO_4 \cdot 7H_2O$, reagent grade.
5. HCl, 1 M (aqueous).
6. Eluent and mobile phase: 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water at pH = 7.0. Dissolve 5.36 g of $Na_2HPO_4 \cdot 7H_2O$ in 2000 mL water. Add 200 mL methanol. Add water until total volume is 3990 mL. Add 1 M HCl until pH is 7.0.
7. Calibration stock solution, 1 mg/mL. Dissolve 25 mg cyanuric acid in eluent to make 25 mL solution. Prepare fresh monthly.
   NOTE: Ultrasonic bath will facilitate dissolution of cyanuric acid.
8. Recovery stock solution, 1.7 μg/μL. Dissolve 42.5 mg cyanuric acid in water to make 25 mL solution.
   NOTE: Ultrasonic bath will facilitate dissolution of cyanuric acid.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 5-μm polyvinyl chloride (PVC) membrane filter in 2-piece cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC), UV absorption detector, 225 nm, recorder, intergrator and column (page 5030-1).
4. Vials, 4-mL, with PTFE-lined caps.
5. Volumetric flasks, 25-mL.
6. Carboy, 4-L.
7. Graduated cylinders, 1-L, readable to 10-mL, 250-mL, readable to 2 mL.
8. Syringes, 500-μL, readable to 10 μL; 100-μL, readable to 1 μL; 10-μL, readable to 0.1 μL.
9. Beakers, 50-mL, internal diameter ≥37 mm.
10. Ultrasonic water bath.
11. Film, plastic, flexible, water-resistant.
12. Filter units, 25-mm PTFE membrane, 0.45-μm pore size, in polypropylene housing.
13. Vacuum oven.
14. Tweezers.
15. pH meter.
16 Adhesive tape.

SPECIAL PRECAUTIONS: Cyanuric acid is a possible tumorigenic agent and a slight eye irritant [3,4]. Methanol is toxic. Ingestion of methanol may cause blindness or death. Methanol is a fire hazard (flash point 12 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 1000 L. Limit the maximum loading of particulate matter on the filter to about 1 mg.
4. Seal the ends of the sampler with plugs. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the PVC filter face down into a 50-mL beaker (the filter should lie flat on the bottom of the beaker). Retain the cassette filter holder (step 9).
6. Add 3 mL eluent to the beaker. Seal the mouth of the beaker with plastic film.
   NOTE: The volume of 3 mL is sufficient when the quantity of cyanuric acid on the filter is 1 mg or less. The limit of solubility of cyanuric acid in eluent is about 2 mg/mL at room temperature.
7. Place the beaker into an ultrasonic bath for 10 min.

8. Filter the solution.
9. If cyanuric acid is found on the PVC filter (steps 13 and 14), prepare additional sample solution by treatment of the interior surface of the front piece of the cassette filter holder with eluent.
   NOTE: The quantity of cyanuric acid collected on the interior surface of the front piece of the cassette filter holder may be significant (see EVALUATION OF METHOD).
   a. Use adhesive tape to secure in place the plug in the inlet of the front piece of the cassette filter holder.
   b. Add eluent (ca. 6 mL) to the front piece until about 95% of the interior surface is in contact with eluent.
   c. Place the front piece into an ultrasonic bath for 5 min.
   d. Transfer the solution from the front piece to a beaker, seal the mouth of the beaker with plastic film, and place the beaker into an ultrasonic water bath for 10 min.
      NOTE: Solid particles may be present in the solution after the first 5 min of ultrasonic agitation. Transfer of the solution to a beaker helps protect the solution from contamination.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.1 to 250 mg cyanuric acid per mL of solution.
    a. Prepare a series of working standards in vials from calibration stock solution and eluent by serial dilution.
    NOTE: Working standards may be stored at −3 °C for at least 18 days without deterioration.
    b. Analyze together with samples and blanks (steps 13 and 14).
    c. Prepare calibration graph (peak area or height vs. μg of cyanuric acid).
11. Determine recovery (R) at least once for each lot of PVC membrane filters used for sampling in the calibration range (step 10). Prepare three filters at each of five levels plus three media blanks.
    a. Place an aliquot of recovery stock solution onto a PVC filter which is situated in the back piece of a cassette filter holder. If the volume of the aliquot is greater than 15 μL, transfer the aliquot to the filter in portions which are about 15 μL in size.
    NOTE: Portions of stock solution will appear as beads on the filter. A maximum of about sixteen 15-μL portions of solution can be distributed on the filter. Thus, a maximum of about 400 mg of cyanuric acid can be applied to the filter with the recovery stock solution. A recovery stock solution which has a much higher concentration of cyanuric acid in water at room temperature can not be prepared because the limit of solubility of cyanuric acid in water at room temperature is about 2.5 mg/mL. If higher loadings are needed, allow the first portions to dry and repeat the process.
    b. Join the front piece of the cassette filter holder with the back piece. Remove the plug from the inlet.
    c. Carefully transfer the filter holder to a vacuum oven.
    d. Dry the filter at about 65 °C and 40 kPa (300 mm Hg). Filter will be dry in ca. 0.3 to 4.5 h.
    e. Prepare sample (steps 5 through 8) and analyze with working standards (steps 13 and 14).
    f. Prepare a graph of R vs. μg cyanuric acid recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

13. Set liquid chromatograph to manufacturer's recommendations and to conditions given on page 5030-1. Inject sample aliquot manually or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, μg (corrected for R), of cyanuric acid found on the filter (W_f) and on the average media blank (B_f).
16. Determine the mass, μg, of cyanuric acid found on the interior surface of the cassette filter holder (W_c) and on the interior surface of a blank cassette filter holder (B_c).
17. Calculate concentration, C, of cyanuric acid in the air volume sampled, V (L):

$$C = \frac{(W_f + W_c - B_f - B_c)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Average recoveries after fortification of 37-mm PVC membrane filters with 12-, 36-, and 412-μg quantities of cyanuric acid were 0.98, 1.00, and 1.00, respectively; precision ($\bar{S}_r$) was 0.020 (16 samples, pooled). The average recovery of 36-μg quantities of cyanuric acid from PVC filters after 22 days of storage at room temperature was 1.08; $\bar{S}_r$ was 0.065 (5 samples). Recovery of 1.08 was not significantly different from 1.00 at the 95% confidence level. Recoveries of 10-, 80-, 200-, and 400-μg quantities of cyanuric acid were 0.88, 1.04, 0.98 and 0.98, respectively, after storage of fortified PVC filters for 69 days at room temperature (one sample at each level). This method was not evaluated with controlled atmospheres in a laboratory. However, the method was employed for measurement of cyanuric acid in air at a plant in which trichloroisocyanuric acid was manufactured from cyanuric acid [1,5]. Significant quantities (ca. 40% of the totals) of cyanuric acid were found on interior surfaces of the front pieces of cassette filter holders.

Working standards of cyanuric acid at concentrations near 1 μg/mL in eluent deteriorated in about 3 weeks during storage at room temperature; standards were stable for at least 18 days during storage at - 3 °C. Deterioration of a C_{18} analytical column took place and caused the LOD of cyanuric acid to increase from 0.1 to 0.25 μg/mL during 6 weeks.

Trichloroisocyanuric acid is an interference because it reacts with water (present in the eluent) to form cyanuric acid. Average yields of cyanuric acid after treatment of 8.4-, 64-, and 424-μg quantities of trichloroisocyanuric acid with eluent in glass vials were 74%, 89%, and 93%, respectively.

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METHOD WRITTEN BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE.

CYCLOHEXANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

CYCLOHEXANOL

See ALCOHOLS III (METHOD 1402) for procedure

CYCLOHEXANONE

See KETONES I (Method 1300) for procedure

CYCLOHEXENE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

1,3-CYCLOPENTADIENE 2523

C_5H_6 MW: 66.10 CAS: 542-92-7 RTECS: GY1000000

METHOD: 2523, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 75 ppm
NIOSH: 75 ppm
ACGIH: TWA 75 ppm
(1 ppm = 2.70 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8021 g/mL @ 20 °C; BP 42 °C; MP −85 °C; dimerizes to solid (MP 32.5 °C); VP not available

SYNONYMS: none

SAMPLING

SAMPLER: SOLID SORBENT TUBE (maleic anhydride on Chromosorb 104, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 75 ppm
-MAX: 5 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 73 to 370 mg/m^3 [1] (3-L samples)

BIAS: 3.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.066 [2]

ACCURACY: ± 16.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-cyclopentadiene-maleic anhydride adduct (see REAGENTS, 1.)

DISSOLUTION: 10 mL ethyl acetate; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: 155 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 5% OV-17 on 100/120 mesh Chromosorb WHP

CALIBRATION: analyte in ethyl acetate

RANGE: 0.2 to 1.2 mg 1,3-cyclopentadiene per sample

ESTIMATED LOD: 0.01 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.031 @ 0.3 to 1.2 mg per sample [1]

APPLICABILITY: The working range is 25 to 150 ppm (67 to 400 mg/m^3) for a 3-L air sample, based on sampler capacity at high relative humidity.

INTERFERENCES: None identified.

OTHER METHODS: This revises P&CAM 294 [2].

REAGENTS:

1. Analyte: 5-norbornene-2,3-dicarboxylic anhydride (Eastman Chemicals).
   NOTE: This is the Diels-Alder adduct formed by reaction of 1,3-cyclopentadiene and maleic anhydride.* Both endo- and exo- forms are present.
2. Calibration stock solution, 50 mg/mL. Dissolve 500 mg analyte in ethyl acetate* to make 10 mL solution.
3. Acetone.*
4. Ethyl acetate.*
5. Maleic anhydride.*
6. Sorbent: acrylonitrile-divinyl benzene copolymer, 60/80 mesh, with surface area 100 to 200 m^2/g (Chromosorb 104, Johns-Manville).
7. Nitrogen, purified.
8. Hydrogen, prepurified.
9. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID, with plastic caps, containing two sections of coated sorbent (front = 100 mg; back = 50 mg), held in place and separated with glass wool plugs. Prior to packing, rinse the empty tube with acetone and dry to eliminate static adhesion of sorbent onto the tube wall. Pressure drop across sampler $\leq$2.5 kPa (25 cm water) at 0.05 L/min airflow.
   NOTE: See APPENDIX for preparation of coated sorbent. Use the coated sorbent within 20 days of preparation. Tubes available by special order (SKC, Inc.).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph with FID, integrator, and column (page 2523-1).
4. Vials, 20-mL, with PTFE-lined caps.
5. Flask, round-bottom, 250-mL.
6. Rotary evaporator.
7. Vacuum oven.
8. Syringes, 10-μL, readable to 0.1 μL.
9. Pipet, volumetric, 10-mL, with pipet bulb.
10. Pipets, micro, 10- to 1000-μL.

SPECIAL PRECAUTIONS: Maleic anhydride is a powerful irritant and can cause burns and pulmonary edema. Avoid exposure to concentrated vapor. Avoid contact with skin, eyes and clothing.

Acetone and ethyl acetate are serious fire risks.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Add 10.0 mL ethyl acetate to each vial. Attach cap to each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 1.2 mg 1,3-cyclopentadiene (0.03 to 3 mg analyte) per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, to ethyl acetate in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine recovery at least once for each lot of coated sorbent used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Prepare (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of recovery vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2523-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 6.5 min under these conditions.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethyl acetate, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for recovery) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1,3-cyclopentadiene in the air volume sampled, V (L) applying the factor 0.403 (MW of 1,3-cyclopentadiene/MW of analyte) for conversion of adduct to 1,3-cyclopentadiene:

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 0.403 \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 294 [2] was issued in 1978 and evaluated over the range 73.4 to 370 mg/m^3 [1,3]. The average recovery for 3-L air samples was 1.036 which represents a non-significant bias. Test atmospheres were generated using a syringe pump delivering 3a,4,7,7a-tetrahydro-4,7-methano-1H-indene (dicyclopentadiene) to a glass pyrolysis tube which thermally decomposed (375 °C) the dimer to monomer. The concentrations of 1,3-cyclopentadiene were confirmed by collecting samples from the generator in bubblers containing 15 mL solution of 74 mg/mL maleic anhydride in ethyl acetate and analysis by GC/FID. Samples were stored at room temperature for one week and found to be stable. Recovery averaged 0.99 in the range 0.75 to 3 mg analyte (equivalent to 0.3 to 1.2 mg 1,3-cyclopentadiene) per sample. Breakthrough capacity exceeded 3.8 mg 1,3-cyclopentadiene when

sampling with freshly prepared (four-day old) coated sorbent and was 1.6 mg with the same batch of coated sorbent 24 days after preparation under similar sampling conditions (360 mg/m^3, 0.045 L/min, >80% RH).

REFERENCES:

[1] Backup Data Report, P&CAM 294 (NIOSH, unpublished, October 13, 1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 294, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
[4] Failure Report, S83 (NIOSH, unpublished, April 14, 1978).

METHOD REVISED BY:

Ardith Grote, NIOSH/DPSE; P&CAM 294 originally developed under NIOSH Contract 210-76-0123.

APPENDIX:

PREPARATION OF COATED SORBENT

1. Add 25 g of sorbent to a 250-mL round-bottom flask.
   NOTE: This will make enough coated sorbent to pack about 150 tubes.
2. Add 100 mL acetone, swirl, and allow sorbent to settle. Decant the acetone. Repeat twice.
   NOTE: This removes the fines and washes the sorbent.
3. Remove the remaining solvent in a rotary evaporator. Dry in a vacuum oven at 30 °C for 1 h.
4. Weigh the dry sorbent and place it in a 250-mL round-bottom flask.
5. Weigh an amount of maleic anhydride equivalent to 20% of the weight of the sorbent and dissolve it in 50 mL acetone.
6. Add the maleic anhydride solution to the sorbent, swirl, and remove the solvent in a rotary evaporator. Dry in a vacuum oven at 30 °C for 15 min. Use the coated sorbent within 20 days of preparation.
   NOTE: Refrigeration in a sealed container may prolong shelf life [1,4].

$C_8H_6Cl_2O_3$ MW: 221.04 CAS: 94-75-7 RTECS: AG6825000

METHOD: 5001, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 10 mg/m^3
NIOSH: 10 mg/m^3
ACGIH: 10 mg/m^3

PROPERTIES: solid; MP 138 °C; VP not significant

SYNONYMS: 2,4-D: (2,4-dichlorophenoxy)acetic acid; hedonal; Trinoxol

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (glass fiber, binderless)	**TECHNIQUE:**	HPLC, UV DETECTION
FLOW RATE:	1 to 3 L/min	**ANALYTE:**	2,4-D anion
VOL-MIN:	15 L @ 10 mg/m^3	**DESORPTION:**	15 mL CH_3OH; stand 30 min
-MAX:	200 L	**INJECTION VOLUME:**	50 µL
SHIPMENT:	routine	**ELUENT:**	0.001 M $NaClO_4$-0.001 M $Na_2B_4O_7$
SAMPLE STABILITY:	at least 1 week @ 25 °C	**FLOW RATE:**	1.7 mL/min
BLANKS:	2 to 10 field blanks per set	**DETECTOR:**	UV @ 284 nm
		COLUMN:	stainless steel, 50 cm x 2-mm ID, packed with Zipax SAX (DuPont) ambient temperature; 6900 kPa (1000 psi)
ACCURACY		**CALIBRATION:**	solutions of analyte in methanol
RANGE STUDIED:	5 to 20 mg/m^3 [1,2] (100-L samples)	**RANGE:**	0.15 to 2 mg per filter
BIAS:	− 1.26%	**ESTIMATED LOD:**	0.015 mg per filter [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.051 (2,4-D) [1]	**PRECISION ($\bar{S}_r$):**	0.01 [1]
ACCURACY:	± 10.21%		

APPLICABILITY: This method determines 2,4-D, 2,4,5-T, and their salts, but not their esters. The working range is 1.5 to 20 mg/m^3 of either compound for a 100-L air sample.

INTERFERENCES: High concentrations of esters of either compound do not interfere but require the use of a pre-column to prevent degradation of the HPLC column.

OTHER METHODS: This method combines and replaces Methods S279 [3] and S303 [3] which are the same except for eluent composition and UV detector wavelength.

REAGENTS:

1. 2,4-dichlorophenoxyacetic acid.*
2. 2,4,5-trichlorophenoxyacetic acid.*
3. Methanol, HPLC grade.
4. LC eluent:
   a. 2,4-D: 0.001 N $NaClO_4$ and 0.001 N $Na_2B_4O_7$. Add 0.122 g $NaClO_4$ and 0.381 g $Na_2B_4O_7 \cdot 10H_2O$ to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and de-gas the solution.
   b. 2,4,5-T: 0.003 M $NaClO_4$ and 0.001 M $Na_2B_4O_7 \cdot 10H_2O$. Add 0.366 g $NaClO_4$ and 0.381 g $Na_2B_4O_7 \cdot 10H_2O$ to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and de-gas the solution.
5. Compressed, filtered air or nitrogen for drying syringes.
6. Ethanol, absolute.
7. Acetone.
8. Calibration stock solution, 400 μg/mL.
   Dissolve 0.400 g 2,4-D or 2,4,5-T in methanol and dilute to 1 L with methanol.
9. Recovery stock solution:
   a. Dissolve 0.248 g 2,4-D in ethanol. Dilute to 10 mL with ethanol.
   b. Dissolve 0.250 g 2,4,5-T, triethylamine salt, in acetone (or 0.250 g 2,4,5-T in methanol).
   Dilute to 10 mL with acetone.
   NOTE: Use the same form (e.g., acid or salt) of 2,4,5-T as in the air sample. Recovery may vary with the chemical form.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: filter, glass fiber, binderless, in a 37-mm polystyrene two-piece cassette filter holder (Gelman type AE or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph, UV detector at 284 nm (2,4-D) and 289 nm (2,4,5-T), integrator and column (page 5001-1).
4. Filter, PTFE, 5-μm, 13-mm diameter in Swinny stainless (13-mm) filter holder.
5. Tweezers.
6. Syringes, 20-mL luer-lock.*
7. Vials, glass, 20-mL.*
8. Volumetric flasks, convenient sizes for preparing standard solutions.*

* Wash all glassware with detergent, thoroughly rinse with tap water and distilled water.

SPECIAL PRECAUTIONS: 2,4-D and 2,4,5-T are suspected animal carcinogens [4]. 2,3,7,8-Tetrachlorodibenzo-1,4-dioxin has been identified as an impurity in 2,4,5-T. Avoid any contact with these substances.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 15 to 200 L. Do not exceed a total dust loading of 2 mg on the filter.
3. Obtain information on the chemical form of the analyte (i.e., ester, salt or free acid) likely to be present in the air sample.

SAMPLE PREPARATION:

4. Remove the filter from the cassette with clean tweezers and place it in a 20-mL vial.
5. Add 15 mL methanol and mix by swirling. Allow to stand at least 30 min.
6. Filter the sample.
   a. Pour the sample solution into a 20-mL syringe which is fitted with a 5-μm PTFE filter.
   b. Filter the sample into a clean vial.
   c. Clean the PTFE filter by backflushing with methanol. Rinse the syringe and plunger with methanol. Dry with air or nitrogen.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards.
   a. Dilute aliquots of calibration stock solution to 10 mL with methanol in volumetric flasks.
   b. Analyze working standards (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg 2,4-D or mg 2,4,5-T).
8. Check recovery with at least four spiked media blanks at each of four levels.
   a. Add aliquot of recovery stock solution to media blank.
   b. Analyze using standards prepared from the recovery stock solution.
   c. Calculate R (mg recovered/mg added).

MEASUREMENT:

9. Establish chromatographic conditions listed on page 5001-1 for either 2,4-D or 2,4,5-T.
10. Inject 50 μL of sample in duplicate. Rinse and dry the syringe between samples.

    NOTE 1: The analyte is the chlorinated phenoxyacetate, whether the air sample contained salts or free acid forms of 2,4-D and 2,4,5-T.

    NOTE 2: Esters of 2,4-D and 2,4,5-T will not elute from the HPLC column and may, if present in large amounts, degrade the HPLC column. Protect the main column with a precolumn of Zipax SAX if esters are known to be present. The sample preparation conditions are sufficiently mild so as to preclude hydrolysis of the esters.

CALCULATIONS:

11. Read the mass of analyte, mg (corrected for recovery), in the sample (W) and average media blank (B) from the calibration curve.
12. Calculate the concentration, C (mg/m^3), of 2,4-D or 2,4,5-T in air volume, V (L), taken:

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Methods S279 (2,4-D) and S303 (2,4,5-T) were issued on February 17, 1978, and March 17, 1978, respectively [3], and validated using 100-L air samples [1,2,5]. Atmospheres were generated using 2,4-D dimethylamine salt for S279 and Weedar Amine BK (Amchem; equal parts of 2,4-D dimethylamine salt and 2,4,5-T triethylamine salt) for S303. Overall precision and recovery for 100-L samples were as shown, representing non-significant bias in each method:

Method	Overall Precision ($\hat{S}_{rT}$)	Range Studied		Recovery	7-Day Storage Stability,
		mg/m^3	mg per sample	@ 0.5 mg	% of Day 1
S279	0.051	5 to 20	0.5 to 2	0.97	99
S303	0.053	5 to 21	0.5 to 2	0.86 to 0.99	104

REFERENCES:

[1] Backup Data Report S279 for 2,4-D prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
[2] Backup Data Report S303 for 2,4,5-T prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Criteria for a Recommended Standard...Occupational Exposure During Manufactur and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).Welfare, Publ. (NIOSH) 79-141 (1979).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; originally validated under NIOSH Contract No. 210-76-0123.

$(C_2H_5O)_2P(=S)O(CH_2)_2SC_2H_5$ (1) MW: 258.34 CAS: 8065-48-3 RTECS: TF3150000
$(C_2H_5O)_2P(=O)S(CH_2)_2SC_2H_5$ (2)

METHOD: 5514, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA: 0.1 mg/m³ (skin)
NIOSH: 0.1 mg/m³; Group I Pesticide
ACGIH: 0.01 ppm (0.11 mg/m³) (skin)
(1 ppm = 10.56 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.18 g/mL @ 20 °C; BP 134 °C @ 270 kPa; MP −25 °C; VP 0.1 kPa (0.001 mm Hg; 1 ppm) @ 33 °C

SYNONYMS: phosphorothioic acid O,O-diethyl O-[2-(ethylthio)ethyl]ester (Demeton O)mixture with O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (Demeton S); Systox; Bayer 8169; Demox; mercaptophos

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (2-μm mixed cellulose ester + XAD-2, 150 mg/75 mg)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 30 L
-MAX: 500 L

SHIPMENT: transfer filter and front sorbent section to same vial

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.03 to 0.19 mg/m³ [1] (480-L samples)

BIAS: 0.49%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.03 [1]

ACCURACY: ± 13.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: (1) Demeton O and (2) Demeton S

DESORPTION: 5 mL toluene, 15 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 210 °C
-COLUMN: 165 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: glass, 1.2 m x 3-mm OD; 1.5% OV-17/1.95% OV-210 on 100/120 mesh Chromosorb WHP

CALIBRATION: solutions of Demeton in toluene

RANGE: 3 to 100 μg per sample

ESTIMATED LOD: 0.1 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.03 [1]

APPLICABILITY: The working range is 0.015 to 10 mg/m³ for a 200-L air sample. The use of a capillary column, e.g., a DB-210, may improve sensitivity and resolution.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S280 [2].

REAGENTS:

1. Demeton O/Demeton S mixture of known concentration, reagent grade.*
2. Toluene, reagent grade.
3. Methanol, reagent grade.
4. Methylene chloride, reagent grade.
5. Calibration stock solution, ca. 2.4 mg/mL Demeton O and 8.3 mg/mL Demeton S. Dilute 100 μL of commercially available mixture to 10 mL with toluene.
6. Hydrogen, prepurified.
7. Nitrogen, purified.
8. Oxygen, purified.
9. Air, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, supported by a stainless steel screen in a polystyrene cassette filter holder followed by a tube, 7 cm long, 8-mm OD, 6-mm ID, packed with two sections (front = 150 mg; back = 75 mg) of 20/50 mesh XAD-2. Two plastic plugs are required for capping the tube after sampling. Tubes are commercially available. (SKC, Inc. 226-30-05, or equivalent).
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Vial, scintillation, with PTFE-lined cap, graduated at 15 mL.
4. Gas chromatograph with phosphorus-sensitive FPD, integrator, and column (page 5514-1).
5. Syringes, 5-, 10- and 25-μL, for making standard solutions and GC injections.
6. Volumetric flasks, 10-mL.
7. Pipets, 5-mL.
8. Tweezers.

SPECIAL PRECAUTIONS: Demeton is a cholinesterase inhibitor and readily absorbed through the skin; baseline and routine red blood cell cholinesterase monitoring is recommended [3,4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of tubes immediately before sampling. Attach filter cassette to inlet of XAD-2 tube with short piece of tubing. Connect the outlet of sampler to pump.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 30 to 500 L.
4. Transfer the filter, the front glass wool plug, and the front sorbent section to the same vial. Cap the tube containing the back sorbent section.
5. Pack the samples securely for shipment.

SAMPLE PREPARATION:

6. Place the back sorbent section of the XAD-2 tube in a separate vial. Discard the remaining glass wool plugs.
7. Add 5.0 mL toluene to each vial. Cap each vial.
8. Allow to stand 15 min with occasional agitation. Analyze within one day.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.1 to 100 μg Demeton per sample for each isomer.
   a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area vs. μg of each isomer).
10. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13).
    e. Prepare a graph of DE vs. μg of each Demeton isomer recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5514-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 4 min for Demeton O and 7.5 min for Demeton S under these conditions.
    NOTE: If peak area is above the linear range of the working standards, dilute with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of Demeton (sum of Demeton O and Demeton S) found on the sample filter plus front sorbent section ($W + W_f$), back (W_b) sorbent section, and on the average media blank filter (B) and front (B_f) and back (B_b) media blank sorbent sections.
15. Calculate concentration, C, of Demeton in the air volume sampled, V (L):

$$C = \frac{(W + W_f) + W_b - B - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S280 for Demeton was issued on August 3, 1979 [2], and validated in the range 0.03 to 0.19 mg/m^3 for 480-L samples [1,5]. The substance used to generate test atmospheres at 25 °C and 760 mm Hg in dry air was a 0.075% solution of Demeton (21% Demeton O, 74.5% Demeton S) in toluene [1,5]. The atmosphere was generated by the aspirator method. Collection efficiencies and recovery were 1.00 for the isomers in the range 5 to 270 mg per sample. Sample filters extracted in toluene immediately and stored one week at ambient conditions gave recoveries of 100%. Overall precision for sampling plus measurement, $\hat{S}_{rT}$, was 0.08. No significant bias was found for either substance. No breakthrough was observed after 12 hours of sampling at 1 L/min in atmospheres containing 0.14 mg/m^3 Demeton O and 0.17 mg/m^3 Demeton S at 80% RH.

REFERENCES:

[1] Backup Data Report, S280 (NIOSH, unpublished, August 3, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S280, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] NIOSH Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[5] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., CDC/ATSDR; S280 originally validated under NIOSH Contract 210-76-0123.

DIACETONE ALCOHOL

See ALCOHOLS III (METHOD 1402) for procedure

DIAZOMETHANE

$CH_2=N^+N^-$ MW: 42.04 CAS: 334-88-3 RTECS: PA7000000

METHOD: 2515, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.2 ppm
NIOSH: 0.2 ppm
ACGIH: 0.2 ppm; suspect carcinogen
(1 ppm = 1.719 mg/m^3 @ NTP)

PROPERTIES: yellow gas; MP −145 °C; BP −23 °C; pure material explodes above 150 °C; impure material explodes at lower temp.

SYNONYMS: azimethylene; diazirine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (octanoic acid-coated XAD-2 resin, 100 mg/50 mg)

FLOW RATE: 0.2 L/min

VOL-MIN: 6 L
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.17 to 0.80 mg/m^3 [1] (10-L samples)

BIAS: −30% at 0.17 mg/m^3 [1]; −10% at 0.36 to 0.75 mg/m^3 [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.084 [1]

ACCURACY: 22.5% at 0.36 to 0.75 mg/m^3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl octanoate

DESORPTION: 1 mL carbon disulfide; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 95 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 3 m x 3-mm OD, 5% SP-1000 on 100/120 mesh Chromosorb WHP preceded by a 15 cm x 3-mm OD stainless steel precolumn packed with 10% Carbowax 20M and 1.2% NaOH on 80/100 mesh Gas Chrom Q

CALIBRATION: methyl octanoate in carbon disulfide with internal standard

RANGE: 2 to 8 µg diazomethane (8 to 32 µg methyl octanoate) per sample

ESTIMATED LOD: not determined

PRECISION ($\hat{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 0.1 to 0.6 ppm (0.2 to 1 mg/m^3) diazomethane for a 10-L air sample.

INTERFERENCES: None reported.

OTHER METHODS: This revises S137 [2].

REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, with internal standard, tridecane (ca. 20 μg/mL).
2. Methyl octanoate, reagent grade.
3. Octanoic acid-coated resin. Pack 20/50 mesh XAD-2 resin (Rohm & Haas Co.) into a column (length to diameter ratio ca. 10:1). Wash with three bed volumes of methanol and two bed volumes of pentane. Check the washings by GC for interfering peaks. Dry at room temperature. Weigh out ca. 10 g washed and dried XAD-2 into a round-bottomed flask. Add 25 mL acetone to form a slurry. Add octanoic acid equivalent to 1% of the sorbent weight. Evaporate the solvent in a rotary evaporator. Dry the coated resin at room temperature.
4. Hydrogen, prepurified.
5. Nitrogen, purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID,with plastic caps; two sections of 20/50 mesh 1% octanoic acid-coated XAD-2 resin preceded, separated and followed by silylated glass wool plugs (front = 100 mg; back = 50 mg). Tubes are commercially available (SKC, Inc. 226-23 or equivalent).
2. Personal sampling pump, 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2515-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); all work with it must be done in a hood away from ignition sources.

Diazomethane is an explosive, insidious poison and a strong irritant which may cause delayed hypersensitivity and cancer [3]. Concentrated solutions may explode violently, especially if impurities are present. Rough surfaces, such as ground glass, may also cause explosions [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.2 ±0.03 L/min for a total sample size of 6 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Add 1.0 mL eluent to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 32 μg methyl octanoate per sample.

a. Add known amounts of methyl octanoate to eluent in 10-mL volumetric flasks and dilute to the mark.
b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of methyl octanoate to that of the internal standard vs. μg methyl octanoate).

9. Determine desorption efficiency (DE) at least once for each lot of coated XAD-2 resin used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of methyl octanoate directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg methyl octanoate recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2515-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of methyl octanoate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Convert μg methyl octanoate to μg diazomethane by multiplying the corrected μg per sample by the conversion factor 0.2657 (molecular weight ratio, 42.04/158.24), and calculate apparent concentration, C_a (mg/m^3), of diazomethane in the air volume sampled, V (L):

$$C_a = \frac{(W_f + W_b - B_f - B_b) \cdot 0.2657}{V}, \text{ mg/m}^3.$$

15. Calculate the recovery (R) from the equation:

$$R = 0.971 - \frac{0.0327}{C_a}.$$

NOTE: This recovery was experimentally determined over the apparent concentration range 0.12 to 0.7 mg/m^3 and may not be valid outside that range [1].

16. Calculate corrected concentration, C (mg/m^3):

$$C = \frac{C_a}{R}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S137 was issued on June 6, 1975 [2]. The precision and bias were determined by analyzing generated atmospheres of diazomethane containing 0.17, 0.36 and 0.8 mg/m^3 at 26 °C and 765 mm Hg using 10-L samples [1]. The recovery (concentration found in air divided by concentration determined by an independent method involving collection in solutions of benzoic acid in xylene) was found to decrease with concentration according to the equation in step 15. Recoveries were 0.68 to 0.93 for six pairs of data in the apparent concentration range 0.12 to 7 mg/m^3. Sample stability was not determined. The method does not meet the 10% bias criterion for a valid NIOSH method.

Breakthrough of the front section of the coated XAD-2 tube was not observed after sampling 53 L of dry test atmosphere containing 0.83 mg/m^3 for 240 min at 0.22 L/min. Desorption efficiencies for samples spiked with methyl octanoate were 1.01 to 1.05. The collection efficiency and reaction of diazomethane with the octanoic acid-coated resin may be strongly dependent on sample flow rates; therefore, all samples must be collected at a flow rate of 0.2 L/min only.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S137, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S137, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] Merck Index, 10th ed., Merck & Co., Inc., NJ (1983).

METHOD REVISED BY:

Julie R. Okenfuss, NIOSH/DPSE; S137 originally evaluated under NIOSH Contract CDC-99-74-45.

DIBORANE 6006

B_2H_6 MW: 27.67 CAS: 19287-45-7 RTECS: HQ9275000

METHOD: 6006, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm
ACGIH: 0.1 ppm
(1 ppm = 1.131 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density (air = 1) 0.96; BP −92.5 °C; MP −165.5 °C
explosive range 0.8 to 98% v/v in air

SYNONYMS: boroethane, boron hydride

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SOLID SORBENT TUBE (PTFE filter + oxidizer-impregnated charcoal, 100 mg/50 mg)	**TECHNIQUE:**	PLASMA EMISSION SPECTROMETRY
FLOW RATE:	0.5 to 1 L/min	**ANALYTE:**	boron
VOL-MIN:	60 L @ 0.1 ppm	**DESORPTION:**	10 mL 3% H_2O_2; stand 30 min; ultrasonic bath 20 min
-MAX:	260 L	**WAVELENGTH:**	249.8 nm
SHIPMENT:	routine	**ENTRANCE SLITS:**	50 x 300 mm
SAMPLE STABILITY:	at least 7 days @ 25 °C [1]	**CALIBRATION:**	aliquots of 1% (v/v) diborane adsorbed on impregnated charcoal
FIELD BLANKS:	2 to 10 field blanks per set	**RANGE:**	7 to 30 μg diborane per sample [1]
		ESTIMATED LOD:	1 μg diborane per sample [1]
ACCURACY		**PRECISION ($\bar{S}_r$):**	0.063 @ 7 to 27 μg diborane per sample [1]
RANGE STUDIED:	0.06 to 0.25 mg/m^3 (120-L samples) [1]		
BIAS:	− 4.8%		
OVERALL PRECISION ($\hat{S}_{rT}$):	0.085 [1]		
ACCURACY:	± 21.5%		

APPLICABILITY: The working range is 0.05 to 0.22 ppm (0.06 to 0.25 mg/m^3) for a 120-L air sample.

INTERFERENCES: The filter removes boron-containing particulates. Avoid borosilicate glassware during sample preparation to prevent boron contamination of samples. Higher boranes (e.g., tetraborane) interfere but are not likely to be encountered in most samples.

OTHER METHODS: This revises P&CAM 341 [2]. The measurement can also be done by inductively-coupled plasma atomic emission spectrometry (e.g., Method 7300).

REAGENTS:

1. Diborane, 1% (v/v), certified gas mixture.*
2. Hydrogen peroxide (H_2O_2), 3% w/v in deionized water.
3. Calibration stock solution, 1000 μg B/mL, commercially available or dissolve 0.572 g boric acid (H_3BO_3) in deionized water to make 100 mL solution. Store in a polyethylene bottle.
4. Argon, for DC plasma excitation.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. PTFE membrane filter, 13-mm diameter, 1-μm pore size (e.g., Millipore FALP), in a plastic cassette (Millipore SX00013 or equivalent).
   b. Glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections (100 mg and 50 mg) of oxidizer-impregnated charcoal; separated and retained by silylated glass wool plugs.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Plasma emission spectrometer with a DC plasmaexcitation source.
4. Pipets, plastic, 10-mL, and 5- to 50-μL.
5. Volumetric flasks, plastic, 10-mL.
6. Bottles, screw-top, plastic, 60-mL.
7. Syringe, plastic, 10-mL, fitted with 0.5-μm PTFE filter.
8. Vials, plastic, 7-mL, screw-on septum caps.
9. Ultrasonic bath.
10. Gas-tight syringes, 0.5- and 5-mL, graduated.

SPECIAL PRECAUTIONS: Diborane is very toxic and flammable, having an Immediately Dangerous to Life or Health (IDLH) level of 40 ppm. It is a strong irritant with a repulsive, sweet odor [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the charcoal tubes immediately before sampling. Attach the filter cassette in front of the charcoal tube with a short piece of tubing. Attach the outlet of the charcoal tube to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 60 to 260 L.
4. Separate the filter and the charcoal tube. Cap the charcoal tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Pipet 10.0 mL 3% H_2O_2 into a series of plastic bottles. Quickly add the front and back charcoal sections to separate bottles and screw on the caps. Discard the glass wool plugs.
6. Allow to stand 30 min and then place in an ultrasonic bath for 20 min.
7. Draw the sample through a 0.5-μm PTFE membrane filter with a syringe.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 3% H_2O_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain boron concentrations in the range 0.1 to 4 μg B/mL.

b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (response vs. μg boron).

9. Determine desorption efficiency (DE) at least once for each lot of impregnated charcoal in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Place 100 mg impregnated charcoal (e.g., unused front sorbent section) in a vial and screw on the septum cap.
   b. Flush the gas-tight syringe with inert gas (e.g., N_2). Inject a known amount (0.1 to 5 mL) of diborane gas mixture with the syringe into the vial. Treat two parallel blanks in the same manner except that no diborane is added.
   c. Allow the vials to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg boron recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set spectrometer to conditions on page 6006-1 and as specified by the manufacturer.
12. Analyze standards and samples.
    NOTE: If response is above the range of the standards, dilute the sample solution with 3% H_2O_2, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of boron found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of diborane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.28}{V}, \text{ mg/m}^3.$$

where: 1.28 = the stoichiometric conversion factor from boron to diborane.

EVALUATION OF METHOD:

The method was tested by analyzing 18 samples, prepared by spiking 100 mg of impregnated charcoal with 6.7, 13.4 or 26.8 mg of diborane gas representing the equivalent of 120-L air samples at 0.05, 0.1 and 0.2 ppm [2]. Desorption efficiency was determined to be 0.889, 0.964, and 0.994 at these three concentrations, respectively. After analysis, the precision at the three concentrations was 8.4, 4.0, and 3.8%, respectively. Test atmospheres at 0.05, 0.1, and 0.2 ppm were generated using diborane gas. The samples were collected at 1 L/min for 2 hours in charcoal tubes containing 100 mg front/50mg back of impregnated charcoal. Eighteen samples were collected, and were desorbed one day later. The backup sections of the samples at 0.2 ppm were analyzed also. Six additional generated samples at 0.1 ppm were stored and analyzed seven days later. The average recovery of the 18 samples was 95.2%, pooled $\bar{S}_r$ = 2.7%. No trace of diborane (boron) was found in the backup section.

The seven-day storage stability samples indicated an average recovery of 101.6 $\pm$ 2.1%.

Breakthrough tests were conducted with a generated test atmosphere at 1.9 ppm with four impregnated charcoal tubes. The sample volume was 120 L. The average collection efficiency in the front sections was 99.8 $\pm$ 0.3%. Breakthrough occurred in only two samples indicating 0.6 and 0.2% breakthrough. An additional breakthrough study was conducted with a generated test atmosphere containing 0.34 ppm diborane at a relative humidity of 60 to 70%. Two impregnated charcoal tubes were collected after

60 min, two after 120 min, and two after 235 min. No breakthrough was detected in any sample. Therefore, the capacity of the charcoal tube is at least 80 μg diborane.

A filter study was conducted with 12 samples collected simultaneously, six with a prefilter and six without the prefilter, at 0.1 ppm. The results indicated that the use of the PTFE filters does not affect the precision or accuracy of the method. Mixed cellulose ester membrane prefilters produced a loss of 7.5% in the collection efficiency and, therefore, are not recommended as prefilters.

REFERENCES:

[1] Arthur D. Little, Inc., Backup Data Report for Diborane, prepared under NIOSH Contract No. 210-80-0099 (June 1, 1981).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 341, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

B.R. Belinky, NIOSH/DPSE and J. Palassis, NIOSH/DTMD.

DIBUTYL PHOSPHATE 5017

$(C_4H_9O_2)(OH)P=O$ MW: 210.21 CAS: 107-66-4 RTECS: TB9605000

METHOD: 5017, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 1 ppm
NIOSH: 1 ppm; STEL 2 ppm
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 8.59 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.06 g/mL; decomposes @ 100 °C; VP unknown

SYNONYMS: phosphoric acid dibutyl ester

SAMPLING

SAMPLER: FILTER (1.0-μm PTFE)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L @ 1 ppm
-MAX: 250 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days at room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.3 to 10 mg/m^3 [1] (180-L samples)

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: dibutyl trimethylsilyl phosphate

DESORPTION: acetonitrile

DERIVATIZATION: N,O-bis(trimethylsilyl)tri fluoroacetamide (BSTFA)

INJECTION VOLUME: 1 μL

CARRIER GAS: He, 30 mL/min

TEMPERATURE-INJECTION: 220 °C
-DETECTOR: 210 °C
-COLUMN: 155 °C

COLUMN: glass; 1.2 m x 6-mm OD; 3% OV-101 on 100/120 mesh Chromosorb WHP

CALIBRATION: dibutyl phosphate in CH_3CN with internal standard

RANGE: 0.4 to 2 mg per sample

ESTIMATED LOD: 0.07 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.017 [1]

APPLICABILITY: The working range is 0.2 to 1.2 ppm (2 to 10 mg/m^3) for a 200-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This method revises P&CAM 297 [2].

REAGENTS:

1. Dibutyl phosphate,* purified 99%, according to Ref. [3].
2. Eluent: Acetonitrile, reagent grade, containing 0.1% (v/v) tributyl phosphate internal standard.
3. Calibration stock solution, 45 mg/mL. Dissolve 0.45 g purified dibutyl phosphate in 10 mL acetonitrile.
4. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), reagent grade.
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE membrane filter, 1-μm, (Millipore FA or equivalent), 37-mm diameter in a two-piece polystyrene cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Jars, squat-form, 60-mL, with PTFE film gaskets, and screw caps.
4. Vial, 2-mL, with PTFE-lined caps.
5. Gas chromatograph with phosphorus FPD, integrator, and column (page 5017-1).
6. Syringes, 5-, 10-, and 25-μL, for making standard solutions and GC injections.
7. Volumetric flasks, 10- and 100-mL.
8. Pipets, 1- and 5-mL.
9. Tweezers.

SPECIAL PRECAUTIONS: Dibutyl phosphate is toxic if inhaled or comes in contact with the eyes or skin [3]. Sample preparations should be conducted in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 50 to 250 L.

SAMPLE PREPARATION:

3. Using tweezers, carefully transfer the filter to a 60-mL jar.
4. Pipet 5.0 mL eluent into each jar. Cap the jar.
5. Allow to stand 30 min with occasional agitation.
6. Transfer 1.0 mL of the extract to a 2-mL vial. Add 100 μL BSTFA. Cap the vial, shake thoroughly, and let stand 30 min.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.1 to 2 mg dibutyl phosphate per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (ratio of peak area of dibutyl phosphate to peak area of internal standard vs. mg dibutyl phosphate).
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

9. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5017-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
   NOTE 1: Under these conditions, approximate retention times are 4 min for dibutyl phosphate and 6 min for tributyl phosphate.
   NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
10. Measure peak area. Divide the peak area of dibutyl phosphate derivative by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

11. Determine the mass, mg of dibutyl phosphate found in the sample (W), and in the average media blank (B).
12. Calculate concentration, C (mg/m^3), of dibutyl phosphate in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 297 was issued on November 8, 1978 [2]. The substance used to generate test atmospheres at 25 °C and 760 mm Hg in dry air was technical grade dibutyl phosphate containing ca. 55% dibutyl phosphate and 45% monobutyl phosphate [1,4]. The collection efficiencies and measurement recoveries were 1.00 in the range 0.5 to 5 mg per sample. Sample filters stored one week at ambient conditions gave recovery of 106 ± 5%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.057. No independent method was available to estimate bias.

REFERENCES:

[1] Backup Data for P&CAM 297, prepared under NIOSH Contract 210-76-0123 (unpublished, November 8, 1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 297, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., ATSDR. P&CAM 297 prepared under NIOSH Contract 210-76-0123.

DIBUTYL PHTHALATE 5020

$C_6H_4(COO(CH_2)_3CH_3)_2$ MW: 278.35 CAS: 84-74-2 RTECS: TI0875000

METHOD: 5020, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3
ACGIH: 5 mg/m^3

PROPERTIES: oily liquid; d 1.047 g/mL @ 20 °C; MP −37 °C; BP 340 °C; VP <1 Pa (<0.01 mm Hg) @ 20 °C

SYNONYMS: di-n-butyl phthalate; phthalic acid dibutyl ester; DBP

SAMPLING

SAMPLER: FILTER (0.8 μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 6 L @ 5 mg/m^3
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 10 mg/m^3 [1] (30-L samples)

BIAS: −8.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ±16.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dibutyl phthalate

DESORPTION: 2 mL CS_2; 30 min in ultrasonic bath

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 300 °C
-DETECTOR: 300 °C
-COLUMN: 200 to 250 °C

CARRIER GAS: He, 30 mL/min

COLUMN: 2 m x 3-mm OD stainless steel, 5% OV-101 on 100/120 mesh Chromosorb W-HP

CALIBRATION: solutions of analyte in CS_2 with internal standard

RANGE: 30 to 500 μg per sample

ESTIMATED LOD: 10 μg per sample

PRECISION ($\hat{S}_r$): 0.05 @ 70 to 300 μg per sample [1]

APPLICABILITY: The working range is 1 to 20 mg/m^3 for a 30-L air sample. Phthalates are widely used as plasticizers for many resins and elastomers.

INTERFERENCES: None identified. An alternate GC column is 10 m x 0.25-mm ID, 0.25-μm DB-1, fused silica capillary.

OTHER METHODS: This method combines and replaces Methods S33 [3] and S40 [4].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.05% (w/v) heneicosane, tetradecane, tricosane, di(2-ethylhexyl)adipate or other suitable internal standard.
2. Analytes: dibutyl phthalate and di(2-ethylhexyl) phthalate.
3. Recovery stock solution, 10 mg/mL. Dissolve 0.1 g of each analyte in CS_2 to make 10 mL solution.
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-mm pore size, 37-mm diameter, in two-piece cassette filter holder with backup pad.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 5020-1).
4. Vials, glass, 5-mL, PTFE-lined caps.
5. Syringes, 1- and 10-μL and other convenient sizes for making standards.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 2-mL, with pipet bulb.
8. Ultrasonic bath.
9. Tweezers.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a dangerous fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove cassette plugs immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 6 to 200 L.
4. Cap the samplers with the cassette plugs and pack securely for shipment.

SAMPLE PREPARATION:

5. Open the cassette and carefully transfer the filter with tweezers to a 5-mL vial. Discard the backup pad.
6. Add 2.0 mL eluent to each vial and attach caps.
7. Agitate for 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 10 to 500 μg analyte per sample.
   a. Add known amounts of analyte (or standard solution of analyte in CS_2) to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg analyte).
9. Determine recovery (R) at least once for each lot of filters used for sampling in the calibration range. Prepare three filters at each of five concentrations plus three media blanks.
   a. Deposit a known amount (1 to 50 μL) of recovery stock solution onto the filter. Allow filters to air dry.

b. Store samples overnight in cassettes.
c. Prepare for analysis (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
d. Prepare a graph of R vs. μg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions on page 5020-1. Inject sample manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for recovery) of analyte found on the filter (W) and in the average media blank (B).
14. Calculate concentration, C, of analyte in the air volume sampled, V(L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S33 (dibutyl phthalate) [3] and S40 [di(2-ethylhexyl) phthalate] [4] were issued on January 17, 1975 and validated over the range 2 to 10 mg/m^3 at 23° and 25 °C and 767 mm and 761 mm Hg, respectively, using 30- and 32-L air samples [1,2]. Test atmospheres of the phthalates were generated using a Royco generator/impinger system and calibrated using the GC assay procedure. Overall precision, $\hat{S}_{rT}$, was 0.057 for both compounds with average recoveries for generated samples of 94 and 107%, respectively. Extraction efficiencies were 97 and 96% in the range 0.07 to 0.30 mg per sample. Collection efficiency for aerosols (less than 5 μm) on this type filter was greater than 99.9%. Storage stability for dibutyl phthalate was at least 6 days at 25 °C. The stability of di(ethylhexyl)phthalate was not determined.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, S33, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] Ibid., S40.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S33, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid., S40.

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S33 and S40 originally validated under NIOSH Contract CDC-99-74-55.

o-DICHLOROBENZENE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

p-DICHLOROBENZENE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

3,3'-DICHLOROBENZIDINE 5509
(See Method 5509, BENZIDINE, for procedure)

$(C_6H_3ClNH_2)_2$ MW: 253.13 CAS: 91-94-1 RTECS: DD0525000

METHOD: 5509, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : carcinogen (29 CFR 1910.1010)
NIOSH: carcinogen (29 CFR 1910.1010)
ACGIH: carcinogen (skin)

PROPERTIES: solid; MP 132 °C

SYNONYMS: 3,3'-dichloro[1,1'-biphenyl]-4,4'-diamine.

SAMPLING

SAMPLER: FILTER (13-mm glass fiber)

FLOW RATE: 0.2 L/min

VOL-MIN: 20 L @ 10 $\mu g/m^3$
-MAX: 100 L

SHIPMENT: ship benzidine samples in dry ice

SAMPLE STABILITY: 12 days @ 23 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	20 to 130 $\mu g/m^3$ [1]
BIAS:	− 4.0%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.07 [1]
ACCURACY:	± 15.2%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 3,3'-dichlorobenzidine

DESORPTION: 0.5 mL 0.17% (v/v) triethylamine in methanol; stand 60 min

INJECTION VOLUME: 15 μL

MOBILE PHASE: 70% acetonitrile/30% water

FLOW RATE: 1.5 mL/min; ambient temperature

COLUMN: μBondapak C_{18}, 10-μm particles, 30 cm x 4-mm

DETECTOR: UV, 254 nm

CALIBRATION: solutions of 3,3-dichlorobenzidine in eluent

RANGE: 0.2 to 7 μg per sample

ESTIMATED LOD: 0.05 μg per sample [1]

PRECISION ($\bar{S}_r$): ≤0.07 [1]

APPLICABILITY: The working range is 4 to 200 mg/m^3 for a 50-L air sample. Benzidinium sulfate and 3,3'-dichlorobenzidine dihydrochloride will be collected and converted to benzidine and 3,3'-dichlorobenzidine, respectively, during sample preparation.

INTERFERENCES: Aniline interferes in the determination of benzidine but may be resolved [2]. 4,4'-Methylenebis(2-chloroaniline) interferes in the determination of 3,3'-dichlorobenzidine [1]. A number of compounds were shown not to interfere [1,2] (see NOTE 2, step 12).

OTHER METHODS: This combines and replaces P&CAM 243 and P&CAM 246 [3].

DICHLORODIFLUOROMETHANE 1018

CCl_2F_2 MW: 120.91 CAS: 75-71-8 RTECS: PA8200000

METHOD: 1018, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
(1 ppm = 4.95 mg/m^3 @ NTP)

PROPERTIES: gas; BP −29.8 °C; MP −158 °C: d 1.35 @ 21.1 °C; nonflammable

SYNONYMS: difluorodichloromethane; Refrigerant 12

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400/200 mg and 100/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 1000 ppm
-MAX: 4 L

SHIPMENT: refrigerated

SAMPLE STABILITY: at least 7 days @ −10 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2940 to 10,500 mg/m^3 [1]

BIAS: − 1.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.063 [1]

ACCURACY: ± 12.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dichlorodifluoromethane

DESORPTION: 20 mL methylene chloride

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 260 °C
-COLUMN: 35 °C for 3 min, 15 °C/min to 75 °C, hold 6 min

CARRIER GAS: He, 1.5 mL/min

COLUMN: DB-1 fused silica capillary, 30 m x 0.32-mm ID, 1-µm film thickness or equivalent

CALIBRATION: standard solutions of analyte in methylene chloride

RANGE: 5 to 30 mg per sample [1]

ESTIMATED LOD: 0.03 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.035 @ 7.4-30 mg per sample [1]

APPLICABILITY: The working ranges are 1000 to 6000 ppm dichlorodifluoromethane (5000 to 30,000 mg/m^3); 700 to 5700 ppm 1,2-dichlorotetrafluoromethane (5000 to 40,000 mg/m^3); and 300 to 4000 ppm chlorodifluoromethane (1000 to 14,000 mg/m^3) for a 1-L air sample. This method was first evaluated for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane with packed column gas chromatography [1]. The method was recently evaluated specifically for chlorodifluoromethane using capillary chromatography [3]. Capillary GC conditions for the separation of the three compounds were established.

INTERFERENCES: None identified.

OTHER METHODS: This combines and revises Methods S111 and S108 [2].

REAGENTS:

1. Chlorodifluoromethane, 99%
2. Dichlorodifluoromethane, 99%
3. 1,2-Dichlorotetrafluoroethane, 99%
4. Methylene chloride*, distilled in glass.
5. Nitrogen, purified.
6. Hydrogen, prepurified
7. Air, filtered, compressed.
8. Helium, purified

* See Special Precautions

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8-mm OD, 6-mm ID, followed by 7 cm long, 6-mm OD, 4-mm ID) connected in series with a short piece of tubing, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (1st 400 mg/200 mg; 2nd 100 mg/50 mg), front and back sections separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 25 mm/Hg. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 mL/min, with flexible connecting tubing.
3. Refrigerant, bagged (Blue Ice, or equivalent).
4. Gas chromatograph with a FID detector, recorder, integrator and column (page 1018-1).
5. Bottles, 22-mL, PTFE-lined septum screw caps.
6. Syringes, gas-tight, 10-mL and other sizes as needed.
7. Pipet, TD, 20-mL, with pipet bulbs.
8. DE apparatus. Glass or plastic T equipped with septum in one arm to allow introduction of analyte to a flowing stream of nitrogen.

SPECIAL PRECAUTIONS: Methylene chloride is an irritant, can be absorbed through the skin, and is a suspect carcinogen [4]. Prepare samples in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 4 L.
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: Refrigerate samples at −10 °C if not analyzed immediately.

5. Pipet 20.0 mL methylene chloride into a series of bottles.
6. Place both sections of the front sampler tube into a bottle containing solvent, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 hrs.
7. Perform step 6 for the back sampler tube.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Pipet 20.0 mL methylene chloride into each of a series of bottles. Cap the bottles.
   b. Using a gas-tight syringe, add known amounts of analyte, e.g., 0.01 to 6 mL (0.0354 to 21.2 mg @ NTP) chlorodifluoromethane, or 0.01 to 6 mL (0.0495 to 29.7 mg @ NTP) dichlorodifluoromethane, or 0.01 to 6 mL (0.0699 to 41.9 mg @ NTP) 1,2-dichlorotetrafluoroethane by bubbling the gas slowly through the methylene chloride. Gently shake the bottles.
   c. Analyze with samples and blanks (steps 11 and 12).
   d. Prepare calibration graph (area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Using a gas-tight syringe, inject a known amount of analyte (0.01 to 6 mL) through the septum of the DE apparatus unto a stream of nitrogen (ca. 20 mL/min) which carries the analyte into a large (400/200 mg) sorbent tube. Allow the nitrogen to flow an additional 30.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12)
   d. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1018-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with methylene chloride, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.
    NOTE: The order of elution is chlorodifluoromethane, dichlorodifluoromethane, 1,2-tetrafluoroethane. If analyzing for two or more of the compounds, a temperature rate of 5 °C/min is required.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Validation this method for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane was done using packed column gas chromatographic techniques. The column was stainless steel 1.2 m x 6-mm OD, packed with 80/100 mesh Chromosorb 102. Chlorodifluoromethane was evaluated using the capillary chromatographic conditions listed on p.1018-1. The use of capillary gas chromatographic analysis was determined to be appropriate for all three compounds.

Dichlorodifluoromethane: Method S111 was issued September 30, 1976 [2], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [1,5]. Average recovery for 18 samples was 98.2%. In breakthrough tests at 12 and 94% relative humidity (RH), the capacity of the sampler was 61 and 44 mg of dichlorodifluoromethane, respectively, when sampling at ca. 0.045 L/min from atmospheres containing ca. 10,000 mg/m^3. Desorption efficiency averaged 0.97 in the range 7.4 to 30 mg per sample.

Dichlorotetrafluoroethane: Method S108 was issued October 29, 1976 [2], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [1,4]. The average recovery for 18 samples was 99.8%. Breakthrough (effluent concentration = 5% of test concentration) occurred after 158 min when sampling 14,600 mg/m^3 at 90% RH at 0.046 L/min. Desorption efficiency averaged 0.99 in the range 10.7 to 42.8 mg per sample.

Chlorodifluoromethane: The precision and accuracy of the method were determined using test gas bag atmospheres generated and monitored with a halide meter. Average recovery for 18 samples over the range of 1780 to 6970 mg/ m^3 was 100 %. In breakthrough tests at 80% relative humidity, the sampler retained 15.4 mg of chlorodifluoromethane when sampling at 0.025 L/min from atmospheres containing 7000 mg/m^3. The desorption efficiency of chlorodifluoromethane from activated charcoal averaged 0.96 in the range 0.53 to 10.4 mg per sample.

REFERENCES:

[1] Backup Data Reports S111 (Dichlorodifluoromethane) and S108 (Dichlorotetrafluoroethane), prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712, from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S111 and S108, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Seymour, M.J., M.F. Lucas. Evaluation of Sampling and Analytical Methods for the Determination of Chlorodifluoromethane in Air, Am. Ind. Hyg. Assoc. J., 54, 253-259 (1993).
[4] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

M.J. Seymour, NIOSH/DPSE.

1,1-DICHLOROETHANE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

1,2-DICHLOROETHYLENE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

DICHLOROETHYL ETHER

$(ClCH_2CH_2)_2O$ MW: 143.01 CAS: 111-44-4 RTECS: KN0875000

METHOD: 1004, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : C 15 ppm (skin)
NIOSH: 5 ppm; STEL 10 ppm (skin); carcinogen
ACGIH: 5 ppm; STEL 10 ppm (skin); carcinogen
(1 ppm = 5.85 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.218 g/mL @ 20 °C;
BP 178 °C; MP −52 °C;
VP 50 Pa (0.4 mm Hg; 530 ppm) @ 20 °C

SYNONYMS: bis(2-chloroethyl) ether; 1,1'-oxybis[2-chloroethane]; 2,2'-dichlorodiethyl ether; sym-dichloroethyl ether

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L @ 15 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 45 to 180 mg/m^3 [1]
(15-L samples)

BIAS: − 7.61%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.059 [1]

ACCURACY: ± 15.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dichloroethyl ether

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 - 225 °C
-DETECTOR: 250 - 275 °C
-COLUMN: 100 - 135 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3-mm ID stainless steel; 10% FFAP on 80/100 mesh DMCS Chromosorb W-AW or equivalent

CALIBRATION: dichloroethyl ether in CS_2

RANGE: 0.15 to 4 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION ($\bar{S}_r$): 0.007 [1]

APPLICABILITY: The working range is 1.7 to 46 ppm (10 to 270 mg/m^3) for a 15-L air sample. This method may be used for simultaneous analysis of two or more analytes by changing the chromatographic conditions (e.g., temperature programming). High humidity during sampling will greatly reduce breakthrough volume.

INTERFERENCES: None identified. Alternate columns, e.g., 10% SP-1000 on 80/100 mesh Supelcoport, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column may be used.

OTHER METHODS: This is Method S357 [2] in a revised format.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing 0.1% (v/v) toluene or other suitable internal standard.
2. Dichloroethyl ether (DCEE).
3. Hexane.
4. Calibration stock solution, 0.244 mg/μL. Dilute 2.44 g DCEE (2.0 mL at 20 °C) to 10 mL with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1004-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 2 to 15 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 4 mg DCEE per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg DCEE).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg DCEE recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1004-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of DCEE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of DCEE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S357 [2] was issued on May 21, 1976, and validated over the range 45 to 180 mg/m^3 at 24 °C and 762 mm Hg using a 15-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.059 with average recovery 90.7%, representing a non-significant bias. The concentration of DCEE was independently verified by a direct hydrocarbon analyzer. Desorption efficiency was 0.94 in the range 0.7 mg to 2.7 mg per sample. Breakthrough (5% on back section) occurred at 115 min when sampling an atmosphere containing 161 mg/m^3 at 0.9 L/min in dry air.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, NIOSH, S357, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S357, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] User check, UBTL, NIOSH Sequence #4121-J (unpublished, November 21, 1983).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon, NIOSH/DPSE; S357 originally validated under NIOSH Contract CDC-99-74-45.

DICHLOROFLUOROMETHANE 2516

$CHCl_2F$ MW: 102.92 CAS: 75-43-4 RTECS: PA8400000

METHOD: 2516, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 10 ppm
ACGIH: 10 ppm
(1 ppm = 4.21 mg/m^3 @ NTP)

PROPERTIES: gas; BP 8.9 °C; d 1.405 g/mL @ 9 °C; vapor density (air = 1) 3.82; not combustible

SYNONYMS: Freon 21; Halon 112; dichloromonofluoromethane

SAMPLING

SAMPLER: SOLID SORBENT TUBES (2 coconut shell charcoal tubes, 400 mg and 200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.25 L @ 1000 ppm
-MAX: 3 L

SHIPMENT: separate front and backup tubes to avoid migration

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1730 to 7640 mg/m^3 [1] (3-L samples)

BIAS: 3.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.061 [1]

ACCURACY: ± 13.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dichlorofluoromethane

DESORPTION: 5 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 125 °C
-DETECTOR: 220 °C
-COLUMN: 55 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 6 m x 3-mm, 10% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: dichlorofluoromethane solutions in CS_2 with internal standard

RANGE: 1 to 35 mg per sample

ESTIMATED LOD: 0.05 mg per sample

PRECISION ($\bar{S}_r$): 0.024 @ 6 to 34 mg per sample [1]

APPLICABILITY: The working range is 120 to 1500 ppm (500 to 6300 mg/m^3) for a 2-L air sample.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S109 [2].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.4% v/v pentane as internal standard.
2. Dichlorofluoromethane, 99%.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes connected in series with a short piece of plastic tubing; each tube 10 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg; back tube = 200 mg). A plug of silylated glass wool is placed at each end of each tube. Pressure drop across sampler less than 3.4 kPa (2.5 cm Hg) at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2516-1).
4. Vials, glass, serum, 10-mL, with PTFE-lined septa and crimp caps.
5. Syringe, 10-μL.
6. Syringes, gas-tight, 10-mL and 100-μL.
7. Syringe needles, 22-gauge.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an extreme fire and explosion hazard (flash point = −30 °C); work with it only in a hood. Dichlorofluoromethane may cause irregular heartbeat if inhaled [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.25 to 3 L.
4. Separate the front and back tubes immediately after sampling. Cap the tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool plugs. Attach crimp cap to each vial. Insert a syringe needle vent through the septum to serve as a vent.
6. Add 5.0 mL eluent to each vial with a syringe. Remove the syringe needle vent from the septum.
   NOTE: To avoid loss of analyte, do not add eluent to the charcoal before sealing the vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.05 to 35 mg (0.01 to 8.2 mL at 20 °C and 101 kPa) dichlorofluoromethane per sample.
   a. Add 5.0 mL eluent to each of a series of vials. Attach crimp cap to each vial.

b. Immediately before adding dichlorofluoromethane, withdraw from each vial an amount of air equal to that of dichlorofluoromethane to be added.
c. Slowly bubble a measured amount of dichlorofluoromethane into the liquid in each vial using a gas-tight syringe.
d. Analyze together with samples and blanks (steps 11 and 12).
e. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg dichlorofluoromethane).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Inject a known amount of dichlorofluoromethane slowly and directly into a medial blank front sorbent section with a gas-tight syringe.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. mg dichlorofluoromethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2516-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 6 min under these conditions.
    NOTE 1: If an autosampler is used, transfer an aliquot of the sample solution to a sealed empty vial using a syringe needle as a vent.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard of the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of dichlorofluoromethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of dichlorofluoromethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S109 was issued on September 30, 1976 [2], and validated over the range 2100 to 12,600 mg/m^3 by analyzing 18 spiked samples and 18 samples collected from dynamically-generated atmospheres of dichlorofluoromethane gas [1,4]. These recoveries were 100.9 and 102.9%, respectively. A combined storage migration study determined that samples of 17 and 35 mg had a 100% recovery after seven days if stored without backup sections. At the same levels, those front sections stored with backup sections had 83.2% recovery. Breakthrough (5%) in an atmosphere of 9120 mg/m^3 and 90% RH, sampling at 0.187 L/min, occurred at 23 min. giving a breakthrough volume of 4.3 L and tube capacity of 39 mg. In a dry atmosphere of 8850 mg/m^3, breakthrough occurred after 64 min sampling at 0.187 L/min, giving a breakthrough volume of 12.0 L and tube capacity of 102 mg. Desorption efficiencies averaged 101% over the range 5.9 to 34 mg dichlorofluoromethane per sample.

REFERENCES:

[1] Backup Data Report, S109, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S109, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Dichlorofluoromethane, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE; S109 originally validated under NIOSH Contract 210-76-0123.

1,1-DICHLORO-1-NITROETHANE

$H_3CC(Cl)_2NO_2$ MW: 143.96 CAS: 594-72-9 RTECS: KI1050000

METHOD: 1601, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : C 10 ppm
NIOSH: 2 ppm
ACGIH: 2 ppm
(1 ppm = 5.89 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.405 g/mL @ 20 °C; BP 124 °C; VP 2 kPa (15 mm Hg; 2% v/v) @ 20 °C

SYNONYMS: dichloronitroethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 1.5 L @ 10 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 27 to 115 mg/m^3 [1] (17-L samples)

BIAS: − 0.12%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 11.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1-dichloro-1-nitroethane

DESORPTION: 1 mL CS_2, stand 30 min

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3-mm stainless steel, 5% SP-1000 on 100/120 mesh Chromosorb WHP, or equivalent

CALIBRATION: analyte solutions in CS_2 with undecane as internal standard

RANGE: 0.09 to 2.7 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.038 [1]

APPLICABILITY: The working range is 1 to 30 ppm (6 to 180 mg/m^3) for a 15-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. Alternate chromatographic columns to circumvent interferences are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column.

OTHER METHODS: This is Method S213 [2] in a revised format.

REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, containing 0.2% v/v undecane or other suitable internal standard.
2. 1,1-Dichloro-1-nitroethane.
3. Calibration stock solution, 0.211 mg/μL. Dilute 2.11 g 1,1-dichloro-1-nitroethane (1.5 mL @ 20 °C) to 10 mL with CS_2. Prepare in duplicate.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated petroleum-based charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector,integrator and column (page 1601-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 1.5 to 15 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 2.7 mg 1,1-dichloro-1-nitroethane per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg 1,1-dichloro-1-nitroethane).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg 1,1-dichloro-1-nitroethane recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1601-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1-dichloro-1-nitroethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of 1,1-dichloro-1-nitroethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S213 [2] was issued on November 21, 1975, and validated over the range 27 to 115 mg/m^3 at 23 °C and 763 mm Hg using a 17-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.055, with average recovery 97.7%, representing a non-significant bias. SKC Lot 104 charcoal was the collecting medium. The concentration of analyte was independently verified by calibrated syringe pump. Desorption efficiency was 0.910 in the range 0.5 mg to 2.0 mg analyte per sample. Breakthrough (5% on back section) occurred at 193 min when sampling an atmosphere containing 116 mg/m^3 1,1-dichloro-1-nitroethane at 0.79 L/min in dry air.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, NIOSH, S213, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S213, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon, NIOSH/DPSE; S213 originally validated under NIOSH Contract CDC-99-74-45.

1,2-DICHLOROTETRAFLUOROETHANE
See DICHLORODIFLUOROMETHANE (METHOD 1018) for procedure

$CClF_2CClF_2$ MW: 170.92 CAS: 76-14-2 RTECS: KI1101000

METHOD: 1018, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
(1 ppm = 6.99 mg/m^3 @ NTP)

PROPERTIES: gas; BP 3.8 °C; MP −94 °C

SYNONYMS: cryofluorane, Refrigerant 114

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400/200 mg and 100/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 1000 ppm
-MAX: 4 L

SHIPMENT: refrigerated

SAMPLE STABILITY: at least 7 days @ −10 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	1800 to 6970 mg/m^3 [3]
BIAS:	0%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.074 [3]
ACCURACY:	± 14.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,2-dichlorotetrafluoroethane

DESORPTION: 20 mL methylene chloride

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR:	200 °C
-DETECTOR:	260 °C
-COLUMN:	35 °C for 3 min, 15 °C/min to 75 °C, hold 6 min

CARRIER GAS: He, 1.5 mL/min

COLUMN: DB-1 fused silica capillary, 30 m x 0.32-mm ID, 1-µm film thickness or equivalent

CALIBRATION: standard solutions of analyte in methylene chloride

RANGE: 5 to 40 mg per sample [1]

ESTIMATED LOD: 0.03 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.038 @ 10-40 mg per sample [1]

APPLICABILITY: The working range is 700 to 5700 ppm 1,2-dichlorotetrafluoroethane (5000 to 40,000 mg/m^3) for a 1-L air sample. This method was first evaluated for dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane with packed column gas chromatography [1].

INTERFERENCES: None identified.

OTHER METHODS: This combines and revises Methods S111 and S108 [2].

DIETHYLAMINE

See AMINES, ALIPHATIC (Method 2010) for procedure

DIETHYLENETRIAMINE
See ETHYLENEDIAMINE, Method 2540, for Procedure

$H_2N(CH_2)_2NH(CH_2)_2NH_2$ MW: 103.2 CAS: 111-40-0 RTECS: IE1225000

METHOD: 2540, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: 1 ppm (skin)
ACGIH: 1 ppm (skin)
(1 ppm = 4.21 mg/m^3)

PROPERTIES: liquid; d 0.96 g/mL @ 20 °C; BP 206.7 °C; VP 0.5 kPa (0.37 mm Hg); flash point 98 °C

SYNONYMS: diethylenetriamine: DETA; aminoethylethandiamine; 3-azapentane-1,5-diamine; bis(2-aminoethyl)amine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (1-naphthylisothiocyanate-coated XAD-2, 80 mg/40 mg)

FLOW RATE: 0.01 to 0.1 L/min [1]

VOL-MIN: 1 L @ 10 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: >30 days @ 20 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.016 to 8 mg/m^3; (10-L samples)

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1]

BIAS: −1.9%

ACCURACY: ±13.5%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: naphthylisothiourea derivative of analytes

DESORPTION: 2 mL dimethylformamide (DMF), ultrasonic 30 min

INJECTION VOLUME: 10 µL

COLUMN: 10-µm radial cyano, 10 cm x 8-mm ID in Waters RCM-100 radial compression mode

MOBILE PHASE: 50/50 isooctane/isopropanol at 3 mL/min

CALIBRATION: standard solutions of derivatives in DMF

RANGE: 1 to 80 µg per sample

ESTIMATED LOD: 0.16 µg per sample

PRECISION ($\bar{S}_r$): 0.007

APPLICABILITY: The working range for DETA is 0.05 to 150 mg/m^3 for a 10-L air sample. This method is the result of evaluation [2] of OSHA Method #60 for DETA, EDA, TETA [1]. The theoretical capacity of each front section is 1.5 mg of DETA.

INTERFERENCES: Other primary or secondary amines may react with the sampler coating reagent, and thereby reduce the sampler capacity.

OTHER METHODS: This replaces NIOSH Method P&CAM 276 [3]. The method of Anderson, et al., for EDA [4] is an alternate method using thiourea derivatization and HPLC analysis.

DI(2-ETHYLHEXYL) PHTHALATE
See DIBUTYL PHTHALATE (Method 5020) for Procedure

$C_6H_4(COOCH_2CH(C_2H_5)(CH_2)_3CH_3)_2$ MW: 390.56 CAS: 117-81-7 RTECS: TI0350000

METHOD: 5020, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3; STEL 10 mg/m^3
NIOSH: 5 mg/m^3; STEL 10 mg/m3 (carcinogen)
ACGIH: 5 mg/m^3; STEL 10 mg/m^3 (suspect carcinogen)

PROPERTIES: oily liquid; d 0.983 g/mL @ 20 °C; MP −50 °C; BP 386 °C; VP < 1 Pa (0.01 mm Hg) @ 20 °C

SYNONYMS: bis(2-ethylhexyl) phthalate; dioctyl phthalate; DOP; DEHP (listed incorrectly as di-sec-octyl phthalate in 29 CFR 1910.23)

SAMPLING

SAMPLER: FILTER (0.8 μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 6 L @ 5 mg/m^3
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 11 mg/m^3 [2] (32-L samples)

BIAS: 7.56%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1,2]

ACCURACY: ± 19.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: di(2-ethylhexyl)phthalate

DESORPTION: 2 mL CS_2; 30 min in ultrasonic bath

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 300 °C
-DETECTOR: 300 °C
-COLUMN: 200 to 250 °C

CARRIER GAS: He, 30 mL/min

COLUMN: 2 m x 3-mm OD stainless steel, 5% OV-101 on 100/120 mesh Chromosorb W-HP

CALIBRATION: solutions of analytes in CS_2 with internal standard

RANGE: 30 to 500 μg per sample

ESTIMATED LOD: 10 μg per sample

PRECISION ($\hat{S}_r$): 0.05 @ 0.07 to 0.3 mg per sample [2]

APPLICABILITY: The working range is 1 to 20 mg/m^3 for a 30-L air sample. Phthalates are widely used as plasticizers for many resins and elastomers.

INTERFERENCES: None identified. An alternate GC column is 10 m x 0.25-mm ID, 0.25-μm DB-1, fused silica capillary.

OTHER METHODS: This revises method S40 [4].

DIFLUORODIBROMOMETHANE 1012

CBr_2F_2 MW: 209.83 CAS: 75-61-6 RTECS: PA7525000

METHOD: 1012, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: 100 ppm
ACGIH: 100 ppm
(1 ppm = 8.58 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.35 g/mL @ 0 °C; BP 24.5 °C; FP −141 °C; VP 83 kPa (620 mm Hg; 82% v/v) @ 20 °C; non-flammable

SYNONYMS: dibromodifluoromethane; Freon 12B2

SAMPLING

SAMPLER: SOLID SORBENT TUBES (2 tubes in tandem, each with 150 mg coconut shell charcoal)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2.5 L
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 470 to 1875 mg/m^3 [1] (10-L samples)

BIAS: 2.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [1]

ACCURACY: ± 18.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: difluorodibromomethane

DESORPTION: 1.0 mL 2-propanol; stand overnight

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 60 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 6 mm OD stainless steel, packed with 10% FFAP on 100/120 Chromosorb WHP or equivalent

CALIBRATION: difluorodibromomethane in 2-propanol

RANGE: 2 to 20 mg per sample

ESTIMATED LOD: 0.4 mg per sample

PRECISION ($\bar{S}_r$): 0.067 @ 4 to 19 mg per sample [1]

APPLICABILITY: The working range is 200 to 2000 mg/m^3 (23 to 230 ppm) for a 10-L air sample. Difluorodibromomethane is used in the synthesis of dyes, pharmaceuticals, and quaternary ammonium compounds, and as a fire extinguishing agent.

INTERFERENCES: Carbon disulfide has about the same GC retention volume as difluorodibromomethane [1].

OTHER METHODS: This is Method S107 in a revised format [2].

REAGENTS:

1. 2-Propanol, chromatographic grade.
2. Difluorodibromomethane.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes in series, each with both ends flame sealed, 7 cm long, 6-mm OD, 4-mm ID, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal; four plastic caps for sealing after use. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds.
   NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1012-1).
4. Vials, 2-mL, glass, with PTFE-lined septa and crimp seals.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flask, 10-mL.
7. Pipets, 1.0-mL.
8. Cold room or cold box for preparing standards at 0 °C or lower.
9. Syringes, gas-tight, 10- and 100-μL.

SPECIAL PRECAUTIONS: Difluorodibromomethane does not have adequate warning properties [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the front and back sorbent tubes immediately before sampling. Connect the tubes with a short piece of plastic tubing and attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2.5 to 10 L.
4. Separate the two sorbent tubes. Cap the ends of each tube with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the charcoal from the front and back sorbent tubes in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL 2-propanol to each vial. Attach crimp cap to each vial.
7. Allow to stand overnight with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.4 to 20 mg dibromodifluoromethane per sample.

NOTE: Prepare the working standards in a cold room or cold box.

a. Add known amounts of cold (<0 °C) difluorodibromomethane to 2-propanol in 10-mL volumetric flasks and stopper.
b. Allow standards to come to room temperature, and dilute to the mark.
c. Analyze together with samples and blanks (steps 11 and 12).
d. Prepare calibration graph (peak area vs. mg difluorodibromomethane).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of cold (<0 °C) difluorodibromomethane directly onto front sorbent section with a microliter syringe.
      NOTE 1: Perform this step in a cold room or cold box.
      NOTE 2: For small quantities (0.4 to 4 mg), use 2 to 20 μL of a 200 mg/mL standard solution of difluorodibromomethane in pentane.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg dibromodifluoromethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1012-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with 2-propanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of difluorodibromomethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of difluorodibromomethane in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S107 was issued on April 11, 1975, and evaluated at 470, 932, and 1876 mg/m^3 [1]. Spiking of samples and standards preparation were done in a cold room (0 °C). Samples of difluorodibromomethane in air were generated and collected on activated coconut charcoal (SKC Lot 105). The air concentration was independently determined by gas chromatographic analysis using a 5-mL sampling loop and comparison to gas bag samples. The mean desorption efficiency over the range 4.4 to 18.5 mg difluorodibromomethane per sampler was 99.5%. The breakthrough volume for 100-mg charcoal beds was 15.6 L at 1875 mg/m^3, low relative humidity, and a flow rate of 0.2 L/min. No storage stability study was done.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S107, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S107, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Y. T. Gagnon, NIOSH/DPSE; S107 validated under NIOSH Contract CDC-99-74-45.

DIISOBUTYL KETONE

See KETONES I (Method 1300) for procedure

DIMETHYLACETAMIDE 2004

$CH_3CON(CH_3)_2$ MW: 87.12 CAS: 127-19-5 RTECS: AB7700000

METHOD: 2004, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: 10 ppm (skin)
ACGIH: 10 ppm (skin)
(1 ppm = 3.56 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 164.5 - 166 °C; MP −20 °C; d 0.937 g/mL @ 25 ° C; VP 1.5 mm Hg @ 20 °C; flash point 70 °C, explosive range 1.8 to 11.5%

SYNONYMS: N,N-dimethylacetamide; acetyldimethylamine; DMAC

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 30 mg/m^3
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 18 to 105 mg/m^3 [1]; (45-L samples)

BIAS: − 0.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [1]

ACCURACY: ± 11.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dimethylacetamide

DESORPTION: 1 mL methanol; 1 h in ultrasonic bath

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 320 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 50 mL/min

COLUMNS: 1.5 m x 6-mm OD glass; 10% UCON 50-HB-5100, 2% KOH on 100/120 mesh Chromosorb WHP

CALIBRATION: analyte in methanol

RANGE: 0.5 to 4 mg per sample [1,2]

ESTIMATED LOD: 0.05 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.032 [1]

APPLICABILITY: The working range is 10 to 80 mg/m^3 of dimethylacetamide or dimethyformamdide for a 50-L air sample. The lower limit is determined by the desorption efficiency which must be determined over the range used. Silica gel has a high affinity for water; high relative humidity may adversely affect the efficiency of analyte adsorption.

INTERFERENCES: None identified. Separation conditions (column, temperature, etc.) may be changed to circumvent problems. Alternate columns include: 60/80 mesh Chromosorb P coated with 20% UCON LB 550X and 2% KOH; 100/120 mesh Chromosorb WHP with 10% Carbowax 20M and 2% KOH; 100/120 mesh Chromosorb WHP with 10% SP-2250; and 30-m x 0.32-mm capillary column coated with 0.5 µm DB Wax..

OTHER METHODS: This combines and replace Methods S254 and S255 [2].

REAGENTS:

1. Methanol, reagent grade.*
2. Analyte: dimethylacetamide, reagent grade, or dimethylformamide, reagent grade.*
3. Acetone, reagent grade.*
4. Desorption efficiency (DE) stock solution, 0.05 mg/mL. Prepare solutions of dimethylacetamide or dimethylformamide fresh daily in acetone.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.
7. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: . glass tube, 7 cm long, 6-mm OD, 4-mm ID, with plastic caps, containing two sections of 20/40 mesh silica gel (front = 150 mg; back = 75 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. The pressure drop across the tube must be less than 3.4 kPa (2.5 cm Hg) at an airflow of 1 L/min. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 2004-1).
4. Vials, 2-mL, PTFE-lined crimp cap, or automatic sampler vials.
5. Microliter syringes, 10-μL and other convenient size for making standards.
6. Pipets, 1.0 mL.
7. Volumetric flasks, 10-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Acetone and methanol are flammable and a dangerous fire and explosion risk. They are moderately toxic by ingestion and inhalation.

Dimethylacetamide and dimethylformamide are strong irritants to skin and tissue and moderate fire risks.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 to 1 L/min for a total sample size of 15 to 80 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL methanol to each vial. Attach crimp cap to each vial.
7. Agitate for 60 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the ranges 0.05 to 4 mg dimethylacetamide or dimethylformamide per sample.
   a. Add known amounts of analyte (neat or diluted with methanol) to methanol in 10-mL volumetric flasks and dilute to the mark.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of pure analyte or DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2004-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, mg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S254 for dimethylacetamide was evaluated over the range of 18 to 105 mg/m^3 at an atmospheric temperature and pressure of 24 °C and 760 mm Hg using a 45-L sample [1]. Breakthrough occurred when sampling a test atmosphere containing 105.6 mg/m^3 of dimethylacetamide at 0.876 L/min for 240 min. The front section of the silica gel tube was found to hold 22.2 mg dimethylacetamide under these conditions. The collection efficiency test conducted at a concentration of 105.6 mg/m^3 was determined to be 1.00. Desorption efficiency at 0.943, 1.886, and 3.77 mg per silica gel tube was 88.8, 93.8, and 94.9%, respectively. A storage study for five days at 1.866 mg per silica gel tube gave a recovery of 93.6%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.067.

Method S255 for dimethylformamide was evaluated over the range of 11 to 61 mg/m^3 at an atmospheric temperature and pressure of 23 °C and 761 mm Hg using a 45-L sample [1]. Breakthrough occurred when a test atmosphere containing 119.5 mg/m^3 of dimethylformamide was sampled at 0.859 L/min for 146 min. The front section of the silica gel tube was found to hold 15 mg of dimethylformamide under these conditions. The collection efficiency test conducted at a concentration of 61.1 mg/m^3 was determined to be 1.00. Desorption efficiency at 0.759, 1.518, and 3.04 mg per silica gel tube was 88.7, 90.4, and 92.2%, respectively. A storage study for five days at 1.5 mg dimethylformamide per silica gel

tube gave a recovery of 91.7%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.056.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S254 (Dimethylacetamide) and S255 (Dimethylformamide), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S254 and S255, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

C. Neumeister, NIOSH/DPSE; S254 and S255 originally validated under NIOSH Contract CDC-99-74-45.

DIMETHYLAMINE

See AMINES, ALIPHATIC (Method 2010) for procedure

N,N-DIMETHYLANILINE

See AMINES, AROMATIC (Method 2002) for procedure

DIMETHYLFORMAMIDE 2004
(See Method 2004, DIMETHYLACETAMIDE, for procedure)

$O=CHN(CH_3)$ MW: 73.10 CAS: 68-12-2 RTECS: LQ2100000

METHOD: 2004, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: 10 ppm (skin)
ACGIH: 10 ppm (skin)
1 ppm = 2.99 mg/m^3 @ NTP

PROPERTIES: liquid; d 0.95 g/mL @ 25 °C; BP 153 °C; MP −61 °C; VP 2.7 mm Hg @ 20 °C; explosive range in air (v/v) 2.2 to 15.2%

SYNONYMS: N-formyldimethylamine; DMF; N,N-dimethylformamide

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 30 mg/m^3
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 11 to 61 mg/m^3 [1]; (45-L samples)

BIAS: − 1.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056 [1]

ACCURACY: ± 11.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dimethylformamide

DESORPTION: 1 mL methanol; 1 h in ultrasonic bath

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 320 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 50 mL/min

COLUMNS: 1.5 m x 6-mm OD glass; 10% UCON 50-HB-5100, 2% KOH on 100/120 mesh Chromosorb WHP

CALIBRATION: analyte in methanol

RANGE: 0.5 to 4 mg per sample [1,2]

ESTIMATED LOD: 0.05 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.037 [1]

APPLICABILITY: The working range is 3.3 to 27 ppm (10 to 80 mg/m^3) for a 50-L air sample. The lower limit is determined by the desorption efficiency which must be determined over the range used. Silica gel has a high affinity for water; high relative humidity may adversely affect the efficiency of analyte adsorption.

INTERFERENCES: None identified. Separation conditions (column, temperature, etc.) may be changed to circumvent problems. Alternate columns include: 60/80 mesh Chromosorb P coated with 20% UCON LB 550X and 2% KOH; 100/120 mesh Chromosorb WHP with 10% Carbowax 20M and 2% KOH; 100/120 mesh Chromosorb WHP with 10% SP-2250; and 30-m x 0.32-mm capillary coated with 0.5 µm DB Wax.

OTHER METHODS: This combines and replace Methods S254 and S255 [2].

$(CH_3)_2NNH_2$ MW: 60.10 CAS: 57-14-7 RTECS: MV2450000

METHOD: 3515, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : C 0.5 ppm (skin)
NIOSH: C 0.06 ppm/120 ppm; carcinogen
ACGIH: C 0.5 ppm (skin); suspected human carcinogen
(1 ppm = 2.46 mg/m^3 @ NTP)

PROPERTIES: liquid; MP - 58 °C; BP 63 °C; d 0.80 @ 20 °C; VP 157 mm Hg @ 25 °C; vapor density (air = 1) 2.07; flash point - 15 °C (closed cup); flammable range 2 to 95% v/v in air

SYNONYMS: dimazine; unsym-dimethylhydrazine; N,N-dimethylhydrazine.

SAMPLING

SAMPLER: BUBBLER
(0.1 M hydrochloric acid)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 2 L @ 0.5 ppm
-MAX: 100 L

SHIPMENT: remove bubbler stem and rinse with 0.1 M hydrochloric acid; seal bubbles with non-reactive stopper

SAMPLE STABILITY: at least 5 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.506 to 2.22 mg/m^3 [1] (91-L samples)

BIAS: − 1.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 14.0%

MEASUREMENT

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: complex of phosphomolybdic acid and 1,1-dimethyl hydrazine

PROCEDURE: add phosphomolybdic acid; heat sample solution at 95 °C for 60 min; cool solution under tap water; transfer sample to 1-cm cell; read absorbance at 730 nm

CALIBRATION: standard solutions of 1,1-dimethylhydrazine in 0.1 M hydrochloric acid

RANGE: 2 to 250 μg per sample [1]

ESTIMATED LOD: 1 μg per sample [2]

PRECISION ($\hat{S}_r$): 0.072 [1]

APPLICABILITY: The working range is 0.008 to 1 ppm (0.02 to 2.5 mg/m^3) for a 100-L air sample. This method is also applicable to ceiling measurements.

INTERFERENCES: Other hydrazines, as well as, stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide, may give a positive interference. Negative interferences in the method may occur by oxidation of the 1,1-dimethylhydrazine by halogens, oxygen (especially in the presence of cooper (I) ion) and hydrogen dioxide.

OTHER METHODS: This revises Method S143 [2]. Method P&CAM 248 [3] describes an acid-coated silica gel sorbent tube/gas chromatographic method for the determination of hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine. Sample stability problems have been noted with P&CAM 248 [4].

REAGENTS:

1. 1,1-Dimethylhydrazine,* ACS reagent grade.
2. Hydrochloric acid, ACS reagent grade.
3. Collection medium, 0.1 M hydrochloric acid. To 300 mL of distilled water in a 1000-mL volumetric flask, add 8.6 mL of concentrated hydrochloric acid with caution. Mix and bring to volume with distilled water.
4. Phosphomolybdic acid solution. Dissolve 15 g of phosphomolybdic acid in 500 mL distilled water, allow to stand one day, and filter through a fluted paper filter.
5. Water, deionized and distilled.
6. Calibration stock solution, 1 mg/mL. Weigh 500 mg of 1,1-dimethylhydrazine in a 100-mL volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

EQUIPMENT:

1. Sampler: 25-mL bubbler with 10 mL 0.1 M hydrochloric acid.
2. Personal sampling pump, 0.2 to 1.0 L/min, with flexible polyethylene or PTFE tubing.
3. Glass or non-reactive stopper for bubbler.
4. Glass tube, 5 cm long by 6-mm I.D., loosely packed with glass wool.
5. Spectrophotometer, set at 730 nm.
6. 1-cm spectrophotometer cells.
7. Test tube, large.
8. Volumetric flasks, 50-mL, 100-mL, 500-mL, 1000-mL.
9. Pipets, 10-, 15-, 25, and 50-μL; 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 95 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

* See SPECIAL PRECAUTIONS.

SPECIAL PRECAUTIONS: 1,1-Dimethylhydrazine may be fatal if inhaled, swallowed or absorbed through the skin [5]. Contact may cause burns to skin and eyes. Vapor may be irritating to the eyes, skin, and mucous membranes. Handle with caution and use appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 10 mL 0.1 M hydrochloric acid to a bubbler.
3. Connect outlet arm of bubbler to the glass-wool-packed tube (to prevent splashover into the pump) and then to the sampling pump with the flexible tubing.
4. Sample at an accurately known rate of 0.2 to 1.0 L/min for total sample size of 2 to 100 L.
5. Remove bubbler stem and rinse with 2 mL of 0.1 M hydrochloric acid into bubbler body. Seal bubbler with an inert stopper for shipment in a suitable container in order to prevent damage during transit.

SAMPLE PREPARATION:

6. Transfer the liquid from the bubbler, quantitatively, to a volumetric flask.
7. Add 10 mL of phosphomolybdic acid solution and bring volume to 50 mL with 0.1 M hydrochloric acid.
8. Transfer an aliquot of this solution to a large test tube and heat to 95 °C for 60 min. Place test tube under running tap water to cool before measurement.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards to cover the range of 1 to 250 μg 1,1-dimethyl hydrazine per sample.

a. Add appropriate aliquots (10, 20, 30, 40 and 50 μL) of calibration stock solution to 10 mL of 0.1 M hydrochloric acid in 50-mL volumetric flasks. Prepare a reagent blank using only 10 mL of 0.1 M hydrochloric acid.
b. Treat with (steps 7 and 8) phosphomolybdic acid solution.
c. Analyze working standards together with samples and reagent blanks (steps 10 through 12) on a spectrophotometer at 730 nm, using a 1-cm cell. Correct standards for reagent blank absorbance.
d. Prepare a calibration graph of absorbance vs. amount (μg) of 1,1-dimethylhydrazine per 50 mL of sample.

MEASUREMENT:

10. Set spectrophotometer according to manufacturer's recommendations to monitor 730 nm.
11. Fill 1-cm sample cell with sample or standard.
12. Measure absorbance.

CALCULATIONS:

13. Determine mass, μg, of analyte found in sample (W) and average reagent blank (B).
14. Calculate concentration (C) of 1,1-dimethylhydrazine in the air volume sampled V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 0.5 to 2.3 mg/m^3 using 91-L samples [1]. Sampling and measurement precision, $\hat{S}_{rT}$ was 0.062 for samples collected at the OSHA standard. Bias could not be determined owing to instability of the 1,1-dimethylhydrazine in the generator. Collection efficiency of the bubblers was determined to be 99.1% at 2.2 mg/m^3. Sample stability during storage was evaluated at 100 μg 1,1-dimethylhydrazine per sample. Samples showed 101.3% recovery after five days of storage at ambient conditions.

REFERENCES:

[1] Backup Data Report for 1,1-Dimethylhydrazine, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd e.d., V. 3, S143, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH Manual of Analytical Methods, 2nd e.d., V. 4, 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] L.R. Cook, R.E. Glenn and G.E. Podolak, Am. Ind. Hyg. Assoc. J., 40, 69-74 (1979).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

E.R. Kennedy, Ph.D., NIOSH/DPSE.

DIMETHYL SULFATE 2524

$(CH_3O)_2SO_2$ MW: 126.13 CAS: 77-78-1 RTECS: WS8225000

METHOD: 2524, Issue 2 **EVALUATION:** PARTIAL **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.1 ppm (skin)
NIOSH: 0.1 ppm/8 hours (skin); carcinogen
ACGIH: 0.1 ppm (skin); suspect carcinogen
(1 ppm = 5.16 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.332 g/mL @ 20 °C;
BP 188 °C with decomposition;
MP -31.8 °C; VP 0.07 kPa (0.5 mm Hg; 700 ppm) @ 20 °C

SYNONYMS: methyl sulfate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Poropak P, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 1 ppm
-MAX: 12 L

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.8 to 24.5 mg/m^3 [1] (1.2-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTOR (SULFUR MODE)

ANALYTE: dimethyl sulfate

DESORPTION: 1 mL diethyl ether, 30 min

INJECTION VOLUME: 4 µL

TEMPERATURE-INJECTION: 180 °C
-COLUMN: 2 min @ 50 °C; then 30 °C/min to 120 °C; hold

CARRIER GAS: He, 20 mL/min

COLUMN: 1.8 m x 3.2-mm OD stainless steel, packed with 5% DEGS on 80/100 mesh Chromosorb WHP

CALIBRATION: dimethyl sulfate in diethyl ether

RANGE: 1 to 120 µg per sample

ESTIMATED LOD: 0.25 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.06 @ 1.1 to 39 µg per sample [1]

APPLICABILITY: The working range is 0.03 to 4 ppm (0.17 to 20 mg/m^3) for a 6-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises P&CAM 301 [2].

REAGENTS:

1. Dimethyl sulfate, 99%.*
2. Diethyl ether,* anhydrous, preserved with ethanol.
3. Calibration stock solution, 12 μg/μL. Add 120 mg (90 μL) dimethyl sulfate to a pre-weighed 10-mL volumetric flask. Re-weigh and dilute to the mark with diethyl ether.
4. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 50/80 mesh Porapak P (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 0.2 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
   NOTE: Some batches of Porapak P initially gave poor recovery. Good recoveries were obtained after the sorbent had been heated at 180 °C in a vacuum oven for 16 hrs.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, electrolytic conductivity detector (sulfur mode), integrator, and column (see page 2524-1).
   NOTE: A new column must be primed before attempting quantitative work by repeatedly injecting aliquots of calibration stock solution until the detector response to dimethyl sulfate reaches a plateau.
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1-μL.
6. Volumetric flasks, 10-mL.
7. Pipets, 1-mL.

SPECIAL PRECAUTIONS: Dimethyl sulfate is a suspect carcinogen, and both the liquid and vapor are extremely severe irritants to skin, eyes, and mucous membranes. It is an insidious hazard -- warning properties are poor and symptoms are delayed up to 10 h or more [3,4]. All transfers involving dimethyl sulfate should be performed in a fume hood. Personal protective equipment should be used to prevent any bodily exposure even to the vapor.

Diethyl ether is an extreme fire (flash point = −45 °C) and explosion hazard (possible peroxide formation); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 12 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the separating plugs.
6. Add 1.0 mL diethyl ether to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.25 to 120 μg dimethyl sulfate per sample (2.5 to 1200 μg/10 mL).
   a. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to the mark with diethyl ether.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg dimethyl sulfate).
9. Determine desorption efficiency (DE) at least once for each lot of Porapak P used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg dimethyl sulfate recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2524-1. Set electrolytic conductivity detector for operation in sulfur mode according to manufacturer's recommendations. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with diethyl ether, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak height.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of dimethyl sulfate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of dimethyl sulfate in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

For the evaluation, a Tracor Model 310 Hall electrolytic conductivity detector was used [1]. It was operated with a furnace temperature of 950 °C, oxygen at 20 mL/min as the reactant gas, and filtered, deionized water at 1 mL/min as the conductivity solvent. The capacity of Porapak P for the collection of dimethyl sulfate was estimated from a log retention volume vs. reciprocal absolute temperature plot of data obtained by chromatographing 30-μg quantities of dimethyl sulfate on a 100-mg sorbent bed. Based on these data, the estimated volumetric capacity decreases from 39 L at 25 °C to 16 L at 35 °C. In a test of humidity and storage effects, six tubes were spiked with 0.6 μg dimethyl sulfate. After passing 12 L of humid air (80% RH) through each, they were stored for seven days. Upon analysis, these samples showed no significant loss of dimethyl sulfate.

This method was compared with an independent method based on collection of dimethyl sulfate on Tenax-GC, derivatization of p-nitrophenol with the collected dimethyl sulfate, and HPLC (UV detection) of the resulting p-nitroanisole. For three sets of six dynamically-generated samples, the concentrations and precisions (relative standard deviations) found using this method were 1.8 (0.061), 4.35 (0.074), and 24.5 (0.070) μg/L. The corresponding results found by the independent method for simultaneously-generated samples were 3.18 (0.153), 7.18 (0.090), and 20.4 (0.086) μg/L. Because of the inconsistency of the results and possible inaccuracy in the independent method, the accuracy of this method remains to be determined.

REFERENCES:

[1] Lunsford, R. A., and P. M. Fey. Backup Data Report for P&CAM 301 (NIOSH, unpublished, December 29, 1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 301, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] The Merck Index, 11th Ed., Merck & Co., Inc., Rahway, NJ (1989).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE.

N,N-DIMETHYL-p-TOLUIDINE

See AMINES, AROMATIC (Method 2002) for procedure

DIOXANE 1602

$C_4H_8O_2$ MW: 88.11 CAS: 123-91-1 RTECS: JG8225000

METHOD: 1602, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 25 ppm (skin)
NIOSH: 1 ppm/30 min; carcinogen
ACGIH: 25 ppm (skin); carcinogen
(1 ppm = 3.60 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.0337 g/mL @ 20 °C;
BP 101 °C; MP 12 °C
VP 3.9 kPa (29 mm Hg; 3.8% v/v) @ 20 °C;
explosive range 2 to 22% v/v in air

SYNONYMS: dioxan; p-dioxane; 1,4-diethylene dioxide; diethylene ether

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 100 ppm
-MAX: 15 L

SAMPLE STABILITY: >1 week @ 25 °C
>6 weeks @ −10 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 157 to 660 mg/m^3 [1]
(10-L samples)

BIAS: + 9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.054 [1]

ACCURACY: ± 18.7

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dioxane

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 75 °C

CARRIER GAS: He, 30 mL/min (60 psig)

COLUMN: 6 m x 3-mm stainless steel packed with 10% FFAP on 80/100 mesh Chromosorb W-HP Chromosorb W-HP

CALIBRATION: solutions of dioxane in CS_2 with internal standard

RANGE: 0.2 to 7 mg per sample [1,2]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION ($\hat{S}_r$): 0.017 [1]

APPLICABILITY: The working range is 5.5 to 190 ppm (20 to 700 mg/m^3) for a 10-L air sample.

INTERFERENCES: None known. An alternate GC column is 30 m x 0.32-mm ID fused silica capillary coated with 1 µm DB-5 [3].

OTHER METHODS: This method combines and replaces S360 [4] and P&CAM 127 [5] for dioxane. A similar method appears in the dioxane criteria document [6].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% (v/v) octane, decane, or other suitable internal standard.
2. Dioxane, reagent grade.*
3. Desorption efficiency (DE) stock solution, 0.1 mg/μL. Dilute 1 g dioxane to 10 mL with pentane.
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1602-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1-μL.
6. Volumetric flasks, 10-mL.
7. Pipet, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C).

Dioxane is toxic, causing central nervous system depression and necrosis of liver and kidneys, as well as a skin irritant [6], and a suspect carcinogen [7]. Use personal protective equipment and work only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 15 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 7 mg dioxane per sample.

a. Add known amounts of dioxane to eluent in 10-mL volumetric flasks and dilute to the mark. By serial dilution, prepare solutions containing 0.01 to 7 mg dioxane/mL.
b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg dioxane).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (1 to 20 μL) of dioxane or DE stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg dioxane recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1602-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of dioxane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of dioxane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S360 [4] was issued on March 14, 1975, and validated over the range 155 to 651 mg/m^3 using atmospheres generated by calibrated syringe pump [1]. Desorption efficiency averaged 0.88 in the range 1.8 to 7.3 mg dioxane per sample. Breakthrough was observed when a test atmosphere containing 651 mg/m^3 of dioxane in dry air was sampled at 0.19 L/min for 210 min (40-L air sample volume). The front section held 26 mg of dioxane. Precision and accuracy are listed on page 1602-1. A similar method, without internal standard, was collaboratively tested in the range 6 to 190 ppm dioxane [2,8].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S360, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents, 4-22, 4-27, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-184 (1975).
[3] UBTL, Inc., NIOSH Sequence Report #4176-K (unpublished, December 19, 1983).
[4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S360, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Ibid., Vol. 1., P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[6] Criteria for a Recommended Standard...Occupational Exposure to Dioxane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-226 (1977).
[7] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[8] Larkin, R. L., J. V. Crable, L. R. Catlett, and M. J. Seymour. Collaborative Testing of a Gas Chromatogrphic Charcoal Tube Method for Seven Organic Solvents, Am. Ind. Hyg. Assoc. J., 38, 543 (1977).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; S360 originally validated under NIOSH Contract CDC-99-74-45.

DIPHENYL 2530

$C_6H_5C_6H_5$ MW: 154.21 CAS: 92-52-4 RTECS: DU8050000

METHOD: 2530, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.2 ppm
NIOSH: 0.2 ppm
ACGIH: 0.2 ppm
(1 ppm = 6.30 mg/m^3 @ NTP)

PROPERTIES: MP 69 °C; BP 255 °C
VP 8 Pa (0.06 mm Hg; 79 ppm)
@ 25 °C; flash point 113 °C

SYNONYMS: biphenyl

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Tenax GC, 20 mg/10 mg))

FLOW RATE: 0.01 to 0.5 L/min

VOL-MIN: 15 L @ 0.2 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: 95% recovery after 7 days @ room temperature

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.64 to 2.4 mg/m^3 [1] (30-L samples)

BIAS: − 6.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.068 [1]

ACCURACY: ± 15.33%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: diphenyl

DESORPTION: 1 mL CCl_4, stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 135 °C

CARRIER GAS: N_2, 50 mL/min

COLUMN: 1.8 m x 4-mm ID glass packed with 5% OV-17 on 80/100 mesh Chromosorb W

CALIBRATION: standard solutions of biphenyl in CCl_4

RANGE: 4 to 120 µg per sample

ESTIMATED LOD: 0.09 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.019 [1] @ 19 to 76 µg per sample

APPLICABILITY: The working range is 0.02 to 0.63 ppm (0.13 to 4 mg/m^3) for a 30-L air sample. Measurement of concentrations down to 0.01 mg/m^3 may be possible if the desorption efficiency remains adequate.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S24 [2].

REAGENTS:

1. Acetone, reagent grade.*
2. Hexane, reagent grade.*
3. Carbon tetrachloride (CCl_4), reagent grade.*
4. Diphenyl, reagent grade.
5. Calibration stock solution, 1.2 mg/mL. Dilute an accurately weighed 120-mg portion of diphenyl to 100 mL with carbon tetrachloride.
6. Desorption efficiency (DE) stock solution, 12 mg/mL. Dilute an accurately weighed 120-mg portion of diphenyl to 10 mL with hexane.
7. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 6 cm long, 6-mm OD, 4-mm ID, containing two sections of cleaned 35/60 mesh Tenax GC (front = 20 mg; back = 10 mg), separated by 2-mm urethane foam plug. A silylated glass wool plug is placed at both ends. Pressure drop across the tube at 0.5 L/min must be less than 3.4 kPa. Cleaned Tenax GC Tubes are commercially available.
   NOTE: Clean bulk Tenax GC by placing it in sintered glass filter fitted to large vacuum flask. Add volume of acetone equal to twice that of sorbent and mix, then remove acetone by filtration. Repeat washing six times. Dry sorbent at 120 °C under vacuum for 4 h.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (see page 2530-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10- and 100-mL.
7. Pipets, 1-mL, and other convenient sizes.
8. Balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hexane (flash point = −22 °C) and acetone (flash point = −18 °C) are highly flammable and carbon tetrachloride is highly toxic. Prepare sorbent, samples, and standards in well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler tube immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.5 L/min for a total sample size of 15 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CCl_4 to each vial. Cap each vial.
7. Allow to stand 15 min with occasional agitation.
   NOTE: Fine particles of Tenax tend to plug an autosampler syringe. For use with autosampler, transfer supernatant solutions to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 120 μg diphenyl per sample. Use serial dilutions for the smallest concentrations.
   a. Add known amount of calibration stock solution to CCl_4 in 10-mL volumetric flask and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak height or area vs. μg diphenyl per sample).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject 2 to 10 μL of DE stock solution (or of a serially diluted solution in hexane) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg diphenyl recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2530-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CCl_4, reanalyze and apply the appropriate dilution factor in calculations.
    NOTE 2: Under these conditions, t_r for diphenyl is approximately 6 min.
12. Measure peak height or area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of diphenyl found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of diphenyl in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S24 was issued on November 25, 1977 [2], and validated over the range 0.64 to 2.4 mg/m^3 using 32-L samples collected on Tenax GC, Lot 04901 (Applied Science Laboratories) [1]. The diphenyl concentration was independently determined by UV analysis of samples collected in methanol. Overall precision, $\hat{S}_{rT}$, was 0.068 with an average recovery of 92.7%. Desorption efficiency averaged 0.987 in the range 19 to 76 μg per sample. For samples collected at 2.5 mg/m^3, 25 °C, and >85% RH, breakthrough to the backup section averaged 3.9% between 31.5 and 48.6 L, and 9.4% between 48.6 and 64.2 L. Recovery from a set of samples stored one week under ambient conditions was 95.0% relative to a set analyzed immediately. Previous work showed desorption efficiency to be poor (<0.7) for diphenyl on SKC Lots 104 and 105 charcoals [1,3].

REFERENCES:

[1] Backup Data Report No. S24, Diphenyl, prepared under NIOSH Contract No. 210-76-0123 (November, 1977), available as "Ten NIOSH Analytical Methods, Set 4," Order No. PB281-038 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S24, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Failure Report S24, NIOSH Contract CDC-99-74-45 (unpublished, 1977).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; S24 originally validated under NIOSH Contract No. 210-76-0123.

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5013, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: lowest feasible; carcinogen
ACGIH: carcinogen

PROPERTIES: colored powders; water soluble; VP not significant

SYNONYMS: Table 1.

SAMPLING

SAMPLER: FILTER (5-μm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 150 L @ 0.1 mg/m^3
-MAX: 500 L

SHIPMENT: keep samples dry and cool; protect from light

SAMPLE STABILITY: at least 7 days @ 25 °C in the dark

FIELD BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: include 1 bulk sample for each dye present on the filter

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: benzidine, o-tolidine, o-dianisidine

DESORPTION: 2 mL H_2O; ultrasonic

REACTION: reductive cleavage of dye to free amine with sodium hydrosulfite

INJECTION VOLUME: 10 μL

MOBILE PHASE: 60% methanol/40% phosphate buffer; ambient temperature

COLUMN: 10 cm x 8-mm ID, Waters Radial Pak C_{18}, 10-μm particles, with Radial Compression Module or equivalent

DETECTOR: UV detector @ 280 nm

CALIBRATION: solutions of benzidine, o-tolidine and o-dianisidine in methanol

RANGE: ca. 15 to 250 μg per sample (Table 1)

ESTIMATED LOD: 3 μg benzidine per sample [1]

PRECISION ($\bar{S}_r$): 0.04 to 0.08 [2,3]

APPLICABILITY: The working range is ca. 0.06 to 8 mg/m^3 for a 250-L air sample. This method determines benzidine, o-tolidine or o-dianisidine from dyes based on these amines, but will not distinguish different dyes based on the same amine. The method will not distinguish benzidine obtained from reduction of the dyes and free benzidine in the dye formulation.

INTERFERENCES: Aniline, azobenzene, p-aminophenol, p-phenylenediamine or p-nitroaniline do not interfere in the measurement when present in equimolar amounts.

OTHER METHODS: This revises P&CAM 325 [2,3]. P&CAM 234 [4,5], a general colorimetric method for diazonium salts and azo dyes, has not been revised.

REAGENTS:

1. Water, deionized and distilled.
2. Methanol, HPLC Grade.
3. Benzidine.*
4. o-Tolidine.*
5. o-Dianisidine.*
6. Calibration stock solutions. Dilute the following amounts to 10 mL with methanol. Stable one month at 4 °C.
   a. Benzidine, 15.6 mg
   b. o-Tolidine, 15.3 mg
   c. o-Dianisidine, 5.6 mg
7. Disodium hydrogen phosphate, Na_2HPO_4.
8. Potassium dihydrogen phosphate, KH_2PO_4.
9. Sodium hydrosulfite, $Na_2S_2O_4$.
10. HPLC mobile phase buffer. Dilute 3.39 g KH_2PO_4 and 4.30 g Na_2HPO_4 to 1 L with water. Prepare daily.
11. Reduction buffer.
    a. Solution A. Dilute 1.179 g KH_2PO_4 and 4.30 g Na_2HPO_4 to 1 L with water. Prepare daily.
    b. Solution B. Dilute 11.79 g KH_2PO_4 and 43.00 g Na_2HPO_4 to 1 L with water. Prepare daily.
12. Reducing solution. Dilute 200 mg $Na_2S_2O_4$ to 10 mL with the appropriate reduction buffer of Solution A or B (see Table 1) immediately before use.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE filter, 5-μm, 37-mm (Millipore Mitex or equivalent), with backup pad in a three-piece plastic cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph equipped with 280-nm UV detector, integrator and column (page 5013-1), Waters Model RCM 100 Radial Compression Module with Waters Radial Pak C_{18} column or equivalent.
4. Syringe or autosampler for HPLC injection.
5. Syringes, volumetric, 10-, 25- and 50-μL.
6. Flasks, volumetric, 10- and 100-mL, 1-L.
7. Vials, 4-mL, with screw caps.
8. Pipets, volumetric, 1-mL.
9. Tweezers.
10. Beakers, 50-mL.
11. Ultrasonic water bath.

SPECIAL PRECAUTIONS: NIOSH recommends that benzidine- and benzidine-congener-based dyes be recognized and handled as human carcinogens because they can be reduced to the free aromatic amine in living systems and eliminated by the usual metabolic pathways [4,6].

Benzidine is a recognized human carcinogen and regulated by the Occupational Safety and Health Administration. o-Tolidine and o-dianisidine are currently suspect carcinogens and should be handled accordingly [4,6]

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 150 to 500 L.

SAMPLE PREPARATION:

3. Remove the filter from the cassette with clean tweezers and place it face up in a 50-mL beaker.
4. Add 1.0 mL H_2O to the beaker and swirl to wet the entire deposit.
5. Add another 1.0 mL H_2O to the beaker and swirl.

6. Turn the filter sample side down and place the beaker in an ultrasonic bath for 15 min.
7. Pipet 1.0 mL desorbed sample solution to a 4-mL vial.
8. Add 1.0 mL freshly prepared reducing solution.
   NOTE: Where the composition of the sample dye is unknown or different from the dyes listed in Table 1, reduce a 1-mL aliquot of the desorbed dye solution with the reducing solution made from buffer A. If precipitation of the dye from solution is observed at this point, reduce the remaining 1-mL aliquot of the desorbed dye solution with the reducing solution made with buffer B.
9. Cap the vial and allow to stand with occasional shaking for at least 1 h or until the change in solution color is completed.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily.
    a. Dilute aliquots of the calibration stock solutions for each of the amines (benzidine, o-tolidine, o-dianisidine) to 10 mL with methanol in volumetric flasks. Prepare at least six working standards to cover the ranges of interest (0.38 to 16 μg/mL benzidine; 0.77 to 15.3 μg/mL o-tolidine; 0.56 to 11.7 μg/mL o-dianisidine).
    b. Analyze the working standards together with samples and blanks (steps 12 through 14).
    c. Prepare separate calibration graphs (peak area vs. μg per sample) for benzidine, o-tolidine. and o-dianisidine. At the completion of step 9, the total effective volume of the solution containing the entire sample is 4 mL.
11. Determine recovery if the filter sample is known to contain only one dye.
    a. Prepare a solution of a known concentration of the bulk sample of the dye in 10 mL H_2O.
    b. Add known volumes of this solution to PTFE filters using a microliter syringe and allow to dry. Prepare three filters at each of five concentration levels.
    c. Analyze the filters by steps 3 through 9 and 12 through 14.
    d. On the day of analysis of the filters, add the same volume of dye solution which was spiked onto the filters to 2.0 mL H_2O. Reduce this solution (steps 7 through 9) and analyze together with samples and standards (steps 12 through 14).
    e. Calculate recovery (μg benzidine, o-tolidine, or o-dianisidine recovered from the filter/μg from step 11.d).
    f. Prepare graph of recovery vs. μg benzidine, o-tolidine or o-dianisidine recovered.

MEASUREMENT:

12. Set the HPLC to conditions given on page 5013-1 and in Table 1.
13. Inject 10 μL sample into the HPLC. Make duplicate injections of samples and standards.
14. Measure peak areas.

CALCULATIONS:

15. Read the mass, μg (corrected for recovery, if applicable) of the free amine corresponding to each peak area for the sample (W) and average media blank (B) from the appropriate calibration graph.
16. Calculate the concentration, C, of benzidine, o-tolidine or o-dianisidine in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was laboratory evaluated over the ranges listed in Table 1 [2]. The concentration of dye remaining after reduction varied from 0 to 6% as determined by visible spectrophotometry. The reduced free amine was confirmed by GC/MS. The lower end of the measurement range was defined as the level which gave at least 75% recovery with approximately 10% $\bar{S}_r$. For C. I. Direct Red 28, the range covered 27.3 to 273 μg dye per sample. The lower level of this range gave 94.4% recovery ($\bar{S}_r$ = 6.3%) based on free benzidine for six replicate samples. For the other three dyes the results were as follows: C. I. Direct Blue 6, 15.0 to 300.0 μg dye per sample, 100.3% recovery ($\bar{S}_r$ = 4.34%); C. I. Direct Brown 95, 24.3 to 243 μg dye per sample, 78.5% recovery ($\bar{S}_r$ = 6.7%); C. I. Direct Black 38, 12.5 to 250.0 μg dye per sample, 78.1% recovery ($\bar{S}_r$ = 12.8%). The pooled precisions ($\bar{S}_r$) for samples at three concentrations in the measurement range for each dye are as follows: Direct Red 28, 0.045; Direct Blue 6, 0.061; Direct Brown 95, 0.072; Direct Black 38, 0.078. Since the method does not distinguish between various benzidine-based dyes, recovery correction factors cannot be applied unless a single known dye is contained on the filter. Recovery studies must be performed on the bulks collected with the samples because of variability in sample purity and variety of benzidine-based dyes. Recovery studies on spiked samples stored at 75% relative humidity indicated no change due to humidity in the recoveries or sample stability.

A user check of this method [1] gave estimated LODs for benzidine (3 μg per sample; 0.7 μg/mL) and dianisidine (4.5 μg per sample; 1.1 μg/mL). The LODs could be lowered to 0.06 μg/mL for benzidine and 0.07 μg/mL for dianisidine by using fluorescent detection with excitation at 285 nm and emission at 375 nm.

REFERENCES:

[1] User check, Wisconsin Occupational Health Laboratory (NIOSH, unpublished, September 27, 1984).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 325, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] Kennedy, Eugene R. and Martha J. Seymour. Development of an Analytical Method for Benzidine-Based Dyes, Chemical Hazards in the Workplace Measurement and Control, ACS Symposium Series 149, American Chemical Society, Washington, DC, 21-35 (1981).

[4] Special Occupational Hazard Review for Benzidine-Based Dyes, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-109 (1979).

[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1, P&CAM 234, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] Preventing Health Hazards from Exposure to Benzidine Congener Dyes, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-105 (1983).

METHOD WRITTEN BY:

Eugene R. Kennedy, Ph.D., Martha J. Seymour and Charles E. Neumeister, NIOSH/DPSE.

TABLE 1. BENZIDINE- AND BENZIDINE-CONGENER-BASED DYES.

Color Index Name	C.I. Number	Molecular Formula	M.W.	Synonyms [4]	Range[a] µg per sampler	Range[a] µg/m³	HPLC Flow rate (mL/min)	Reduction Buffer[b]
BENZIDINE-BASED:								
C.I. Direct Red 28	22120	$C_{32}H_{22}N_6S_2O_6Na_2$	696.67	Congo Red; CAS #573-58-0 RTECS QK1400000	27.3-273	54.6-546	2	B
C.I. Direct Blue 6	22610	$C_{32}H_{20}N_6S_4O_{14}Na_4$	932	Amidine Blue 2B; CAS #2602-46-2 RTECS QJ6400000	15.0-300	30.0-600	2	B
C.I. Direct Brown 95	30145	$C_{31}H_{18}N_6O_9Na_2Cu$	759	Chrome Leather Brown; CAS #16071-86-6 RTECS GL7375000	24.3-242	48.6-485	2	B
C.I. Direct Black 38	30235	$C_{34}H_{25}N_9S_2O_7Na_2$	781	Amidine Black GA; CAS #1937-37-7 RTECS QJ6160000	12.5-250	25.0-500	1	A
o-TOLIDINE-BASED:								
C.I. Direct Red 2	23500	$C_{34}H_{26}N_6S_2O_6Na_2$	724.74	Benzopurpurine 4B; CAS #992-59-6 RTECS QK1765000	16.7-334	33.4-668	1	A
o-DIANISIDINE-BASED:								
C.I. Direct Blue 8	24140	$C_{34}H_{24}N_4S_2O_{10}Na_2$	758.69	Direct Azurine G; Benzo Azurine G; CAS #2429-71-2	10.2-204	20.4-408	1	A

[a] Air concentrations calculated from analytical results with an air volume of 500 L assumed.
[b] The letters "A" and "B" refer to the reduction buffer solutions described in the REAGENTS section, items 11.a and b.

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E - N

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August 1994

M.W.: Table 1 FORMULA: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 8005, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

BIOLOGICAL INDICTOR OF: exposure to the following elements or their compounds: antimony, cadmium, chromium, cobalt, copper, iron, lanthanum, lead, lithium, magnesium, manganese, molybdenum, nickel, platinum, silver, strontium, thallium, vanadium, zinc and zirconium.

SYNONYMS: vary according to compound.

BIOLOGICAL SAMPLING		MEASUREMENT	
SPECIMEN:	BLOOD OR TISSUE	**METHOD:**	INDUCTIVELY-COUPLED ARGON PLASMA-ATOMIC EMISSION SPECTROSCOPY (ICP-AES)
VOLUME:	10 mL (blood) or 1 g (tissue)	**ANALYTE:**	elements above
PRESERVATIVE:	heparin (blood); none for tissue	**DIGESTION ACID:**	3:1:1 (v/v/v) HNO_3:$HClO_4$:H_2SO_4
SHIPMENT:	frozen for blood and "wet" tissue; routine for "dry" tissue	**FINAL SOLUTION:**	10% H_2SO_4; 10 mL (blood), 5 mL (tissue)
STABILITY:	not established	**WAVELENGTH:**	varies with element; Table 2
CONTROLS:	collect at least 3 blood specimens from unexposed workers	**BACKGROUND CORRECTION:**	spectral wavelength shift
		CALIBRATION:	elements in 10% H_2SO_4 or yttrium internal standard
		QUALITY CONTROL:	spiked blood or tissue; reference materials
		RANGE:	10 to 10,000 μg/100 g blood; 2 to 2000 μg/g tissue
		ESTIMATED LOD:	1 μg/100 g blood; 0.2 μg/g tissue
		PRECISION ($\bar{S}_r$):	Table 2
		ACCURACY:	Table 2

APPLICABILITY: This method is useful for monitoring the blood of workers exposed to several metals simultaneously. This is a simultaneous multielemental analysis, but is not compound-specific.

INTERFERENCES: Spectral interferences are sometimes encountered. These are minimized by judicious wavelength selection and interelement correction factors. Background corrections (spectral wavelength shift) are also made [1,2].

OTHER METHODS: This method uses a measurement technique similar to that of Methods 7300 (Elements; for air samples) and 8310 (Metals in urine).

REAGENTS:

1. Nitric acid, conc. (HNO_3) (high purity).*
2. Perchloric acid, conc. ($HClO_4$) (high purity).*
3. Sulfuric acid, conc. (H_2SO_4) (high purity).*
4. Digestion acid, 3:1:1 (v/v/v) HNO_3:$HClO_4$:H_2SO_4.* Mix three volumes conc. HNO_3 with one volume conc. $HClO_4$ and one volume conc. H_2SO_4.
5. Element standards, 1000 µg/mL. Commercially available or prepared per instrument manufacturer's recommendations.
6. Reference materials of known elemental composition. SRM #1577a, Bovine Liver, from the U.S. National Institute of Standards and Technology is recommended.
7. Argon.
8. Deionized water.
9. Yttrium standard, 5 µg/mL in 5% HNO_3. Combine 50 mL conc. HNO_3, ca. 500 mL deionized water, and 5 mL 1000 µg Y/mL standard. Dilute to 1 L.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Blood collection tubes, heparinized, lead-free, specially prepared for collecting blood samples for blood lead determinations.
   NOTE: Heparin may contain significant amounts of Ca, Cu, Mn, Sr and Zn and should not be used if these elements are to be determined [3].
2. Vacutainer needles (21-gauge) and holder.
   NOTE: These may be significant sources of contamination in some cases [4].
3. Tourniquet and alcohol swabs.
4. Bottles, glass or polyethylene, with PTFE-lined caps, 20-mL (e.g., scintillation vials).*
5. Inductively-coupled plasma-atomic emission spectrometer equipped for determination of elements of interest.
6. Regulator, two-stage, for argon.
7. Analytical balance, readable to 1 mg.
8. Beaker, Griffin (50-mL) or Phillips (125-mL), with watchglass covers.*
9. Hotplate, for use at 110 and 250 °C.
10. Pipets, 5- and 10-mL, with pipet bulb.*
11. Volumetric flasks, 5- and 10-mL and 1-L.*
12. Plastic,* glass* or single element (e.g., tantalum) knives and forceps for cutting tissue samples, as needed [3,4,5].
13. Work station with plastic work surfaces, with air cleaned by a vertical, laminar flow device and high efficiency particulate air filter or by electrostatic precipitator.
14. Gloves, plastic, metal-free. *All glassware and plasticware which contacts standards, blanks, or samples should be detergent-washed, thoroughly rinsed with tap and deionized water, soaked 12 h in 10% (v/v) HNO_3 and soaked 12 h in deionized water.

SPECIAL PRECAUTIONS: Concentrated acids are extremely corrosive; work with them only in a fume hood and wear appropriate safety equipment (safety glasses or face shield, gloves and labcoat).

Samples of blood and tissue collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood and tissue specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect blood samples in heparinized blood collection tubes. Mix immediately. Collect tissue samples (ca. 0.25 g for "dry" tissue or ca. 1 g for "wet" tissue) in bottles.
   NOTE: If unheparinized blood collection tubes are used, freeze samples immediately.

2. Ship samples in dry ice and store frozen (<15 °C) prior to digestion.

SAMPLE PREPARATION:

3. Allow sample to equilibrate to room temperature.
4. Transfer accurately weighed portions of 10 g blood, 0.25 g "dry" tissue, or 1.0 g "wet" tissue to a beaker.
5. Add 10.0 mL digestion acid to each blood sample or 5.0 mL digestion acid to each tissue sample. Heat at 110 °C for 2 h.
   NOTE: Start reagent blanks, in triplicate, at this step.
6. Increase hotplate temperature to 250 °C and heat until ca. 1 mL (for blood) or ca. 0.5 mL (for tissue) remains (2 to 3 h).
7. Allow beaker to cool.
8. Choose one of the following:
   a. **External standard method.** Transfer contents of beaker to a volumetric flask (10 mL for blood; 5 mL for tissue). Dilute to the mark with deionized water.
   b. **Internal standard method.** Add, via pipet, 10.0 mL (for blood) or 5.0 mL (for tissue) yttrium standard to the beaker.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate the spectrometer according to manufacturer's recommendations.
   NOTE: Typically, an acid blank and 10 μg/mL multielement solutions are used.
10. Analyze a standard for every ten samples.
11. Check measurement recoveries for all elements of interest with at least three spiked, unexposed samples or with reference materials of known elemental composition. These quality control samples should constitute 15 to 20% of all samples analyzed.
    NOTE: For blood or tissue spikes, split a control sample and spike one fraction. Subtract the element quantity found in the unspiked portion from the element quantity found in the spiked portion and determine measurement recovery. Correct all samples for this measurement recovery. This is especially important for blood samples because routine interelement corrections will not adequately compensate for the high levels of iron present, which has numerous spectral emission wavelengths.

MEASUREMENT:

12. Set the spectrometer to conditions specified by the manufacturer.
13. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the sample solutions with 10% H_2SO_4, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

14. Obtain the solution concentration found for each element in the sample, C_s (μg/mL), and the average blank, C_b (μg/mL), from the measurement data.
15. According to the method of standardization, calculate the concentration, C (μg/g), of each element in the mass of sample taken, M (g).
    a. **External standard method.** Use the final solution volumes of sample, V_s (mL) and blank, V_b (mL):
    b. **Internal standard method.** Use the yttrium standard concentration, C_y (μg/mL), the volume of yttrium standard added, V_y (mL), and the concentration of yttrium found in the

$$C = \frac{(C_s V_s - C_b V_b)}{M}, \mu g/g.$$

sample, C_{sy} (μg/mL). Treat the blank solution similarly [i.e., C_b is the concentration (μg/mL) of analyte on the blank and C_{by} is the concentration of yttrium in the blank]:

$$C = \frac{\frac{C_s C_y V_y}{C_{sy}} - \frac{C_b C_y V_y}{C_{by}}}{M}, \mu g/g.$$

GUIDELINES TO INTERPRETATION:

Acceptable and unacceptable levels for elements have not been determined by this method. Iyengar [6] reports metals concentrations in tissues and body fluids. Lauwerys [7] discusses metals and can be consulted for guidance and interpretation. For tissue, trace element concentrations will vary with the tissue type or organ. Iyengar [6] reports metals concentrations for different tissues of non-occupationally exposed people. Blood metal concentrations of non-occupationally exposed individuals are given in Table 2.

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TABLE 1. GENERAL INFORMATION

Element (Formula)	Atomic Weight	CAS#	RTECS
Antimony (Sb)	121.75	7440-36-0	CC4025000
Cadmium (Cd)	112.40	7440-43-9	EU9800000
Cobalt (Co)	58.93	7440-48-4	GF8750000
Chromium (Cr)	52.00	7440-47-3	GB4200000
Copper (cu)	63.54	7440-50-8	GL5325000
Iron (Fe)	55.85	7439-89-6	NO4565500
Lanthanum (La)	138.91	7439-91-0	--
Lead (Pb)	207.19	7439-92-1	OF7525000
Lithium (Li)	6.94	7439-93-2	OJ5540000
Magnesium (Mg)	24.31	7439-95-4	OM2100000
Manganese (Mn)	54.94	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	7439-98-7	QA4680000
Nickel (Ni)	58.71	7440-02-0	QR5950000
Platinum (Pt)	195.09	7440-06-4	TP2160000
Silver (Ag)	107.87	7440-22-4	VW3500000
Strontium (Sr)	87.62	7440-24-6	--
Thallium (Tl)	204.37	7440-28-0	XG3425000
Vanadium (V)	50.94	7440-62-2	YW1355000
Zinc (Zn)	65.37	7440-66-6	ZG8600000
Zirconium (Zr)	91.22	7440-67-7	ZH7070000

TABLE 2. RECOVERY OF METALS FROM BLOOD [1,2].

Element (Formula)	Wavelength (nm)	Value[a] (μg/100 mL)	Metal "Nonexposed" Added (μg/Sample)	Quantity Recovery (%)	Precision (% s_r) n = 4	Accuracy (±%)
Antimony (Sb)	217.58	0.4	10	106	4.9	15.6
Cadmium (Cd)	226.5	0.5	10	120	1.1	22.2
Cobalt (Co)	231.2	1.0	10	81	21	60.2
Chromium (Cr)	205.6	4.5	10	114	4.7	23.2
Copper (Cu)	324.8	100	10	101	5.8	12.4
Iron (Fe)	45,000	0	--[b]	--[b]		--
Lanthanum (La)	--[c]	10	119	2.4		23.7
Lead (Pb)	220.4	23	10	113	0.85	14.7
Lithium (Li)	670.8	1.0	10	113	1.1	15.2
Magnesium (Mg)	279.6	3,800	110	104	12	27.5
Manganese (Mn)	257.6	4.0	10	98	2.1	6.1
Molybdenum (Mo)	281.6	4.0	10	126	3.1	32.1
Nickel (Ni)	231.6	5.0	10	86	16	45.4
Platinum (Pt)	203.7	--[c]	10	92	14	35.4
Silver (Ag)	328.3	3.5	10	115	0.8	16.6
Strontium (Sr)	421.5	2.8	10	113	0.88	14.7
Thallium (Tl)	190.9	1.0	10	97	8.7	20.0
Vanadium (V)	310.2	1.2	10	131	1.1	33.2
Zinc (Zn)	213.9	700	60	103	17	36.3
Zirconium (Zr)	339.2	1.5	10	71	8.7	46.0

[a]"Nonexposed" value is the average concentration for the respective element in blood of non-occupationally exposed individuals. These values were tabulated from References [6] through [19].

[b]Recovery not determined (blood Fe concentration was above quantitation limit of spectrometer).

[c]Concentration not reported.

MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 7300, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

ELEMENTS:

aluminum*	chromium*	lithium*	phosphorus	tellurium	zinc
arsenic	cobalt*	magnesium	platinum*	thallium	zirconium*
beryllium*	copper	manganese*	selenium	titanium	
cadmium	iron	molybdenum*	silver	vanadium	
calcium	lead*	nickel	sodium	yttrium	

* Some compounds of those elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-μm, cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY

ANALYTE: elements above

ASHING REAGENTS: conc. HNO_3, 4 mL; and conc. $HClO_4$, 1 mL

CONDITIONS: room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 10 mL

WAVELENGTH: depends upon element; Table 3

BACKGROUND CORRECTION: spectral wavelength shift

CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$

RANGE: 2.5 to 1000 μg per sample [1]

ESTIMATED LOD: 1 μg per sample [1]

PRECISION ($\bar{S}_r$): Table 3

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m^3 for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. An alternative microwave digestion procedure is included. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1,2].

OTHER METHODS: This method replaces P&CAM 351 [2] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

REAGENTS:

1. Nitric acid, conc., ultra pure.
2. Perchloric acid, conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
4. Calibration stock solutions, 1000 μg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3, 1% $HClO_4$. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10- and 100- mL.**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or the Appendix for a microwave digestion procedure [8].
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [2-7]. For example, aqua regia may be needed for Mn [4,9].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 10-mL volumetric flasks.
11. Dilute to volume with dilution acid.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 10 μg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO_3/1% $HClO_4$:
    a. Ag, Ca, Co, Mn, Pb, V, Zn;
    b. Al, Be, Cd, La, Li, Ni, Tl;
    c. As, B, Ba, Mg, Mo, P;
    d. Cu, Fe, Na, Pt, Sr, Te, Y;
    e. Cr, K, Se, Ti, Zr; and
    f. Si, W (distilled water only)
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked media blanks per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (μg/mL), and the average media blank, C_b (μg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 351 was evaluated in 1981 [1,2]. The precision and recovery data were determined at 2.5 and 1000 μg of each element per sample on spiked filters. The precision and recovery data, instrumental detection limits, sensitivity, and analytical wavelengths are listed in Table 3. The values in Table 3 were determined with a Jarrell-Ash Model 1160 ICP operated according to manufacturer's instructions.

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METHOD WRITTEN BY:

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James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Labortories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties		Air Volume, L @ OSHA PEL	
	Atomic Weight	MP, °C	MIN	MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Sodium (Na)	22.99	98	13	2000
Nickel (Ni)	58.71	1453	25	1000
Phosphorus (P)	30.97	44	50	2000
Lead (Pb)	207.19	328	1250	2000
Platinum (Pt)	195.09	1769	13	2000
Selenium (Se)	78.96	217	5	2000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m^3 (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total) 5 (respirable)	5	10 (dust) 5 (fume)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	--	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.2, C 0.6 (dust) 0.1, C 0.3 (fume)	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05	0.05 (dust, fume)
Chromium (II) (Cr)	22541-79-3	GB6260000	0.5	0.5	0.5
Chromium (III) (Cr)	16065-83-1	GB6261000	0.5	0.5	0.5
Chromium (VI) (Cr)	18540-29-9	GB6262000	C 0.1	0.001 (dust)	0.05 (soluble) 0.05 (insoluble), Ca
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	1309-37-1	NO7400000	10 (dust, fume)	5 (dust, fume)	5 (fume)
Lithium (Li)	--	--	--	--	--
Magnesium (Mg)	1309-48-4	OM3850000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble) 5 (respirable insol.)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.05, Ca
Lead (Pb)	7439-92-1	OF7525000	0.05	<0.1	0.15
Platinum (Pt)	7440-06-4	TP2160000	0.002	1 (metal)	1 (metal)
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti) TiO_2	7440-32-6 13463-67-7	XR1700000 XR2275000	as TiO_2, 15 as TiO_2, 5 (respirable)	lowest feasible, Ca	10
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V) V_2O_5	7440-62-2 1314-62-1	YW240000 YW1355000	C 0.5 (respirable) as V_2O_5 C 0.1 (fume) as V_2O_5	C 0.05	0.05 (respir.) as V_2O_5
Yttrium (Y)	7440-65-5	ZG2980000	1	1	1
Zinc (Zn)	1314-13-2	ZH4810000	5 (ZnO fume) 15 (ZnO dust) 5 (ZnO respirable)	5; STEL 10 (ZnO fume) 5; C 15 (ZnO dust)	5; STEL 10 (ZnO fume) 10 (ZnO dust)
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA [a].

Element	Wavelength (nm)	Instrumental LOD (ng/mL)	Sensitivity (Intensity/ μg/mL)	Recovery @ 2.5 μg/ filter [b]	Recovery @ 1000 μg/ filter	Precision ($\tilde{S}_r$) (N = 3) @ 2.5 μg/ filter	Precision ($\tilde{S}_r$) (N = 3) @ 1000 μg/ filter
Ag	328.3	26	0.65	111	91	0.02	0.075
Al	308.2	14	0.23	93	100	0.092	0.023
As	193.7	13	0.57	103	99	0.062	0.026
Be	313.0	1.5	1.29	107	90	0.040	0.034
Ca	315.9	10	0.49	99	95	0.036	0.014
Cd	226.5	1.6	0.83	107	99	0.032	0.020
Co	231.2	7.4	0.38	101	95	0.040	0.005
Cr	205.6	1.3	0.50	98	106	0.053	0.016
Cu	324.8	2.1	0.72	98	99	0.036	0.022
Fe	259.9	3.9	0.13	94	97	0.068	0.016
Li	670.8	2.8	0.48	89	95	0.171	0.043
Mg	279.6	24	0.22	105	106	0.084	0.027
Mn	257.6	0.4	0.74	84	93	0.062	0.035
Mo	281.6	7.0	0.18	94	88	0.023	0.049
Na	589.0	10	0.76	(c)	101	(c)	0.045
Ni	231.6	3.4	0.41	105	97	0.027	0.020
P	214.9	22	0.17	(c)	91	(c)	0.056
Pb	220.4	17	0.42	105	95	0.060	0.011
Pt	203.7	15	0.69	106	91	0.041	0.075
Se	190.6	21	0.28	105	97	0.068	0.049
Sn[d]	190.0	64	0.49	74	67	0.33	0.16
Te	214.3	29	0.41	102	94	0.050	0.063
Ti	334.9	1.2	0.55	96	108	0.051	0.029
Tl	190.9	17	0.22	103	99	0.043	0.017
V	310.2	3.2	0.88	99	94	0.043	0.014
W[d]	207.9	13	2.58	35	23	0.053	0.60
Y	371.0	0.8	2.35	99	100	0.015	0.013
Zn	213.9	0.6	0.60	101	94	0.013	0.013
Zr	339.2	1.9	0.88	75	98	0.049	0.008

(a) Values reported were obtained with a Jarrell-Ash Model 1160 ICP; performance may vary with instrument and should be independently verified.
(b) 2.5 μg/filter corresponds to 5 $\mu g/m^3$ for a 500-L air sample.
(c) Blank levels too high to make accurate determinations.
(d) Qualitative only because of low recovery.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements

   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.

c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.

d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six, or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180°C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180°C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in Table 1.

Table 1

Program Variables for Paint Chips Sample Digestion with Nitric Acid

Stage		(1)	(2)	(3)
Power		90%	90%	0%
Pressure, psi		50	100	0
Run Time, min		10:00	20:00	05:00
Time @ P, min		05:00	15:00	00:00
Temperature		180°C	180°C	0°C
Fan Speed		100%	100%	100%
Number of Vessels:	12			
Liquid Volume per Vessel:	5 mL			
Sample Weight:	0.1 g			

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.

ENDRIN

$C_{12}H_8OCl_6$ MW: 380.93 CAS: 72-20-8 RTECS: IO1575000

METHOD: 5519, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3 (skin)
NIOSH: 0.1 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.1 mg/m^3 (skin)

PROPERTIES: crystals; MP 200 °C; decomposes @ 245 °C; VP 0.27 x 10^{-7} kPa (2 x 10^{-7} mm Hg) @ 25 °C

SYNONYMS: Mendrin; Nendrin; Hexadrin

SAMPLING

SAMPLER: FILTER + SOLID SORBENT TUBE (0.8 µm cellulose ester membrane + Chromosorb 102, 100/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 12 L @ 0.1 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.06 to 0.31 mg/m^3 [1,2] (120-L samples)

BIAS: - 0.7%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [2]

ACCURACY: ± 13.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: endrin

EXTRACTION: 5 mL toluene, stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 280 °C
-COLUMN: 160 °C

CARRIER GAS: 95% argon/5% methane @ 60 mL/min

COLUMN: 2 m x 4-mm ID glass, packed with 3% OV-1 on 100/120 Chromosorb Q

CALIBRATION: standard solutions of endrin in toluene

RANGE: 1.2 to 36 µg per sample [2]

ESTIMATED LOD: 0.02 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.016 @ 1.2 to 24.5 µg per sample [1]

APPLICABILITY: The working range is 0.01 to 0.33 mg/m^3 for a 120-L air sample. Smaller concentrations can be determined if desorption efficiency is satisfactory. The use of a capillary column, e.g., DB-1, may improve resolution and sensitivity.

INTERFERENCES: None identified.

OTHER METHODS: This is a modification of the method of Hill and Arnold [3] and it replaces NIOSH method S284 [2].

REAGENTS:

1. Toluene, ACS reagent grade or better.
2. Hexane, ACS reagent grade or better.
3. Xylene, ACS reagent grade or better.
4. Endrin.*
5. Calibration stock solution, 3 mg/mL. Dissolve 30 mg endrin in 1 mL xylene and dilute to 10 mL with hexane.
6. 95% Argon/5% methane mixture, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 0.8-μm pore size MCEF filter supported by a stainless steel screen in cassette filter holder followed by a 7 cm x 8-mm OD x 6-mm ID, glass tube, flame-sealed with plastic caps, containing 20/40 mesh Chromosorb 102 (front = 100 mg; back = 50 mg), separated by 3-mm silanized glass wool plug. Pressure drop across the tube at 1 L/min must not exceed 3.4 kPa. Tubes commercially available (SKC #226-49-20-102 or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator and column (page 5519-1).
4. Vials, glass, scintillation, 20-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1-μL.
6. Volumetric flasks, 10-mL.
7. File, triangular.
8. Pipets, 5- and 10-mL.
9. Tweezers.

SPECIAL PRECAUTIONS: Endrin is absorbed through the skin. Gloves and safety glasses must be used to avoid direct contact with this compound. Handle all chemicals and organic solvents in the laboratory hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the tube immediately before sampling. Connect the Chromosorb tube to the cassette with a short piece of tubing. Connect the tube to the pump with backup section nearest the sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 12 to 400 L.
4. Remove the cassette from the sampling train, carefully remove the filter from the cassette with tweezers and place it in a clean vial. Reassemble the cassette and plug the inlet and outlet.
5. Score the Chromosorb tube in front of the front section and break the tube at score line. Transfer the front (larger) section of sorbent and the glass wool plug to the scintillation vial containing the filter.
6. Cap the ends of the sampling tube containing the backup section and ship along with the sample vial.
7. In a separate package, ship bulk sample of the suspected material in a vial.

SAMPLE PREPARATION:

8. Transfer the backup sorbent section and associated glass wool plugs to a clean vial.
9. Add 5.0 mL toluene to each vial (filter + front sorbent section in one vial and back sorbent section in another vial). Cap each vial. Allow to stand, with occasional swirling, for 15 min.

10. Wash the filter cassette parts as follows: Pipet 10.0 mL hexane into a clean vial and mark the level. Remove the hexane and allow to dry. Place the bottom part-cassette on the open, marked vial. Invert the top part-cassette and place it on the bottom part-cassette. Hold the metal screen over the set-up with clean tweezers. Rinse the screen with 10.0 mL hexane, allowing the rinse to drain from top cassette through bottom cassette to the marked vial. Remove any remaining rinse from the cassette parts with clean disposable pipet and transfer to the marked vial. Dilute with hexane to the marked levels. Cap immediately.
NOTE: Analysis should be done within 24 hours of desorption.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards covering the range of samples.
    a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark. Use serial dilution as needed to obtain endrin concentrations in the range 0.004 to 7 μg/mL.
    b. Analyze (steps 14 through 16) the working standards and blank in duplicate.
    c. Prepare a calibration graph (peak area vs. μg endrin); analyze two additional check standards for each ten sample injections.
12. Determine the analytical method recovery at least once for each lot of filter and Chromosorb 102 used. Prepare four samplers at each of five levels plus three media blanks.
    a. Place a MCEF filter and 100 mg of Chromosorb 102 in a vial.
    b. Inject calibration stock solution onto the combined filter and Chromosorb 102 in the container with a microliter syringe. Include blank samples.
    c. Cap the vial and let stand overnight.
    d. Analyze in duplicate; prepare graph of recovery vs. μg endrin.
13. Check recovery at two levels for each sample set in duplicate. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

14. Set gas chromatograph to conditions given on page 5519-1.
15. Inject 5 μL sample aliquot using solvent flush technique. Make duplicate injections of sample and standards.
    NOTE: Under these conditions, t_r for endrin is ca. 5 min.
16. Measure peak areas.

CALCULATIONS:

17. Determine the mass, μg (corrected for recovery) of endrin found on the sampler (filter plus front section of Chromosorb 102), W_1, back of section, W_2, and the rinse from screen and cassette, F, and in the average media blank (filter plus front tube section, B_1, and back tube section, B_2.
    NOTE: If $W_2 > W_1 + F/10$, report breakthrough and possible sample loss.
18. Calculate the concentration of endrin, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_1 + W_2 + F - B_1 - B_2)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S284 was validated on July 8, 1979 [1,2,4]. The substance used to dynamically generate test atmospheres at 25 °C and 760 mm Hg was: 1.6 EC, Velsicol Chemical Corporation. Collection efficiencies were close to 1.00 in the range 28 to 33 μg per sample. The analytical recoveries from

sorbent tubes (range: 1.2 to 6.1 μg per sample) and from the filter sampler (range: 6.1 to 24.5 μg per sample) were 99% with a combined precision of 0.016. No significant breakthrough was observed after 240 min of sampling an atmosphere containing 0.257 mg/m^3 endrin at a flow rate of approximately 1 L/min. Samples stored one week at room temperature and extracted with toluene gave recoveries of 96 to 100%. Overall precision ($\hat{S}_{rT}$) was 0.07. No significant bias was found.

REFERENCES:

[1] NIOSH Backup Data Report S284 (July 8, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S284, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] Hill, R. H. and J. E. Arnold., "A Personal Air Sampler for Pesticides", Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., ATSDR; S284 originally validated under NIOSH Contract No. 210-76-0123.

EPICHLOROHYDRIN

CH_2OCHCH_2CL MW: 92.53 CAS: 106-89-8 RTECS: TX4900000

METHOD: 1010, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: lowest feasible (carcinogen)
ACGIH: 2 ppm (skin) (carcinogen)
(1 ppm = 3.78 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.812 g/mL @ 20 °C; BP 117.9°C; MP −25.6 °C; VP 1.67 kPa (12.5 mm Hg; 16,400 ppm) @ 20 °C; explosive range 3.8 to 21% v/v in air

SYNONYMS: chloropropylene oxide; 1-chloro-2,3-epoxypropane; chloromethyloxirane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 5 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 12 to 43 mg/m^3 [2] (20-L samples)

BIAS: 4.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [2]

ACCURACY: ± 14.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: epichlorohydrin

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 215 °C
-COLUMN: 135 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: 1.8 m x 2-mm ID glass; 80/100 Chromosorb 101 [1]

CALIBRATION: epichlorohydrin in CS_2

RANGE: 0.04 to 1.2 mg per sample [2]

ESTIMATED LOD: 1.0 µg per sample

PRECISION ($\bar{S}_r$): 0.031 [2]

APPLICABILITY: The working range is 0.5 to 16 ppm (2 to 60 mg/m^3) for a 20-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S118 in a revised format [3]. A similar method appears in the criteria document [4].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Epichlorohydrin, reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Calibration stock solution, 9.45 mg/mL. Dissolve 80 μL epichlorohydrin in 10 mL CS_2.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, FID, integrator and column (page 1010-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 10- and 100-μL.
7. Volumetric flasks, 1- and 10-mL.
8. Metal file.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = −30 °C); work with it only in a hood.

Epichlorohydrin is a strong irritant and sensitizer and may cause kidney injury [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 30 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 1200 μg epichlorohydrin per sample.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg epichlorohydrin).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of epichlorohydrin (or a solution of epichlorohydrin) directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg epichlorohydrin recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1010-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of epichlorohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of epichlorohydrin in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S118 was issued on May 9, 1975 and validated over the range 11.7 to 43.1 mg/m3 using approximately 20-L sample volumes [2] of a generated atmosphere of epichlorohydrin. During sampling, a total hydrocarbon analyzer was used to independently verify the analyte concentration. Epichlorohydrin at the OSHA standard, 0.38 mg, was stable on coconut charcoal for six days at ambient temperature. Over the analytical range, the average DE was 0.905. Breakthrough of the front section occurred at 44.4 L while sampling 43.1 mg/m^3 at 0.185 L/min.

Epichlorohydrin was also sampled at 40 μg/L for 49 L without breakthrough to the back section using 80% relative humidity [1]. In this later evaluation, epichlorohydrin on lot 105, PCB 20/40, charcoal was found to be stable for at least two weeks. A DE of 0.82 was used to correct results of 8.1 and 11.6 μg per tube.

REFERENCES:

[1] Hill, R.J., Jr., J.A. Arnold and W.J. Woodfin. Collection and Determination of Epichlorohydrin in Air, NIOSH, Method evaluation report (unpublished, 1976).
[2] Documentation of the NIOSH Validation Tests, S118, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S118, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Criteria for a Recommended Standard...Occupational Exposure to Epichlorohydrin, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-206 (1976).

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S118 validated under NIOSH Contract CDC-99-74-45.

$C_{14}H_{14}NO_4PS$ W: 323.31 CAS: 2104-64-5 RTECS: TB1925000

METHOD: 5012, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: solid; MP 36 °C; d 1.268 g/mL @ 25 °C
VP 0.04 Pa (0.0003 mm Hg, 5 mg/m^3) @ 100 °C

SYNONYMS: phenylphosphonothioic acid O-ethyl-O,p-nitrophenyl ester

SAMPLING

SAMPLER: FILTER (glass fiber)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L @ 0.5 mg/m^3
-MAX: 700 L

FIELD TREATMENT: transfer filters within 1 h of sampling to vial

SHIPMENT: in vials

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.3 to 1.2 mg/m^3 [1] (120-L samples)

BIAS: 0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1,2]

ACCURACY: ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME PHOTOMETRIC

ANALYTE: EPN

DESORPTION: 15 mL isooctane

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 215 °C
-DETECTOR: 215 °C
-COLUMN: 205 °C

CARRIER GAS: N_2 or He, 60 mL/min

COLUMN: 2 m x 6-mm glass, packed with 3% OV-1 on 100/120 mesh Gas Chrom Q

CALIBRATION: solutions of the EPN in isooctane

RANGE: 6 to 170 µg per sample

ESTIMATED LOD: 2 ng per sample [1]

PRECISION ($\bar{S}_r$): 0.04 [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 EPN for 120-L air samples. Malathion and Parathion have also been determined by this procedure.

INTERFERENCES: None known.

OTHER METHODS: This method replaces Method S285 [2]. The method of Hill and Arnold [3] has also been used for analysis of pesticides. Method 5600 is an alternative method for organophosphorus pesticides.

REAGENTS:

1. EPN.*
2. Isooctane, chromatoquality.*
3. Calibration stock solution, 15 mg/mL isooctane (prepare fresh daily):
   NOTE: 4 μL of this solution contains a mass of EPN (0.06 mg) equivalent to a 120-L air sample at OSHA PEL.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filter (Gelman Type AE or equivalent), 37-mm, in a two-piece polystyrene cassette supported by a backup pad.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Gas chromatograph, column bypass valve, flame photometric detector, phosphorus filter, integrator and column (page 5012-1).
4. Vials, 20-mL, glass with PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, 15-mL, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: EPN is a highly toxic cholinesterase inhibitor with cumulative effects [4,5]. Special care must be taken to avoid inhalation or skin contact.

Isooctane is flammable. Prepare all samples in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 2 L/min for a total volume of 15 to 700 L. Do not exceed 2 mg total dust loading on the filter.
3. Within 1 h after sampling, transfer the glass fiber filter with tweezers to a clean 20-mL vial.

SAMPLE PREPARATION:

4. Pipet 15 mL isooctane into each vial. Cap each vial and swirl the contents for 1 h.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least six working standards covering the analytical range of the method, by diluting aliquots of the calibration stock solutions to 15 mL with isooctane.
   a. Analyze calibration standards in triplicate with the unknowns, blanks and other quality control spiked samples following steps 7 through 9.
   b. Prepare calibration graph (peak area or peak height vs. μg of EPN).
6. Analyze recovery (R) samples with each sample set, in duplicate.
   a. Place filter media blanks in clean 20-mL vials.
   b. Inject analyte calibration stock solution directly onto the filter with a microliter syringe.
   c. Cap the vial and allow to stand overnight.
   d. Analyze according to steps 4 and 7 through 9.
   e. Calculate recovery (μg found on filter divided by μg added to filter).

MEASUREMENT:

7. Set gas chromatograph to conditions given on page 5012-1, optimizing the air, hydrogen and oxygen according to the GC manufacturer's instructions.
8. Inject 5-μL sample aliquots using solvent flush technique.

a. Vent the solvent peak by opening the column bypass valve at the time of injection. Close the column bypass valve after the solvent peak has eluted (ca. 30 sec) and before the analyte peak elutes.
b. Make replicate injections of samples and standards.

9. Measure peak area or peak height.

CALCULATIONS:

10. Read the mass, μg per sample, of EPN found on the sample filters, W, and average media blank filters, B, from the calibration graph.
11. Calculate the concentration, C, of EPN in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S285 for EPN was issued on April 26, 1976 [2]. The precision and bias were obtained by generating atmospheres of EPN at one-half, one and two times the OSHA standards [1,6]. Test atmospheres were generated using Trion-6 EPN (Wilbur Ellis Co.). Gelman Type AE glass fiber filters were used for all sampling and measurement recovery studies. Collection efficiency of the glass fiber filter was determined to be 1.0 and losses from vaporization of known amounts of EPN deposited on a glass fiber filter were negligible [4]. Filters spiked with solutions of EPN gave quantitative recoveries after storage for 7 days at 25 °C.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S285, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S285, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Hill, Robert H., Jr. and James E. Arnold. A Personal Air Sampler for Pesticides, Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).
[4] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[5] NIOSH/OSHA Occupational Safety and Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Paula Fey O'Connor, NIOSH/DPSE; Method S285 originally validated under NIOSH Contract CDC 99-74-45.

TABLE 2 MW: TABLE 1 CAS: TABLE 2 RTECS: TABLE 2

METHOD: 1450, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 2

COMPOUNDS: (synonyms in Table 2)	n-amyl acetate	t-butyl acetate	isobutyl acetate	sec-amyl acetate
	2-ethoxyethyl acetate	methyl isoamyl acetate	n-butyl acetate	ethyl acrylate
	n-propyl acetate	sec-butyl acetate	isoamyl acetate	

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ OSHA PEL
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 2X OSHA PEL [1] (10-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.05 to 0.09; see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE - INJECTION: 200 - 225 °C
- DETECTOR: 250 - 300 °C
- COLUMN: 60 to 100 °C (Table 1)

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 3 m x 3-mm, 5% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: solutions of compounds in CS_2

RANGE: Table 1

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.02 [1]

APPLICABILITY: This method can be used for simultaneous analysis of 2 or more substances by changing the gas chromatographic conditions (e.g., temperature programming). High humidity greatly reduces sampler capacity and breakthrough volume.

INTERFERENCES: None identified. Alternate columns (e.g., 10% SP-1000 on Chromosorb WHP) may be useful if interferences are encountered.

OTHER METHODS: This method combines and replaces Methods S31, S32, S35, S37, S41, S44 through S48, and S51 [3]. Method 1457 (Ethyl Acetate) gives a capillary column procedure which may be useful for the esters in this method.

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 0.1% (v/v) benzene or 1% (v/v) tridecane, dodecane, undecane or other suitable internal standard
2. Analyte, reagent grade
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
4. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1450-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-μL, readable to 0.1 μL, 25-, 50- and 100-μL.
7. Volumetric flasks, 10-mL
8. Pipet, volumetric, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

   NOTE: The desorption efficiency of 2-ethoxyethyl acetate has been found to decrease with the resident time of the desorbed solution with charcoal [4]. After 30 min. desorption transfer the supernatant solution of 2-ethoxyethly acetate to a clean 2-mL vial and seal with a crimp cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.02 to 10 mg analyte per sample.

a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1450-1. Inject sample aliquot with autosampler, or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The methods listed below were issued on December 6, 1974, except for S51, which was issued on January 17, 1975 [2]. Atmospheres of each compound were generated in dry air by calibrated syringe drive and 10-L air samples were taken [1]. Collection efficiency in humid air and sample stability were not tested. Spiked samplers were used to study measurement precision and desorption efficiency (DE). Results are as follows:

		Overall					Measurement		
Compound	Method [3]	Range, mg/m^3	Breakthrough[1] (<)	Bias %	$\hat{S}_{rT}$	Accuracy (± %)	Range, mg per sample	DE[2]	$\hat{S}_r$
n-amyl acetate	S51	208-871	34.2	0.3	0.051	10.3	2.6-10	0.87	0.019
sec-amyl acetate	S31	349-1460	20.9	-4.1	0.071	15.4	3.3-13	0.93	0.012
n-butyl acetate	S47	352-1475	20.5	0.3	0.069	10.4	3.5-14	0.94	0.020
sec-butyl acetate	S46	478-2005	16.5	-2.4	0.054	11.3	4.7-19	0.93	0.017
t-butyl acetate	S32	424-1780	14.3	-8.6	0.091	22.2	4.7-19	0.94	0.039
2-ethoxyethyl acetate	S41	262-1100	34.6	9.6	0.062	19.4	2.5-11	0.79	0.024
ethyl acrylate	S35	50-210	>45	-7.1	0.054	15.7	0.5-2	0.95	0.029
isoamyl acetate	S45	208-874	32.3	-7.1	0.056	15.6	2.6-10	0.91	0.010
isobutyl acetate	S44	306-1280	21.5	1.8	0.065	11.1	3.5-14	0.94	0.016
methyl isoamyl acetate	S37	143-601	>45	-2.6	0.058	11.6	1.5-6	0.93	0.021
n-propyl acetate	S48	384-1610	17.9	6.9	0.056	16.8	4.2-17	0.93	0.018

[1] 5% breakthrough, 0.2 L/min, at high end of concentration range in dry air.
[2] Averaged over mass range shown.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #4121-N (unpublished, November 15, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Corelson, D., SRI, Menlo Park, CA., Personal communication with NIOSH (1988).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. Operational details.

Compound	M.W. mg/m3 = 1 ppm @ NTP / MW mg/m^3 = 1 ppm		Working range mg/m^3 @ 10 L	Measurement Range, mg per sample	Column Temperature, °C
n-amyl acetate	130.18	5.32	50 to 1575	0.5 to 16	90
sec-amyl acetate	130.18	5.32	65 to 1950	0.65 to 20	95
n-butyl acetate	116.16	4.75	71 to 2130	0.7 to 21	90
sec-butyl acetate	116.16	4.75	95 to 2850	1 to 28	60
t-butyl acetate	116.16	4.75	95 to 2850	1 to 28	70
2-ethoxyethyl acetate	132.16	5.40	54 to 1620	0.5 to 16	100
ethyl acrylate	100.11	4.09	10 to 300	0.1 to 3	70
isoamyl acetate	130.18	5.32	50 to 1575	0.5 to 16	90
isobutyl acetate	116.16	4.75	70 to 2100	0.7 to 21	70
methyl isoamyl acetate	144.22	5.90	30 to 900	0.3 to 9	90
n-propyl acetate	102.13	4.18	84 to 2520	0.8 to 25	70

Table 2. General information

Compound, Formula, and RTECS	Synonyms	OSHA/NIOSH/ACGIH, ppm	BP, °C	VP @ 20 °C, kPa (mm Hg)	Liquid Density, g/mL @ 20 °C
n-amyl acetate $CH_3COO(CH_2)_4CH_3$; $C_7H_{14}O_2$ AJ1925000	acetic acid 1-pentanol ester; CAS #628-63-7	TWA (STEL) 100/100/100	149	0.5(4)	0.876
sec-amyl acetate $CH_3COOCHCH_3(CH_2)_2CH_3$; $C_7H_{14}O_2$ AJ2100000	acetic acid 2-pentanol ester; CAS #626-38-0	125/125/125	134	0.9(7)	0.866
n-butyl acetate $CH_3COO(CH_2)_3CH_3$; $C_6H_{12}O_2$ AF7350000	acetic acid butyl ester; CAS #123-86-4	150/150(200)/150(200)	126	1.3(10)	0.883
sec-butyl acetate $CH_3COOCH(CH_3)CH_2CH_3$; $C_6H_{12}O_2$ AF7380000	acetic acid 1-methyl propyl ester; CAS #105-46-4	200/200/200	112	1.3(10)	0.865
t-butyl acetate $CH_3COOC(CH_3)_3$; $C_6H_{12}O_2$ AF7400000	acetic acid 1, 1-dimethylethyl ester; CAS #540-88-5	200/200/200	98	not available	0.867
2-ethoxyethyl acetate $CH_3COO(CH_2)_2OCH_2CH_3$; $C_6H_{12}O_3$ KK8225000	Cellosolve acetate; acetic acid ethylene glycol monoethyl ether ester; CAS 111-15-9	100*/0.5*/5*	156	0.3(2)	0 973
ethyl acrylate $CH_2=CHCOOCH_2CH_3$; $C_5H_8O_2$ AT0700000	2-propenoic acid ethyl ester; CAS #140-88-5	25*/4 LOQ[b]/5*[b] (15 ppm)	99	3.9(30)	0.923
isoamyl acetate $CH_3COO(CH_2)_2CH(CH_3)_2$; $C_7H_{14}O_2$ NS9800000	acetic acid 3-methyl-1-butanol ester; CAS #123-92-2	100/100/100	142	0.5(4)	0.876
isobutyl acetate $CH_3COOCH_2CH(CH_3)_2$; $C_6H_{12}O_2$ AI4025000	acetic acid isobutyl ester; CAS #110-19-0	150/150/150	117	1.7(13)	0.871
methyl isoamyl acetate $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$; $C_8H_{16}O_2$ SA7525000	acetic acid 4-methyl-2-pentanol ester; 1,3-dimethyl butyl acetate; "sec-hexyl acetate"; CAS #108-84-9	50/50/50	146	0.5(3.8)	0.858
n-propyl acetate $CH_3COO(CH_2)_2CH_3$; $C_5H_{10}O_2$ AJ3675000	acetic acid n-propyl ester; CAS #109-60-4	200/200 (250)/200 (250)	102	3.3(25)	0.890

[a] Skin
[b] Carcinogen

ETHANOL

See ALCOHOLS I (Method 1400) for procedure

2-ETHOXYETHANOL

See ALCOHOLS IV (Method 1403) for procedure

2-ETHOXYETHYL ACETATE

See ESTERS I (Method 1450) for procedure

ETHYL ACETATE

$CH_3COOC_2H_5$ MW: 88.10 CAS: 141-78-6 RTECS: AH5425000

METHOD: 1457, Issue 1 **EVALUATION:** FULL **Issue 1:** 15 August 1994

OSHA : 400 ppm
NIOSH: 400 ppm
ACGIH: 400 ppm
(1 ppm = 360 mg/m^3 @ NTP)

PROPERTIES: liquid, d = 0.8945 g/mL @ 25 °C; BP = 77 °C; VP = 9.7 kPa (73 mm Hg) @ 20 °C

SYNONYMS: acetic ether; acetic ester; ethyl ethanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/minute

VOL-MIN: 0.1 L @ 1400 mg/m^3
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 6 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 704 to 2950 mg/m^3 [2] (6-L samples)

BIAS: −2.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.058 [2]

ACCURACY: ±11.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl acetate

EXTRACTION: 1 mL CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C, 2 min; 10 °C/min to 150 °C

COLUMN: DB-Wax; 30 m, 0.32-mm ID, 1-µm film thickness

CARRIER GAS: He, 1 mL/min

MAKEUP GAS: Na, 30 mL/min

CALIBRATION: standard solutions of ethyl acetate in CS_2

RANGE: 1.5 to 1,000 µg per sample [1]

ESTIMATED LOD: 0.5 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.019 @ 40.5 to 810 µg per sample [1]

APPLICABILITY: The working range is 0.07 to 790 ppm (0.25 to 2800 mg/m^3) for a 6-L air sample [2]. The method may be adapted for other esters with appropriate changes in chromatographic conditions.

INTERFERENCES: Any compounds with similar retention times.

OTHER METHODS: This revises Method S49 [2]. Improved recovery of analyte may be achieved with the addition of 5% butyl carbitol to the CS_2 desorption procedure [3,4].

REAGENTS:

1. Carbon disulfide,* chrom. grade.
2. Ethyl acetate, reagent grade.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1457-1).
5. Vials, glass, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C.) Use only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.2 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
   NOTE: Decane or other suitable internal standard at 0.1% v/v may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 8 to 1000 μg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area of analyte vs. mg ethyl acetate).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
10. Determine desorption efficiency (DE) for each lot of charcoal tubes used for sampling in the calibration range (step 9).
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
    e. Prepare a graph of DE vs. μg ethyl acetate recovered.
11. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1457-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE), of ethyl acetate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of ethyl acetate in the air volume sampled, V (L), at the sampling site:

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S49 [2] was evaluated over the range of 704 to 2950 mg/m^3 for 6-L samples at 23 °C and a pressure of 759 mm Hg. The overall sampling and analytical precision ($\hat{S}_{rT}$) was 0.058 with an average recovery of 97.9% and the breakthrough capacity was found to be 25 mg of ethyl acetate [5]. The method was updated later for a lower range (40.5 to 810 μg/sample) with a capillary column [1]. Desorption efficiencies ranged from 44.5% to 87.5% with an analytical precision ($\bar{S}_r$) of 0.058. Samples of ethyl acetate on coconut charcoal are stable for 6 days at 5 °C with a recovery of 91.0% based on samples analyzed immediately after collection [1].

REFERENCES:

[1] S.M. Pendergrass, Ethyl Acetate Method Development (unpublished report), NIOSH/MRSB, 1990, NIOSH Seq. Report 7716-F (unpublished, Feb. 5, 1993).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S49, U.S. Dept. of Health, Education, and Welfare, Publ. (NIOSH) 77-157B (1977).

[3] Analysis of NIOSH Samples for Ethyl Acetate, NIOSH/MRSB/MDS, Sequence #7133 - Cincinnati, Ohio (unpublished, 1991).

[4] Beck, S., T. Stock, and L. Whitehead, Improved Efficiency of Desorption of Oxygenated Solvents from Activated Charcoal Using a New Polar Additive to Carbon Disulfide, Appl. Occup. Environ. Hyg., 5(3), 171-177, 1990.

[5] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185(1977).

METHOD REVISED BY:

S.M. Pendergrass, NIOSH/DPSE.

ETHYL ACRYLATE

See ESTERS I (Method 1450) for procedure

ETHYLBENZENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

ETHYL BROMIDE

CH_3CH_2Br MW: 108.97 CAS: 74-96-4 RTECS: KH6475000

METHOD: 1011, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: no REL
ACGIH: 5 ppm (skin); suspected carcinogen
(1 ppm = 4.46 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.461 g/mL @ 20 °C; BP 38 °C; MP −119 °C; VP 51 kPa (380 mm Hg; 50% v/v) @ 20 °C; explosive range 6.8 to 11% v/v in air

SYNONYMS: bromoethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 200 ppm
-MAX: 4 L

SAMPLE STABILITY: not known

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 550 to 2200 mg/m^3 [1] (4-L samples)

BIAS: − 6.4%

OVERALL PRECISION ($\hat{S}_{rt}$): 0.054 [1]

ACCURACY: ± 15.0%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl bromide

DESORPTION: 1 mL 2-propanol; overnight

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 60 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel; 10% FFAP; on 80/100 mesh Chromosorb W-AW

CALIBRATION: standard solutions of ethyl bromide in 2-propanol

RANGE: 0.4 to 10 mg per sample

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.025 @ 1.8 to 8.5 mg per sample [1]

APPLICABILITY: The working range is 22 to 560 ppm (100 to 2500 mg/m^3) for a 4-L air sample. Ethyl bromide is used in organic synthesis as a solvent and as a refrigerant, anesthetic, and grain and fruit fumigant.

INTERFERENCES: None reported. An alternate GC column is 30 m x 0.32-mm fused silica capillary coated with 0.5-µm DBWAX at 50 °C isothermal [2].

OTHER METHODS: This revises Method S106 [3].

REAGENTS:

1. 2-Propanol, chromatographic grade.*
2. Ethyl bromide, reagent grade.*
3. Calibration stock solution, 0.073 mg/μL. Dilute 0.5 mL ethyl bromide to 10 mL with 2-propanol.
4. Nitrogen or helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1011-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, 1- and 5-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Ethyl bromide is flammable, a dangerous fire hazard (flash point = 26 °C), respiratory irritant, narcotic, and a hepato- and renal toxin [4].

2-Propanol is flammable and a dangerous fire risk with a flash point of 11 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 4 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL 2-propanol to each vial. Attach crimp cap to each vial.
7. Allow to stand overnight with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.02 to 10 mg ethyl bromide per sample.
   a. Add known amounts of ethyl bromide or calibration stock solution to 2-propanol in 10-mL volumetric flasks and dilute to the mark. Make serial dilutions as necessary to obtain solutions in the range 0.02 to 10 mg ethyl bromide/mL.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area vs. mg ethyl bromide).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of ethyl bromide or calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg ethyl bromide recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1011-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with 2-propanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of ethyl bromide found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of ethyl bromide in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S106 was issued on April 11, 1975 [3], and validated over the range 550 to 2200 mg/m^3 using 4-L air samples [1]. The concentrations of ethyl bromide were independently determined by gas chromatographic analysis of the synthetic atmospheres using a 5-mL sampling loop. The average recovery of generated samples was 93.8% with a relative standard deviation of 6.3%. No storage stability study was done. The breakthrough volume was 6.4 L when dry air containing 2213 mg/m^3 of ethyl bromide was sampled at 0.2 L/min. Desorption efficiencies averaged 0.84 over the range 1.8 to 7.1 mg per sample. At 0.03 mg per sample, a desorption efficiency of 0.63 was found [2].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] User check, UBTL, Inc., NIOSH Sequence #4585-K (NIOSH, unpublished, October 31, 1984).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S106, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Y. T. Gagnon, NIOSH/DPSE; S106 originally validated under NIOSH Contract CDC-99-74-45.

ETHYL BUTYL KETONE

See KETONES II (Method 1301) for procedure

ETHYL CHLORIDE 2519

CH_3CH_2Cl MW: 64.52 CAS: 75-00-3 RTECS: KH7525000

METHOD: 2519, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: handle with caution
ACGIH: 1000 ppm
(1 ppm = 2.64 mg/m^3 @ NTP)

PROPERTIES: gas; BP 12.2 °C;
vapor density (air = 1) 2.22;
explosive range 3.8 to 15.4% v/v in air

SYNONYMS: chloroethane; monochloroethane

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(2 coconut shell charcoal tubes,
400 mg and 200 mg)

FLOW RATE: 0.02 to 0.05 L/min

VOL-MIN: 0.3 L
-MAX: 3 L

SHIPMENT: separate front and back tubes

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1586 to 6500 mg/m^3 [1]
(3-L samples)

BIAS: − 1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.096 [1]

ACCURACY: ± 21.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl chloride

DESORPTION: 2 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 190 °C
-COLUMN: 110 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 6 m x 3 mm OD, 10% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: standard ethyl chloride solutions in CS_2 with internal standard

RANGE: 1 to 16 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.024 @ 3.4 to 15 mg per sample [1]

APPLICABILITY: The working range is 330 to 5300 mg/m^3 (130 to 2000 ppm) for a 3-L air sample; lower concentrations may be measured if desorption efficiency is adequate.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S105 [2].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.4% (v/v) nonane as internal standard.
2. Ethyl chloride, 99.7%.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes connected in series with a short piece of plastic tubing; each tube 10 cm long, 8 mm OD, 6 mm ID, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg; back tube = 200 mg). A plug of silylated glass wool is placed at each end of each tube. Four plastic caps are required for sealing the tubes after use. Pressure drop across sampler less than 3.4 kPa (2.5 cm Hg) at 1 L/min airflow.
2. Personal sampling pump, 0.02 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2519-1).
4. Vials, glass, serum, 3-mL, with PTFE-lined rubber septa and crimp seals.
5. Syringes, 0.5- and 5-mL.
6. Syringe, gas-tight, 10-mL.
7. Syringe needle, 22-gauge.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an extreme fire and explosion hazard (flash point = −30 °C). Ethyl chloride is a narcotic and toxic [3]. Work with these only in a hood and away from spark sources.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.05 L/min for a total sample size of 0.3 to 3 L.
4. Separate the front and back tubes immediately after sampling. Cap the tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool plugs. Seal each vial with a septum and crimp seal. Insert a syringe needle through the septum to serve as a vent.
6. Add 2.0 mL eluent to each vial with a syringe. Remove the syringe needle from the septum.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 16 mg (0.004 to 6 mL of ethyl chloride gas at 20 °C and 101 kPa) ethyl chloride per sample. Use serial dilutions for the smallest concentrations.
   a. Add 2.0 mL eluent to each of a series of vials. Attach septum with crimp seal to each vial.

b. Immediately before adding ethyl chloride, withdraw from each vial a volume of air equal to that of ethyl chloride to be added. Weigh the vial.
c. Slowly bubble a measured amount of ethyl chloride into the liquid in each vial using a gas-tight syringe.
d. Reweigh the vial. Calculate the mass of ethyl chloride added.
e. Analyze together with samples and blanks (steps 11 and 12).
f. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg ethyl chloride).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
a. Weigh media blank front tube and caps.
b. Inject ethyl chloride slowly and directly onto a media blank front sorbent section with a gas-tight syringe.
c. Immediately cap the tube. Reweigh the tube. Calculate the mass of ethyl chloride added. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg ethyl chloride recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2519-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 3 min for ethyl chloride and 4.5 min for nonane under these conditions.
NOTE: If peak area is above the linear range of the working standards, dilute with 2-propanol, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of ethyl chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of ethyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S105 [2] was evaluated over the range 1300 to 5200 mg/m^3 by analyzing 18 spiked samples and 24 dynamically-generated samples [1,5]. The average concentrations found for the dynamically-generated samples, including six which were stored at ambient temperature for seven days, were not significantly different from the concentration calculated for the generated atmospheres using the system flow rates and the rate of injection of ethyl chloride into the system. Desorption efficiencies averaged 101% over the range 3.4 to 15 mg ethyl chloride per sample.

The breakthrough volume for the 400-mg charcoal bed was 4.3 L when an atmosphere containing 5560 mg/m^3 ethyl chloride at 21 °C and 90% relative humidity was sampled at 0.06 L/min, yielding a breakthrough capacity of 24 mg under these conditions.

REFERENCES:

[1] Backup Data Report, S105, available as "Ten NIOSH Analytical Methods, Set 4," Order No. PB 281-038 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S105, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE; S105 originally validated under NIOSH Contract 210-76-0123.

ETHYL ETHER

$(C_2H_5)_2O$ MW: 74.14 CAS: 60-29-7 RTECS: KI5775000

METHOD: 1610, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 400 ppm
NIOSH: no recommended standard
ACGIH: 400 ppm; STEL 500 ppm
(1 ppm = 3.03 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.7134 g/mL @ 20 °C; BP 34.6 °C; MP −116 °C; VP 59 kPa (440 mm Hg); FI 58% v/v) @ 20°C; explosive range 1.7 to 48% v/v in air

SYNONYMS: diethyl ether; 1,1'-oxybisethane; ethyl oxide

SAMPLING

SAMPLER: SOLID SORBENT TUBES (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 400 ppm
-MAX: 3 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 606 to 2400 mg/m^3 [1] (3-L samples)

BIAS: 5.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.053

ACCURACY: ± 14.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl ether

DESORPTION: 1.0 mL ethyl acetate; 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 195 °C
-DETECTOR: 250 °C
-COLUMN: 175 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel; 1.2 m x 6-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: solutions of ethyl ether in ethyl acetate

RANGE: 0.3 to 11 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.024 @ 1.8 to 7.1 mg per sample [1]

APPLICABILITY: The working range is 100 to 2700 mg/m^3 (33 to 880 ppm) for a 3-L air sample. During sampling, high humidity may greatly decrease the breakthrough volume. A sampling period of 15 min may be monitored for STEL compliance using a flow rate of 0.2 L/min.

INTERFERENCES: Carbon disulfide, hexane, and 2-butanone have similar GC retention times [1]. A 30-m x 0.32-mm ID fused silica capillary column with 1-µm DB-1 at 50 °C may be used [2].

OTHER METHODS: This revises Method S80 [3].

REAGENTS:

1. Ethyl acetate, reagent grade.*
2. Ethyl ether, reagent grade.*
3. Nitrogen, prepurified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1610-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Flasks, volumetric 10-mL.
7. Pipet, volumetric, 1-mL with pipet bulb.

SPECIAL PRECAUTIONS: Ethyl ether is a dangerous fire and explosion hazard (flash point = −45 °C) and tends to form explosive peroxides [4]. Ethyl acetate is flammable (flash point = −4 °C). Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 3 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL ethyl acetate to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range 0.01 to 11 mg ethyl ether per sample.
   a. Add known amounts of ethyl ether to ethyl acetate in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain ethyl ether concentrations in the range 0.01 to 11 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg ethyl ether).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard the back sorbent section of a media blank sampler.
b. Inject a known amount (1 to 20 μL) of ethyl ether or a standard solution of ethyl ether in ethyl acetate directly onto the front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg ethyl ether recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1610-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with ethyl acetate, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE), of ethyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of ethyl ether in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S80 was issued on February 14, 1975 [3], and evaluated over the range 630 to 2500 mg/m^3 at 22 °C and 766 mm Hg for 3-L air samples desorbed in 0.5 mL ethyl acetate [1]. The concentrations were verified by using a total hydrocarbon analyzer. Breakthrough (5% on the backup section) occurred at 33 min when sampling a concentration of 2470 mg/m^3 in dry air at a flow rate of 0.185 L/min., corresponding to a capacity of 15 mg. The average DE was 0.98 over the range 1.8 to 7.1 mg ethyl ether per sample. Sample storage stability was not determined.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S80, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] UBTL, Inc., NIOSH Sequences 3610-J (unpublished, August 23, 1982) and 3726-J (unpublished, December 28, 1982).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S80, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; S80 originally validated under NIOSH Contract CDC-99-74-45.

ETHYL FORMATE 1452

CH_3CH_2COOH MW: 74.08 CAS: 109-94-4 RTECS: LQ8400000

METHOD: 1452, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 100 ppm
NIOSH: 100 ppm; Group I Pesticide
ACGIH: 100 ppm
(1 ppm = 3.03 mg/m^3)

PROPERTIES: liquid; BP 54.5 °C; d 0.917 g/mL @ 20 °C; VP 26 kPa (194 mm Hg) @ 20 °C; vapor density (air = 1) 2.6; explosive range 2.8 to 16% v/v

SYNONYMS: formic acid, ethyl ester; ethyl methanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.3 L @ 100 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 171-666 mg/m^3 (10-L samples) [1]

BIAS: 7.3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.0782 [1]

ACCURACY: ± 21.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl formate

EXTRACTION: 1 mL CS_2; stand 30 min.

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 65 °C

CARRIER GAS: helium, 30 mL/min

COLUMN: stainless steel, 10% FFAP on 80/100 Chromosorb W AW-DMCS (20 ft. x 1/8 in.)

CALIBRATION: standard solutions of ethyl formate in carbon disulfide with n-nonane as internal standard.

RANGE: 0.1 to 6 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample

PRECISION ($\bar{S}_r$): 0.019 @ 1.71 to 6.66 mg per sample [1]

APPLICABILITY: The working range is 3.3 to 210 ppm (10 to 630 mg/m^3) for a 10-L air sample.

INTERFERENCES: Any compound having the same retention time as ethyl formate under the same analytical conditions is an interference. A different temperature program or column with a different phase may eliminate the problem.

OTHER METHODS: This revises Method S36 [2].

REAGENTS:

1. Ethyl formate, ACS reagent grade.
2. Eluent: carbon disulfide, chromatographic quality, with 0.1% v/v n-nonane, ACS reagent grade (optional internal standard).
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID flame-sealed ends with plastic caps, containing two sections of 20/40 mesh of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column.
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL and other convenient sizes for preparing standards.
6. Flasks, volumetric, 10-mL.
7. Pipet, 1-mL graduated in 0.1 mL increments with bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a sample size of 0.3 to 10 L.
4. Replace the caps on the sampling tube and pack securely for shipment.
5. Obtain a small quantity (5 mL) of the bulk material in a glass container with a Teflon-lined cap. Ship to the laboratory in a separate container from the charcoal tube samples.

SAMPLE PREPARATION:

6. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
7. Add 1.0 mL eluent to each vial. Attach cap to each vial.
8. Allow to stand for 30 min. with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range 0.01 to 6 mg/sample.
   a. Add known amounts of ethyl formate to eluent in 10-mL volumetric flasks with a concentration equal to 70% of that of the highest standard.
   b. Analyze together with the samples (steps 12 and 13).

c. Prepare a calibration graph of the ratio of peak area of ethyl formate to that of n-nonane vs. mg of ethyl formate).

10. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels and three media blanks.
    a. Remove and discard the back sorbent section of a media blank sample.
    b. Inject a known amount of ethyl formate or a standard solution directly onto the front sorbent section with a microliter syringe.
    c. Cap the tubes. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze together with the working standards (steps 12 and 12).
    e. Prepare a graph of DE vs. mg ethyl formate recovered.
11. Analyze three quality control blind spikes and three analysts spikes to ensure that the results are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1452-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of ethyl formate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$ report breakthrough and possible sample loss.
15. Calculate concentration, C, of ethyl formate in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 171 to 666 mg/m^3 at 23 °C and 766 mm Hg using 10-L samples. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.0782, with average recovery of 104%. Desorption efficiency from charcoal was 82% in the range of 1.48 to 5.91 mg per sample. Break through volume was 14 L when sampling an atmosphere containing 666 mg/m^3 at 0.190 L/min. This corresponds to a capacity of 9.5 mg of ethyl formate. Storage stability was not determined.

REFERENCES:

[1] Backup Data Report for Ethyl Formate, prepared under NIOSH Contract No. CDC-99-74-45.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S36, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

Robert Kurimo, NIOSH/DPSE.

ETHYLENE CHLOROHYDRIN

$ClCH_2CH_2OH$ MW: 80.51 CAS: 107-07-3 RTECS: KK0875000

METHOD: 2513, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: C 1 ppm (skin)
ACGIH: C 1 ppm (skin)
(1 ppm = 3.29 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.201 g/mL @ 25 °C; BP 129 °C; MP −67 °C; VP 0.67 kPa (5 mm Hg; 6600 ppm) @ 20 °C; explosive range 4.9 to 15.9% v/v in air

SYNONYMS: 2-chloroethanol, glycol chlorohydrin

SAMPLING

SAMPLER: SOLID SORBENT TUBE (petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 5 ppm
-MAX: 35 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7 to 30 mg/m^3 [1] (20-L samples)

BIAS: − 11.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 31.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethylene chlorohydrin

DESORPTION: 1 mL 5% (v/v) 2-propanol in CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 170 °C
-DETECTOR: 210 °C
-COLUMN: 130 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: 3.0 m x 2-mm ID stainless steel; 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: ethylene chlorohydrin in eluent containing internal standard

RANGE: 0.03 to 1 mg per sample [2]

ESTIMATED LOD: 3 µg per sample

PRECISION ($\bar{S}_r$): 0.052 [1]

APPLICABILITY: The working range is 1.5 to 50 mg/m^3 (0.5 to 15 ppm) for a 20-L air sample. During sampling, high humidity may greatly decrease the breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S103 [2] in a revised format.

REAGENTS:

1. Eluent: carbon disulfide,* (chromatographic grade), containing 5% (v/v) 2-propanol (reagent grade) and 0.1% (v/v) n-pentadecane as internal standard.
2. Ethylene chlorohydrin (reagent grade).*
3. Calibration stock solution, 50 mg/mL.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of petroleum-derived activated charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 0.2 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2513-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL, readable to 0.1 μL, and 100-μL, readable to 1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = −30 °C); work with it only in a hood.

Ethylene chlorohydrin is highly toxic, has poor warning properties, and as a liquid, is readily absorbed through the skin and penetrates rubber [3]. Toxic effects may be cumulative. Wash liquid from skin immediately if contacted.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 35 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range 3 to 1000 μg ethylene chlorohydrin per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg ethylene chlorohydrin).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard the back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution, or a dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg ethylene chlorohydrin recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2513-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of ethylene chlorohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of ethylene chlorohydrin in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S103 was issued on April 11, 1975 [2] and evaluated over the range 7 to 30 mg/m^3 at 25 °C and 742 mm Hg using a 20-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.076 with an average recovery of 0.914. The concentration of ethylene chlorohydrin was independently verified using a GC-FID calibrated with gas mixtures of ethylene chlorohydrin in nitrogen. Breakthrough volume (effluent concentration = 5% of influent concentration) was >48 L; the test was conducted in dry air containing 31 mg/m^3 ethylene chlorohydrin with a sampling flow rate of 0.2 L/min. Desorption efficiency was 0.94 in the range 0.16 to 0.64 mg per sample. For the DE determination experiments, an 80 mg/mL solution of ethylene chlorohydrin in 2-propanol was used for spiking.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S103, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S103, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S103 originally validated under NIOSH Contract CDC-99-74-45.

ETHYLENEDIAMINE

$H_2N(CH_2)_2NH_2$ MW: 60.1 CAS: 107-15-3 RTECS: KH8575000

METHOD: 2540, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm
NIOSH: 10 ppm
ACGIH: 10 ppm (skin)
(1 ppm = 2.46 mg/m^3)

PROPERTIES: liquid; d 0.90 g/mL @ 20 °C; BP 116 - 117 °C; VP 1.43 kPa; (10.7 mm Hg); flash point 34 °C

SYNONYMS: ethylenediamine: EDA; 1,2-diaminoethane; 1,2-ethanediamine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (1-naphthylisothiocyanate-coated XAD-2, 80 mg/40 mg)

FLOW RATE: 0.01 to 0.1 L/min [1]

VOL-MIN: 1 L @ 10 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: >30 days @ 20 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.016 to 8 mg/m^3; (10-L samples)
OVERALL PRECISION ($\hat{S}_{rT}$):	0.06 [1]
BIAS:	−6.6%
ACCURACY:	±17.4%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: naphthylisothiourea derivative of analytes

DESORPTION: 2 mL dimethylformamide (DMF), ultrasonic 30 min

INJECTION VOLUME: 10 µL

COLUMN: 10-µm radial cyano, 10 cm x 8-mm ID in Waters RCM-100 radial compression mode

MOBILE PHASE: EDA, 80/20 isoctane/isopropanol; DETA and TETA, 50/50 isoctane/isopropanol at 3 mL/min

CALIBRATION: standard solutions of derivatives in DMF

RANGE: 5 to 465 µg per sample

ESTIMATED LOD: 0.9 µg per sample

PRECISION ($\bar{S}_r$): 0.013

APPLICABILITY: The working range for EDA is 1 to 130 mg/m^3 for a 10-L air sample. This method is the result of evaluation [2] of OSHA Method #60 for DETA, EDA, TETA [1]. The theoretical capacity of each front section is 1.3 mg of EDA.

INTERFERENCES: Other primary or secondary amines may react with the sampler coating reagent, and thereby reduce the sampler capacity.

OTHER METHODS: This replaces NIOSH Method P&CAM 276 [3]. The method of Anderson, et al., for EDA [4] is an alternate method using thiourea derivatization and HPLC analysis.

REAGENTS:

1. XAD-2 resin, reagent grade.
2. 1-Naphthylisothiocyanate (NTIC), reagent grade.
3. Methylene chloride, reagent grade.
4. Dimethylformamide (DMF), HPLC grade.
5. Isooctane, HPLC grade.
6. Isopropanol, HPLC grade.
7. Ethylenediamine (EDA),* high purity.
8. Diethylenediamine (DETA),* high purity.
9. Triethylenetetramine (TETA),* high purity.
10. Calibration stock solution, 4.8 mg/mL DETA,4.50 mg/mL EDA, 4.9 mg/mL TETA. Dissolve 95.4 mg DETA, 90.0 mg EDA, and 98.2 mg TETA in 600 mg of NTIC, allow to react for at least 60 minutes, and dilute to 20 mL with DMF.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing 2 sections of 16/50 mesh XAD-2 resin coated with 10% 1-naphthylisocyanate (front = 80 mg; back = 40 mg) separated by a plug of PTFE wool (see APPENDIX). Tubes are commercially available.
2. Personal sampling pump calibrated to 0.01 to 0.1 L/min.
3. High performance liquid chromatograph (HPLC), UV, 254 nm, cyano column and integrator (page 2540-1).
4. Vials, 4-mL.
5. Syringes, microliter, readable to 0.1 μL.
6. Pipets, 2-mL.
7. Flasks, volumetric, 25- and 50-mL.
8. Ultrasonic water bath.

SPECIAL PRECAUTIONS: The vapors of these amines are painful and irritating to the eyes, nose, throat, and respiratory system. The liquids can cause severe damage to the eye and serious burns to the skin [1,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling.
3. Attach the sampler to personal sampling pump with flexible tubing.
4. Sample at an accurately known flow rate between 0.01 to 0.1 L/min for a total sample size of 1 to 20 L.
5. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

6. Transfer each sorbent section to separate sampling vials.
7. Add 2.0 mL DMF to each vial.
8. Agitate in an ultrasonic water bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards in the range of the samples.
   a. Prepare working standards by serial dilution of the stock standards with DMF.
   b. Analyze together with samples, blanks, and QC samples (steps 12 and 13).
   c. Prepare separate calibration graph (peak area vs. μg per sample) for EDA, DETA, and TETA.
10. Determine the desorption efficiency (DE) at least once for each lot of XAD-2 resin used for sampling. Prepare three tubes at each of five levels plus 3 media blanks.
    a. Inject a known amount of analyte onto the NTIC-coated resin.
    b. Allow to stand overnight.

c. Desorb and analyze together with the working standards.
d. Prepare a graph of DE vs. μg amine recovered.

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration curve and DE graph are in control.

MEASUREMENT:

12. Set liquid chromatograph according to manufacturer's recommendations and conditions given on page 2540-1.
13. Inject sample aliquot manually or with autosampler. Measure peak area.
    NOTE: If the peak response is above the range of the working standards, dilute the standards with DMF, reanalyze and apply the appropriate dilution factors in calculations.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of each analyte found in the sample front sorbent (W_f) and the sample back sorbent (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.
15. Calculate concentration, C, of each analyte in the air volume sampled, (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was developed by and subjected to the evaluation procedures of the OSHA Organics Methods Evaluation Branch [1]. NIOSH evaluated the method for recovery, storage stability, precision, and accuracy and found comparable results [2]. The detection limits obtained by OSHA [1] corresponded to air concentrations of 0.004 ppm, 0.15 ppm, and 0.004 ppm for DETA, EDA, and TETA respectively, for a 10-L air volume. The method was validated over the range of 0.8 to 80 μg/sample for DETA, 4.6 to 465 μg/sample for EDA, and 1.3 to 119 μg/sample for TETA [1]. Desorption efficiency studies as performed by OSHA [1] using 6 samples at 3 levels gave a recovery of 99.0% for DETA, 99.2% for EDA, and 99.8% for TETA. The recovery of DETA, EDA, and TETA from samples used in a 15-day storage study was 89, 94, and 91%, respectively. These samples were generated by spiking the amines onto a glass wool plug in front of a sampling tube and drawing approximately 10 liters of air at 80% relative humidity through them. A 30-day storage study conducted by NIOSH [2] showed similar recoveries. Collection efficiency studies were done [1] by drawing 10-L of air at 80% relative humidity through Teflon wool plugs positioned ahead of the samplers and spiked with the pure amine. No DETA or TETA was found on the back section with a loading of 57.2 μg of DETA or 32.5 μg of TETA. At a loading of 414 μg of EDA, the back section was found to contain 12.2 μg of EDA.

REFERENCES:

[1] Elskamp, Carl J. "OSHA Method #60, Ethylenediamine (EDA), Diethylenetriamine (DETA), Triethylenetetramine (TETA)." Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah. September, 1986.

[2] Neumeister, Charles. NIOSH/MRSB In-House Evaluation of OSHA Method #60, (NIOSH, Unpublished, June 17, 1988).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 276, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[4] Anderson, K., Hallgren, C., Levin, J., and Nilsson, C. "Determination of Ethylenediamine in Air Using Reagent-Coated Adsorbent Tubes and High-Performance Liquid Chromatography on the 1-Naphthylisothiourea Derivative, "Am. Ind. Hyg. Assoc. J., 46(4), 225-229 (1985).

[5] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN BY:

Charles Neumeister, NIOSH/DPSE.

APPENDIX:

PREPARATION OF NTIC-COATED XAD-2 RESIN:

a. Weigh sufficient XAD-2 resin (16/50 mesh 120 mg XAD resin per tube) to allow preparation of tubes for sampling, blanks, quality control, and recovery studies.
b. Dissolve sufficient 1-naphthylisothiocyanate in methylene chloride to coat the XAD-2 resin at a 10% loading (w/w).
c. Place the XAD-2 resin in the NTIC solution, mix, and remove methylene chloride using rotary evaporation.
d. Load the coated XAD-2 resin into 7 cm long, 6-mm OD, 4-mm ID, glass tubes so that the front section contains 80 mg and the back section contains 40 mg. Use PTFE-wool plugs to separate and contain the two sections. Cap the finished tubes with plastic caps.

ETHYLENE DIBROMIDE 1008

BrH_2CCH_2Br MW: 187.88 CAS: 106-93-4 RTECS: KH9275000

METHOD: 1008, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 20 ppm; C 30 ppm; PEAK 50 ppm/5 min
NIOSH: 0.045 ppm; C 0.13 ppm/15 min; Group I Pesticide
ACGIH: carcinogen (skin)
(1 ppm = 7.68 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.169 g/mL @ 25 °C;
BP 131 °C; MP 10 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 25 °C

SYNONYMS: EDB, 1,2-dibromoethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 0.1 L @ 0.1 ppm
-MAX: 25 L

SHIPMENT: insulated container, dry ice

SAMPLE STABILITY: 2 weeks at −25 °C or below [1,2].

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: ethylene dibromide

DESORPTION: 10 mL 99:1 benzene:methanol (v/v); stand 1 h

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 315 °C
-COLUMN: 50 °C

CARRIER GAS: N_2, 35 mL/min

COLUMN: 1.8 m x 4-mm ID, borosilicate glass packed with 3% OV-210 on 80/100 Gas Chrom Q

CALIBRATION: ethylene dibromide in 99:1 benzene:methanol (v/v) with internal standard

RANGE: 0.1 to 0.5 µg per sample [1]

ESTIMATED LOD: 0.01 µg per sample [1,2]

PRECISION ($\bar{S}_r$): 0.044 [3]

APPLICABILITY: The working range is 0.0003 to 1 ppm (0.002 to 8 mg/m^3) for a 25-L air sample. The range of an ECD most useful for quantitation depends on the type of detector and chromatograph used. For reliable quantitation, the ECD must be optimized for the smallest possible amount of analyte.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems. An alternate chromatographic column packing is GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Chromosorb WHP [2].

OTHER METHODS: This revises P&CAM 260 [1] and Method 1008 (dated 2/15/84). Method S104 [4], which has not been revised, can also be used but uses the less sensitive flame ionization detector.

REAGENTS:

1. Benzene, pesticide quality.*
2. Methanol, pesticide quality.*
3. Ethylene dibromide, high purity (density = 2.169 g/mL @ 25 °C).*
4. An appropriate internal standard such as 1,1,2,2-tetrachloroethane (density = 1.587 g/mL @ 25 °C) or 1,2-dibromopropane (density = 1.923 g/mL @ 25 °C).
5. 99:1 benzene:methanol (v/v).
6. Eluent*: 99:1 benzene:methanol (v/v) containing 0.1 μg internal standard/mL.
7. Calibration stock solution, 10 ng/μL. Dissolve 50 mg ethylene dibromide in benzene to make 25 mL solution. Dilute 50 μL of this solution to 10 mL with benzene. Stable 3 weeks if refrigerated.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron-capture detector, integrator and column (page 1008-1).
4. Syringe*, 10-μL, readable to 0.1 μL, and 50-μL, readable to 1 μL.
5. Volumetric flasks, 10-mL, 25-mL, and 500 mL.
6. Pipet, 10-mL with pipet bulb.

SPECIAL PRECAUTIONS: Benzene and ethylene dibromide [1] are carcinogens and can be absorbed through the skin. Benzene and methanol are flammable. All work with these should be performed in a hood, while wearing gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 0.1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely in an insulated container with dry ice for shipment.

SAMPLE PREPARATION:

NOTE: Store the samplers at −25 °C or below until preparation begins.

5. Place the front and back sorbent sections of the sampler tube in separate 10-mL volumetric flasks. Discard the glass wool and foam plugs.
6. Add 10.0 mL eluent to each flask.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 0.5 μg ethylene dibromide per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg ethylene dibromide).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard the back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg ethylene dibromide recovered.
10. Analyze three quality control blind spikes and five analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1008-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Retention times under these conditions are: ethylene dibromide, 2.2 min; 1,2-dibromo propane, 2.9 min; and 1,1,2,2-tetrachloroethane, 4.1 min.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of ethylene chlorohydrin found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of ethylene dibromide in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 260 [1] was evaluated with coconut shell charcoal (SKC Lot 106 and MSA Lot 6) fortified with solutions of ethylene dibromide. Average recoveries ranged from 0.85 to 0.93; overall precision (s_r) was 0.044 (31 samples, pooled) [3]. Samples based on 0.2- and 2-μg quantities of ethylene dibromide were stable on charcoal during storage below -20 °C for 13 and 12 days, respectively. Gasoline samples which contained ethylene dibromide were placed into U-tubes; ethylene dibromide vapor was collected with charcoal tubes (flow rate of air was 0.6 L/min). Recoveries were 0.91 and 0.93 for 0.2- and 2.4-μg quantities of ethylene dibromide, respectively. No significant breakthrough from front sections of charcoal occurred with 200-μg quantities of ethylene dibromide in the vapor phase (flow rate of air was 0.6 L/min); quantities of ethylene dibromide (if any) on the back sections of charcoal were less than 0.04 μg (<0.02%).

Breakthrough was determined for SKC Lot 105 charcoal [5]. At an ethylene dibromide concentration of 446 mg/m^3 in dry air, the effluent concentration was 2% of the test concentration after 4 h of sampling (48 L air). Thus, the capacity of the charcoal was at least 21 mg ethylene dibromide under these conditions. In the analysis of a large set of field samples over a period of seven days, DE was found to vary day-to-day in the range of 0.76 to 0.87 at 0.1 μg ethylene dibromide per sample [6]. Overall precision ($\hat{S}_{rT}$) and bias were not determined.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, P&CAM 260, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
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[3] Tucker, S. P., J. J. Sweeney and A. W. Teass. "A Charcoal Tube Method for Determining 1,2-Dibromoethane in Air," NIOSH (unpublished, 1979).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Documentation of the NIOSH Validation Tests, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[6] Report of NIOSH Seq. #5332-A (unpublished, May 5, 1986).

METHOD REVISED BY:

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ETHYLENE DICHLORIDE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

ETHYLENE GLYCOL DINITRATE
See NITROGLYCERINE (Method 2507) for Procedure

$O_2NOCH_2CH_2ONO_2$ MW: 152.06 CAS: 628-96-6 RTECS: KW5600000

METHOD: 2507, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : C 0.2 mg/m^3 (skin)
NIOSH: STEL 1 mg/m^3 (skin)
ACGIH: 0.31 mg/m^3 (skin)
(1 ppm = 6.22 mg/m^3 @ NTP)

PROPERTIES: liquid; MP −22 °C; explodes 114 °C; d 1.49 g/mL @ 25 °C; VP 6.8 Pa (0.05 mm Hg; 68 ppm) @ 20 °C

SYNONYMS: EGDN; ethylene dinitrate.

SAMPLING

SAMPLER: SOLID SAMPLER TUBE (Tenax-GC, 100 mg/50 mg)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 3 L @ 1 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 25 days @ 25 °C [5]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 1.8 mg/m^3 [3]

BIAS: −0.02%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089 [2]

ACCURACY: ±20.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: EGDN

DESORPTION: 2 mL ethanol; stand 30 min

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 280 °C
-COLUMN: 125 °C

CARRIER GAS: 95% argon/methane, 75 mL/min

COLUMN: glass, 1 m x 4-mm, 2-mm ID 10% OV-17 on 60/80 mesh Gas Chrom Q

CALIBRATION: solutions of EGDN in ethanol

RANGE: 3 to 45 µg per sample

ESTIMATED LOD: 0.6 µg per sample

PRECISION ($\hat{S}_r$): 0.063 [2]

APPLICABILITY: The working range is 0.03 to 0.5 ppm (0.2 to 3 mg/m^3) for a 15-L air sample, provided that the linear range of the ECD is not exceeded.

INTERFERENCES: A high concentration of 2-hydroxyethyl nitrate (ethylene glycol mononitrate) tails into the EGDN peak but does not prevent a satisfactory determination of EGDN.

OTHER METHODS: This method combines and replaces Methods S216 [2,5] and P&CAM 203 [4].

ETHYLENE OXIDE

$CH_2(O)CH_2$ MW: 44.05 CAS: 75-21-8 RTECS: KX2450000

METHOD: 1614, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1 ppm
NIOSH: 0.1 ppm; C 5 ppm/10 min; carcinogen; Group I Pesticide
ACGIH: 1 ppm; suspect carcinogen
(1 ppm = 1.801 mg/m^3 @ NTP

PROPERTIES: gas; d (liquid) 0.8694 g/mL @ 20 °C; BP 10.7 °C; MP −111 °C; explosive limits 3 to 100% (v/v) in air

SYNONYMS: 1,2-epoxyethane; oxirane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (HBr-coated petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.15 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: 90% recovery after 17 days @ 25 °C in the dark [3]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.04 to 0.98 ppm (24-L samples) [1]
BIAS:	−6.9% [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.062 [1]
ACCURACY:	±19%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: 2-bromoethylheptafluorobutyrate

DESORPTION: 1 mL dimethylformamide; stand 5 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 100 °C

CARRIER GAS: 5% CH_4 in Ar, 25 mL/min

COLUMN: 3 m x 4 mm glass; 10% SP-1000 on 80/100 Chromosorb WHP

CALIBRATION: standard solutions of 2-bromoethanol in dimethylformamide

RANGE: 2 to 42 µg ethylene oxide per sample

ESTIMATED LOD: 1 µg EtO per sample [2]

PRECISION ($\hat{S}_r$): 0.020 @ 18 to 71 µg EtO per sample [1]

APPLICABILITY: The working range is 0.05 to 4.6 ppm (0.08 to 8.3 mg/m^3) for a 24-L air sample. The method is applicable to short-term (10-min) samples.

INTERFERENCES: 2-Bromoethanol, if present in the sample interferes. No other significant interferences have been found [1].

OTHER METHODS: This is a modification of OSHA Method 50 [1] and replaces NIOSH method 1607, which has smaller sample capacity, and S286 [3], which is useful for higher levels. Method 3702 (Ethylene Oxide by Portable GC) describes field-readable gas chromatography for the determination of ethylene oxide.

REAGENTS:

1. N,N-Dimethylformamide (DMF), high purity.
2. Isooctane (2,2,4-trimethylpentane), reagent grade.
3. Benzene, reagent grade.*
4. N-Heptafluorobutyrylimidazole (HFBI; N-heptafluorobutanoylimidazole; Alfa Chemical #31594, Alfa Products, Ward Hill, MA 01835).
5. Water, high purity (e.g., deionized distilled).
6. 2-Bromoethanol (2-FrEt), 95 to 98%.
7. Sodium hydroxide (NaOH), reagent grade.
8. Potassium hydrogen phthalate (KHP), reagent grade, dried at 90 °C.
9. HCl, conc., reagent grade.*
10. Pyridine, reagent grade.
11. Phenolphthalein, 1% (w/v) in ethanol or methanol.
12. Hydrobromic acid (HBr), 48%, reagent grade.*
13. Charcoal, petroleum-based (SKC Lot 208 or equivalent, SKC, Eighty-Four, PA).
14. Ethylene oxide (EtO), liquid or gas, 99.7% purity.*
15. Sodium hydroxide, 0.5 N. Dissolve 20 g NaOH in distilled water to make 1 L of solution. Standardize with KHP to a phenolphthalein endpoint (APPENDIX B).
16. HCl in pyridine, 0.2 N. Dissolve 8.5 mL conc. HCl in pyridine to make 500 mL solution. Standardize (APPENDIX C).
17. Ethylene oxide stock solution,* ca. 40 μg/μL. Bubble EtO gas (or pipet 4 mL EtO liquid) into 85 mL benzene in a graduated cylinder until solution volume increases ca. 4 mL. Seal tightly and store in freezer. Standardize weekly (APPENDIX D).
18. HFBI, 2% in isooctane. Dissolve 2 mL HFBI in isooctane to make 100 mL solution. Store in refrigerator.
19. 5% Methane in argon.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 6-mm OD x 4-mm ID x 45 mm glass tube, flame-sealed, with plastic caps, contaiing HBr-coated charcoal (see APPENDIX A), two sections, 100-mg front, 50-mg back, separated and contained with silanized glass wool plugs. Tubes are commercially available (Supelco Orbo-78, SKC 226-38-03, or equivalent.
2. Gas chromatograph, electron capture detector, integrator, and column (p. 1614-1).
3. Burette, 50-mL, 0.1-mL graduations.
4. Flask, round-bottom, 100-mL, with ground-glass joint.
5. Condenser, reflux, with ground-glass joint to fit round-bottom flask.
6. Heating mantle, with heat control, to fit round bottom flask.
7. Graduated cylinder, glass, 100-mL, with stopper that seals tightly.
8. Vials, glass, 5-mL, with PTFE-lined screw caps.
9. {o[ets. vp;i,etroc. 2- tp 500-μL and 1-,2-,4- and 40-mL, with pipet bulb.
10. Syringes.
11. Vials, glass, 2-mL, with PTFE-lined septum screw caps.
12. Flasks, Erlenmeyer, 125-mL.
13. Gloves.
15. Fume hood.
16. File, triangular.
17. Evaporator, rotary.

SPECIAL PRECAUTIONS: Ethylene oxide and benzene are toxic and serious fire and explosion hazards; they are also suspect carcinogens [4-6].

Hydrobromic and hydrochloric acids are eye, skin, and inhalation hazards [6]. Work with these substances only in a hood. Use protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.

3. Sample at an accurately known flow rate between 0.05 and 0.15 L/min for a total sample size of 1 to 24 L.
4. Cap each tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
6. Transfer front sorbent section and first glass wool plug to a 2-mL vial. Transfer middle glass wool plug and back sorbent section to a separate vial.
7. Add 1.0 mL DMF to each vial. Cap each vial.
8. Shake at least 10 sec. Allow to stand at least 5 min.
9. Pipet a 20-μL aliquot of the DMF solution to another 5-mL vial containing 2.0 mL 2% HFBI (v/v) in isooctane.
   NOTE: Pipet 20 μL of each working standard (step 13) into vials containing 2% HFBI at this step.
10. Cap and shake 1 min: Allow to stand at room temperature at least 5 min.
11. Add 2.0 mL high purity water. Mix 1 min to ensure complete hydrolysis of excess HFBI.
12. Transfer at least 1.0 mL of isooctane (top) layer to 2-mL vial.
    NOTE: If the sample concentration is higher than the standards, dilute an aliquot of sample with DMF, reanalyze starting at step 9, and apply the appropriate dilution factor in calculations. The desorbed sample (in DMF) keeps well in a freezer [1].

CALIBRATION AND QUALITY CONTROL:

13. Calibrate daily with at least six working standards over the range 1 to 42 μg EtO per sample. For example:
    a. Pipet 1.0 mL 2-BrEt (density 1.763 g/mL @ 20 °C) into a 10-mL volumetric flask. Dilute to volume with DMF. This is stock solution "A." Dilute 3 mL of "A" to 25 mL with DMF to give standard "B." Dilute 1 mL of "B" to 10 mL with DMF to give standard "C."
       NOTE: A sample calculation with 95% pure 2-BrEt (MW = 124.98) expressed as its equivalent weight in EtO (MW = 44.05) is:

       Standard Solution "A":

$$\frac{1.763\ \text{g 2-BrEt}}{10\ \text{mL}} \cdot 0.95 \cdot \frac{44.05}{124.97} \cdot 10^6\ \mu\text{g} = 59{,}036\ \mu\text{g EtO/mL}.$$

       Standard Solution "B":

$$3\ \text{mL} \cdot 59{,}030/25\ \text{mL} = 7084\ \mu\text{g EtO/mL}.$$

       Standard Solution "C":

$$1\ \text{mL} \cdot 7084/10\ \text{mL} - 708.4\ \mu\text{g EtO mL}.$$

    b. Prepare working standards by injecting microliter volumes of "B" and "C" into vials containing 1.0 mL DMF. The following serial dilution scheme is suggested:

Working Standard	Aliquot added to 1.0 mL DMF	Final μg EtO/mL
D	2.5 μL "C"	1.77
E	5.0 μL "C"	3.54
F	10.0 μL "C"	7.08
G	2.5 μL "B"	17.7
H	3.5 μL "B"	24.8
I	5.0 μL "B"	35.4
J	6.0 μL "B"	42.5

Higher standards may be used if detector output remains acceptable. (Some detectors may become saturated at higher levels.)

c. Analyze working standards together with samples and blanks.
d. Prepare calibration graph (μg EtO per sample vs. peak area). Use a nonlinear (e.g., parabolic) least squares fit if necessary to obtain the best fit of the data.

14. Determine recovery (R) at least once for each lot of charcoal used for sampling in the concentration range of interest. Prepare three tubes at each concentration of interest plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (2 to 15 μL) of EtO stock solution or a serial dilution thereof directly onto the charcoal with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 9 through 12 and 16 and 17).
15. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

16. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1614-1. Inject sample aliquot manually using solvent-flush technique or with autosampler.
17. Measure peak area.

CALCULATIONS:

18. Determine the mass, μg (corrected for R), of EtO found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
19. Calculate concentration, C, of EtO in the air volume sampled, V(L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method uses HBr-coated charcoal to collect EtO and rapidly convert it to 2-bromoethanol. This method was evaluated at the OSHA Analytical Laboratory, Salt Lake City, UT, as OSHA Method 50 [1]. Fifteen-min and 30-min air samples were collected from a constant 5-ppm test atmosphere (80% relative humidity, ambient temperature) at 0.1 L/min with observed recoveries in the range 88 to 100%.

Fifteen pairs of side-by-side area samples were collected and analyzed by OSHA using this method and the Qazi-Ketcham method. The sampling rate was ca. 50 mL/min for 4 to 7.5 H. Results showed no statistical difference in the two methods, with no bias over the range 0.3 to 7 ppm EtO. test atmospheres of 0.1, 0.5, 1.0, and 16 ppm at 70 to 80% relative humidity and ambient temperature were sampled for 4 h at 0.1 L/min with no breakthrough. The 5% breakthrough volume for sampling a 16-ppm atmosphere of EtO at 0.15 L/min was 39 L. No significant storage effects were observed for samples in the 0.1 to 16 ppm range at high humidity and stored at ambient temperature for a minimum of two weeks.

The precision, S_r, of chromatographic response of working standards in the range 18 to 71 μg EtO per sample was 0.028 [1]. Recovery of EtO spikes in NIOSH laboratories averaged 75% at 11, 22, 33, and 44 μg EtO per sample.

REFERENCES:

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[7] Siggia, S. and J.G. Hanna. Quantitative Organic Analysis via Functional Groups, 4th ed., Chapter 5, John Wiley & Sons, Inc., New York, NY (1979).

METHOD REVISED BY:

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APPENDIX A: PREPARATION OF SOLID SORBENT

Slowly add a mixture of 25 mL 48% hydrobromic acid and 125 mL acetonitrile to 75 g petroleum-based charcoal (SKC Inc., Lot 208) contained in a 500-Ml round-bottom flask. Allow the slurry to cool to room temperature. Dry the coated charcoal by rotary evaporation using gentle heat and keep it overnight under vacuum at ambient temperature. The product is stable for four months when stored in a tightly sealed amber glass jar at room temperature [1]. Recovery may be lower as the sample medium ages.

APPENDIX B: STANDARDIZATION OF NaOH

1. Transfer duplicate, accurately weighed, ca. 1.5-gram portions of KHP (W, mg) to separate 125-mL Erlenmeyer flasks. Dissolve in 20 to 30 mL distilled water, warming if necessary.
2. Add one drop phenolphthalein solution to each flask.
3. Fill the burette with 0.5 N NaOH. Titrate, with constant mixing, to a pink endpoint in each flask. Record the volume, V (mL), of 0.5 N NaOH used.
4. Calculate the normality, N_b, of the NaOH solution.

$$N_b = \frac{W}{(204.22 \cdot V)}.$$

APPENDIX C: STANDARDIZATION OF HCl IN PYRIDINE

1. Pipet 40.0 mL 0.2 N HCl in pyridine into a 100-mL round-bottom flask.
2. Add 4.0 mL benzene.
3. Attach the flask to a water-cooled condenser and heat flask with a heating mantle to boiling. Reflux for 20 min.
4. Cool to near room temperature. Add 5 mL distilled H_2O through condenser and collect washings in the flask.
5. Remove reflux condenser and add a drop of phenolphthalein solution to the flask.
6. Titrate, with mixing, 0.5 N NaOH from the burette to the flask to a pink endpoint. Record volume, V_b (mL), of NaOH used.

7. Repeat steps 1 through 7 and average the results. Calculate the normality, N_o, of the HCl-pyridine solution using N_b from APPENDIX B:

$$N_o = \frac{N_b V_b}{40}.$$

APPENDIX D: STANDARDIZATION OF ETHYLENE OXIDE STOCK SOLUTION [7]

1. Pipet 20.0 mL standardized HCl-pyridine solution into a 100-mL round bottom flask.
2. Add 2.0 mL EtO stock solution.
3. Attach the flask to the condenser. Reflux for 20 min.
   NOTE: The reaction is: EtO + HCl(xs) → chloroethanol. The excess HCl is back-titrated in step D-6.
4. Cool to near room temperature. Add 5 mL distilled H_2O through the condenser, collecting washings in the flask.
5. Remove the condenser and add a drop of phenolphthalein solution to the flask.
6. Titrate, with mixing, 0.5 N NaOH from the burette to a pink endpoint. Record volume, V_c (mL), of NaOH used.
7. Calculate the normality, N_s, of the excess HCl using N_b from APPENDIX B:

$$N_s = \frac{N_b V_c}{20\ mL}.$$

8. Repeat steps 1 through 7 to obtain an average of two titrations. Results should agree to within 1%. Rinse flask thoroughly before reuse.
9. Calculate the concentration of the EtO stock solution:

$$\frac{mg\ EtO}{mL\ EtO\ stock\ solution} = (N_o - N_s) \cdot \frac{20\ mL}{10^3\ mL} \cdot \frac{44.05\ g}{1\ equivalent} \cdot \frac{1}{2\ mL} \cdot \frac{10^3\ mg}{1\ g} = (N_o - N_s) \cdot 440.5$$

ETHYLENE OXIDE by Portable GC 3702

C_2H_4O MW: 44.05 CAS: 75-21-8 RTECS: KX2450000

METHOD: 3702, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1 ppm
NIOSH: 0.1 ppm; C 5 ppm/10 min; carcinogen; Group I Pesticide
ACGIH: 1 ppm; suspect carcinogen
1 ppm = 1.801 mg/m^3 @ NTP

PROPERTIES: gas; d (liq.) 0.8694 g/mL @ 20 °C; BP 10.7 °C; MP −111 °C; explosive limits 3 to 100% (v/v) in air

SYNONYMS: 1,2-epoxyethane; oxirane

SAMPLING

SAMPLER: AMBIENT AIR OR BAG SAMPLE

FLOW RATE: ≥ 0.02 L/min; spot samples possible (See Step 1)

SHIPMENT: calibration and carrier gas shipment must comply with hazardous materials shipment regulations

SAMPLE STABILITY: bag samples stable 24 h @ 25 °C [1]

FIELD BLANKS: clean air, either in bag or from non-work area

ACCURACY

RANGE STUDIED: 0.1 to 700 ppm [1]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): <0.09 [1]

ACCURACY: ± 17%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: ethylene oxide

COLUMN: 1.2 m x 3 mm OD PTFE, packed with Carbopak BHT 40/100 mesh

CARRIER GAS: ultrapure air, 15 mL/min

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.001 to 1000 ppm

ESTIMATED LOD: 2.5 pg per injection @ .001 ppm (1-mL injection)

PRECISION ($\bar{S}_r$): <0.07 @ 0.05 to 0.2 ppm [1]

APPLICABILITY: The working range is 0.001 to 1000 ppm in relatively non-complex atmospheres (e.g., sterilization facilities).

INTERFERENCES: Freon 12, carbon dioxide, and alcohols do not interfere. Other compounds with similar retention times under the same chromatographic conditions are potential interferences.

OTHER METHODS: This method complements Method 1614 [2] which utilizes solid sorbent collection, derivatization, and gas chromatographic measurement for ethylene oxide.

REAGENTS:

1. Uncontaminated air for preparation of standards and purging samplers.
2. Carrier gas, air, ultra-pure.*
3. Ethylene oxide (EtO) for standards, pure or in known concentration (i.e., 88/12 Freon 12/EtO mixture).*
   NOTE: Commercial sterilant mixtures are sold on a weight/weight ratio. An 88/12 mixture is 27% EtO by volume.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC) with photoionization detector, column (page 3702-1), and (if appropriate) portable strip chart recorder or integrator, and battery chargers, regulators, and other peripherals necessary for individual instruments.
2. Personal sampling pump, 0.02 to 4 L/min or other rate suitable for filling bag, with flexible connecting tubing.
3. Syringes, gas-tight (0.01 to 1-mL, 1-L), for standards preparation, sample collection and sample injection.
4. Bags, inert plastic (e.g., aluminized polyester or Tedlar), 2- to 20-L, for standard preparation, and (if needed) sample collection.
   NOTE: Care must be taken to assure that the pump, bag, and tubing are all inert and impermeable to the analyte (step 3).

SPECIAL PRECAUTIONS: Ethylene oxide is flammable. Shipment of compressed calibration gas and carrier gas must comply with 49 CFR regulations on shipment of hazardous materials.

SAMPLING:

1. Collect samples by one of the following methods:
   NOTE: Other techniques such as liquid displacement or use of an evacuated vessel may be adaptable to this method but have not been evaluated.
   a. **Draw air directly into a syringe.** Collect syringe samples by first purging a gas-tight syringe several times with clean air to remove any residual ethylene oxide from previous samples, then draw air into the syringe at the time and location of interest.
      NOTE: This technique requires less equipment and also has the advantage of allowing for a grab sample. It is not easily applied to TWA measurements. Since this is a one-time analysis, the concentration of the sample must be estimated in advance so that the proper size sample can be collected. An injection volume as small as ten microliters can be used if the concentration is expected to be several hundred ppm, while a 1.0- mL syringe is more appropriate if a concentration on the order of 0.01 ppm is expected.
   b. **Bag samples for TWA.**
      (1) Evacuate the sampling bag.
      (2) Allow the pump to be purged with sample air before opening the valve on the sampling bag. Collect bag sample by using pump to pull air from a point of interest and push it into the bag.
      NOTE: This technique can obtain a sample in a relatively short time (e.g., at 4 L/min, a few seconds sampling time will yield the fraction of a liter necessary for several replicate analyses). By selecting a low flow rate and larger bag (i.e., 10 mL/min flow and 5 L bag), an 8-h TWA sample can be obtained. A few mL will allow for replicate injections of 1 mL or less, although in practice several hundred mL to 1 L is a more reasonable minimum. The maximum volume is limited only by the size of bags available and space in which to store them.

CALIBRATION AND QUALITY CONTROL:

2. Calibrate the GC daily in the field.
   a. Prepare bag standards by adding a known volume of EtO to a known volume of clean air in a bag. This creates a standard of known concentration in ppm (μL EtO/L air).
      (1) Evacuate a 5- to 10-L bag completely by drawing the air out with a large (1- to 2-L) syringe.
      (2) Draw clean air (or oxygen or nitrogen) from a supply cylinder into the syringe for measured transfer into the bag. Alternately, if a clean air supply is not available, draw room air through charcoal sorbent into the syringe. Repeat until the bag contains 5 L of air.
      (3) Add a known amount of pure EtO or standard EtO mixture to the bag by means of gas-tight syringe.
      Example:
      Using a gas-tight syringe, take 50 μL from a cylinder of pure EtO and inject it into 5 L of air to create a 10 ppm standard. Alternately, 200 μL of a 27% v/v EtO mixture (i.e., 88/12 w/w Freon 12 and EtO) can be added to the 5 L of air to obtain a 10.8 ppm standard.
      (4) Allow the bag to equilibrate, with occasional kneading, for at least 5 min.
   b. Analyze aliquots of various sizes to establish a calibration graph (steps 4 and 5). Analyze three or more replicates at each point.
      NOTE: On a high instrument attenuation (low sensitivity), injections of 0.2, 0.4, 0.6, 0.8 and 1.0 mL might be possible. This would correspond to injections of 2, 4, 6, 8, and 10 nL. On a more sensitive attenuation, injections of 0.02, 0.04, 0.06, 0.08 and 0.10 mL would be typical. Results will vary from instrument to instrument, and from time to time on the same instrument.
   c. Plot nL EtO vs. peak height or area. This plot should be a straight line.
   d. Periodically throughout the day, check calibration by repeating some of these injections of standards. Ideally, each sample would be bracketed, before and after, with injections of standards, although this is seldom practical.
3. Check the sampling equipment to prevent contamination.
   a. Use different syringes for sampling and for standard preparation. Identify each syringe with a unique number.
      NOTE 1: So called gas-tight syringes appear to be so only when new. Leakage results in injections less than indicated, resulting in inaccurate reporting of the actual concentration.
      NOTE 2: Even after more than a dozen purges, a syringe used to transfer pure ethylene oxide continues to elute small amounts of EtO.
   b. Bag sampling.
      (1) Check inertness and impermeability of the entire sampling train. This is best accomplished in the laboratory before going to the field. Purge a bag of the type to be used for sampling with clean air, and then fill it with clean air and an amount of EtO to create a concentration in the range of interest. Take replicate samples from that bag and inject them into the GC. Measure peak heights. Pump the contents of this bag through a sampling train of the type to be used in the field, into a second bag. Analyze replicate samples from the second bag immediately after transfer and hourly thereafter. If the concentrations found immediately after transfer are equal to those prior to transfer, the sampling train is not altering the EtO concentration (i.e., is inert). If the concentrations do not change over time, the bags are inert.
      (2) Consider any residual analyte which may remain in a bag after use, since practicality dictates reuse of bags. One or two purges with clean air are usually sufficient to remove residual EtO unless the concentration of the previous sample was extremely high. Analyze a sample of "clean" air taken from the bag during its final purge. If no measurable EtO is found, the bag is ready for reuse.
      NOTE: Some bags continue to show traces of analyte, even after several purges, and these bags should be discarded.

(3) Segregate bags used for sample collection from those used for calibration standards.

MEASUREMENT:

4. Fill a gas-tight syringe, purged several times with sample, from the sample bag. Then empty it to the desired volume, and inject that volume into the chromatograph with a quick firm motion. Record identity of syringe. Use replicate analyses to determine the repeatability of the analysis.
   NOTE 1: If no estimate of concentration is available, use an injection volume of 10 to 25 μL at a high attenuation to reduce the possibility of column and detector overload. Depending on the results of this injection, larger volumes and/or more sensitive attenuations may be selected.
   NOTE 2: The procedure for analysis of samples collected directly in a gas tight syringe is the same as for bag samples, with the obvious elimination of the step where the sample is withdrawn from the bag.
5. Along with the sample identification, record the injection volume (mL), the instrument attenuation, and the resultant peak height or area.

CALCULATIONS:

6. Divide the EtO volume (nL) from the calibration graph, by the injection volume (mL) to calculate sample EtO concentration (ppm):

$$ppm = \frac{\mu L\ (gas)}{L\ (gas)} = \frac{nL\ (gas)}{mL\ (gas)}.$$

EVALUATION OF METHOD:

This method was evaluated in the laboratory where the accuracy and precision were determined by a comparison of measured values with accepted concentrations from a dynamic (permeation tube) generation system with confirmation by lab G.C. with flame ionization detector [1]. Field evaluations were conducted in hospital and manufacturing sterilization facilities which used commercial mixtures of EtO with Freon 12 and carbon dioxide, respectively.

REFERENCES:

[1] Burroughs G. E., and Busch, K. A., "Field Validation of Direct-Reading Instrumental Methods for the Sampling and Analysis of Environmental Contaminants," unpublished NIOSH report (1985).
[2] NIOSH Manual of Analytical Methods, 3rd ed., Vol. 1, Method 1614, Department of Health and Human Services (NIOSH) Publ. No. 84-100 (1984).

METHOD WRITTEN BY:

G. E. Burroughs, NIOSH/DPSE.

ETHYLENE THIOUREA

$C_3H_6N_2S$ MW: 102.17 CAS: 96-45-7 RTECS: NI9625000

METHOD: 5011, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : suspect carcinogen
NIOSH: lowest feasible; carcinogen
ACGIH: no TLV

PROPERTIES: solid; MP 203 to 204 °C

SYNONYMS: 2-imidazolidinethione, ETU; 4,5-dihydroimidazole-2(3H)-thione.

SAMPLING

SAMPLER: FILTER (5-μm PVC or mixed cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 200 L @ 0.05 mg/m^3
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; high-volume air or settled dust

ACCURACY

RANGE STUDIED: 0.03 to 1.5 mg/m^3 (100-L sample)

BIAS: not significant [3]

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: ETU-pentacyanoamineferrate coordination complex

EXTRACTION: distilled water, stand 45 min @ 60 °C

COMPLEXATION: pentacyanoamineferrate reagent

WAVELENGTH: 590 nm

CALIBRATION: solutions of ETU in water

RANGE: 10 to 150 μg per sample

ESTIMATED LOD: 0.75 μg per sample

PRECISION ($\bar{S}_r$): 0.03

APPLICABILITY: The working range is 0.05 to 0.75 mg/m^3 for a 200-L air sample. Ethylene thiourea is used in the manufacture of fungicides, rubber vulcanization and in dyes, pharmaceuticals, synthetic resins and electroplating baths [1]. The method was also applied to tetramethyl thiourea [1].

INTERFERENCES: Compounds containing a thione (C=S) group will complex with the pentacyanoamineferrate reagent and may interfere with the ETU absorbance band at 590 nm.

OTHER METHODS: This method was originally designated P&CAM 281 [2], which it replaces.

REAGENTS:

1. Bromine, Br_2, ACS reagent.*
2. Disodium pentacyanonitrosyl ferrate dihydrate (sodium nitroferricyanide; sodium nitroprusside), $Na_2Fe(CN)_5NO \cdot 2H_2O$, ACS reagent.
3. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, ACS reagent.
4. Sodium bicarbonate, $NaHCO_3$, ACS reagent.
5. Hexane, spectrophotometric quality.
6. Methanol, spectrophotometric quality.
7. Water, distilled or deionized.
8. Complexing reagent (see APPENDIX).
9. Dilute complexing reagent. Mix 1 volume complexing reagent with 2 volumes water. Prepare fresh daily.
10. Ethylene thiourea (ETU) (see APPENDIX).
11. Calibration stock solution, 1000 μg/mL. Dilute 0.250 g recrystallized ETU to 250 mL with distilled water.

* See Special Precautions

EQUIPMENT:

1. Sampler: PVC filters, 5-μm pore size, 37-mm diameter or mixed cellulose ester filters, 0.8-μm pore size, 37-mm diameter; plastic filter holders (cassettes).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Spectrophotometer to operate at 590 nm.
4. Matched glass cuvettes, 5-cm optical path length.
5. Analytical balance capable of weighing to the nearest 0.1 mg.
6. Mortar and pestle.
7. Waterbath thermostatically controlled to 60 ± 1 °C.
8. Glass vials, 20-mL capacity, with PTFE-lined screw caps.
9. Beakers, assortment of 50- to 250-mL.
10. Adjustable pipettes (5- to 50-μL, 50- to 250-μL, 0.5- to 5-mL) with disposable tips.
11. Volumetric pipettes, assortment of 1- to 25-mL, with pipet bulb.
12. Volumetric flasks, 25-, 100-, 200- and 250-mL capacity.
13. Miscellaneous: tweezers, microspatula, rubber suction bulb, wood applicator stick weighing paper, filter paper and filter funnel with stand.

SPECIAL PRECAUTIONS: Bromine is very corrosive and causes severe burns; vapors are extremely irritating and toxic. Wear gloves and handle only in a hood.

Ethylene thiourea is an animal teratogen and carcinogen [3,4]. Extra care must be taken to avoid inhalation, ingestion or skin contact. Keep ETU in a bottle labelled "animal carcinogen" and place the bottle in a resealable thick-walled plastic bag in locked storage.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 200 to 800 L. Do not exceed 2 mg dust loading on the filter.
3. Collect a high-volume air sample or rafter dust sample. Ship in a glass vial in a separate container from the filters.

SAMPLE PREPARATION:

4. Remove the top portion of the filter holder. Hold the bottom portion containing the filter and filter support over a piece of weighing paper. Remove the plug from the bottom of the filter holder and insert the applicator stick through the hole. Gently raise the filter and grasp the edge with tweezers. Very carefully transfer the filter to a 20-mL glass vial and push it gently to the bottom. Add to the vial any material remaining in the filter holder or collected on the weighing paper.

5. Pipet 7.0 mL distilled water into the vial to completely immerse the filter. Cap the vial.
6. Place vials in a 60 °C waterbath (thermostatically controlled) for 45 min. The waterbath level must be above the water level in the vial. Shake each vial every 5 min.
   NOTE: Do not use an ultrasonic bath, because it breaks up the filters.
7. Lift the filter with tweezers above the water level in the vial. Wash the filter two times with 4-mL aliquots of water using a 5-mL adjustable pipette. Collect the rinsings in the vial. Discard the filter.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standrds over the range of 0 to 150 μg/mL.
   a. Prepare a 15 μg/mL ETU standard solution by pipetting 3.0 mL of the 1000 μg/mL calibration stock solution into a 200-mL volumetric flask and diluting to the mark with distilled water.
   b. Prepare working standards by pipetting 0- to 10-mL aliquots of the 15 μg/mL standard solution into clean vials. Bring the total volume to 15 mL with distilled water. Follow steps 10 and 11 to analyze the working standards.
   c. Prepare a calibration graph (absorbance vs. μg per sample).
9. Determine recovery at least once for each lot of filters used.
   a. Place eight filters on a plastic test tube rack. Using an adjustable pipette, add to the center of each filter 0, 7.5, 15, 30, 45, 60, 90, 120, and 150 μL of 1000-μg/mL calibration stock solution. Let filters air dry overnight at room temperature. Extract (steps 4 through 7) and analyze (steps 10 and 11).
   b. Convert the absorbance of each sample to μg from the calibration graph. Calculate recovery, R (μg found/μg taken).

MEASUREMENT:

10. Complexation.
    NOTE: Perform this step at the same time for both standards and samples to reduce errors due to color degradation.
    a. Pipet a 1.5-mL aliquot of dilute complexing reagent into each vial.
    b. Allow the vials to stand for at least 30 min before analysis to insure full color development. Shake the vials every 10 min.
       NOTE: The color of the complexed samples varies with increasing concentration from yellow to light green to turquoise. Very high concentrations have Prussian blue color; dilute these with distilled water and use the appropriate dilution factor in the calculations.
11. Measurement.
    a. Transfer the solution to a clean 5-cm cuvette. Wipe cuvette with a lens paper to remove any droplets on the cuvette windows.
    b. Place the cell in the sample compartment and measure absorbance at 590 nm vs. a reference sample (15 mL distilled water and 1.5 mL dilute complexing reagent) in a 5-cm cuvette. Record the absorbance for each sample.
       NOTE: Scan the absorbance of the bulk sample (dissolve several mg of bulk sample in 15 mL water and treat as in steps 10 and 11) in the range 350 to 700 nm to detect possible interferences.

CALCULATIONS:

12. Determine the mass of ETU, μg (corrected for recovery), for the sample (W) and average media blank (B).

13. Calculate the concentration of ETU, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was tested with 21 PVC (VM-1)/ETU spiked samples in the range 15 to 150 μg per sample with an average recovery of 98.0 ± 3.2% [1]. It was also tested with 20 mixed cellulose ester filters spiked with ETU in the range of 15 to 150 μg per sample, giving an average recovery of 99.2% ± 3.6% [1]. All calibration graphs indicated a minimum linear correlation coefficient of 0.9999 [1]. The method was also used on 50 field samples on VM-1 filters in two surveys [1]. The amounts of ETU found ranged from 5 to 56 μg per sample. Storage stability was not determined, nor was overall method bias determined.

REFERENCES:

[1] Palassis, J. Sampling and Analytical Determination of Airborne Tetramethyl and Ethylene Thiourea, Am. Ind. Hyg. Assoc. J., 41, 91-97 (1980).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 281, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Special Occupational Hazard Review...Ethylene Thiourea, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-109 (1978).
[4] NIOSH Current Intelligence Bulletin No. 22: Ethylene Thiourea, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-144 (1978).

METHOD WRITTEN BY:

John Palassis, NIOSH/DTMD.

APPENDIX:

1. PREPARATION OF COMPLEXING REAGENT
   a. Weigh 0.500 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in a 50-mL beaker. Dissolve in 10 mL distilled water.
   b. Grind together 0.500 g $NH_2OH \cdot HCl$ and 1.00 g $NaHCO_3$ in a mortar.
   c. In a hood, add the ground mixture to the solution from (a.). When bubbling ceases, add 0.10 mL bromine. When reaction stops, add ca. 10 mL distilled water. Filter. Rinse beaker with 4 mL distilled water and filter. Transfer filtrate to a 25-mL volumetric flask and dilute with distilled water to the mark. Refrigerate. Stable at least two weeks at 4 °C [3].

2. PURIFICATION OF ETU
   a. In a 250-mL Erlenmeyer flask, weigh 3 to 5 g ETU. Dissolve in 100 mL 1:1 methanol:water. Heat to boiling in a hood. Cool 5 min at room temperature. Add 5 mL hexane. Shake 30 sec. Cover with watchglass. Let stand 1 h at room temperature. Filter the ETU crystals, and wash with 100 mL 1:1 methanol:water. Let the crystals air dry in a hood.

ETHYLENIMINE

C_2H_5N MW: 43.07 CAS: 151-56-4 RTECS: KX5075000

METHOD: 3514, Issue 2 **EVALUATION:** FULL **Issue 1:** 2 May 1979 **Issue 2:** 15 August 1994

OSHA : carcinogen
NIOSH: carcinogen
ACGIH: 0.5 ppm (skin)
(1 ppm = 1.76 mg/m^3)

PROPERTIES: liquid; mp, −74.0 °C; bp, 56-57 °C; d 0.8321 g/mL @ 24 °C; VP 21 kPa (160 mm Hg) @ 20 °C

SYNONYMS: aziridine, azacyclopropane

SAMPLING

SAMPLER: BUBBLER (Folin's reagent)

FLOW RATE: 0.2 L/min

VOL-MIN: 1 L @ 0.5 ppm
-MAX: 48 L

SHIPMENT: ship at 5 °C in dark

SAMPLE STABILITY: 14 days @ 5 °C in dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.16 to 21 mg/m^3 (2.6- to 39-L samples)

BIAS: − 2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069

ACCURACY: ± 15.5%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 4-(1-aziridinyl)-1,2-naphthoquinone

EXTRACTION: 4 mL of $CHCl_3$, 15 sec. (twice)

FINAL VOLUME: 10 mL

INJECTION VOLUME: 10 µL

MOBILE PHASE: 59.5% hexane:40% chloroform (with 1% ethanol):0.5% 2-propanol

FLOW RATE: 1.3 mL/min

COLUMN: Lichrosorb DIOL 25 cm x 4.6-mm)

DETECTOR: UV @ 254 nm

CALIBRATION: 4-(1-aziridinyl)-1,2-naphthoquinone in $CHCl_3$

RANGE: 1 to 795 µg per sample

ESTIMATED LOD: 0.3 µg per sample

PRECISION ($\bar{S}_r$): 0.024

APPLICABILITY: The working range is 0.014 to 11 ppm (0.025 to 20 mg/m^3) for a 40-L air sample. A variation of this method has been used to measure ethylenimine in air at 0.02 to 0.10 mg/m^3 at a manufacturing plant [1,2]. The modifications of the method included use of a µBondapak-CN column in place of the Lichrosorb DIOL column and 50:48:2 hexane:dichloromethane:2-propanol for the mobile phase.

INTERFERENCES: Propylenimine and 2-bromoethylamine interfere.

OTHER METHODS: This method replaces Method P&CAM 300 [3] and is a variation of the method of Evans et al. [4]. The product of ethylenimine and Folin's reagent can be measured spectrophotometrically [5,6].

REAGENTS:

1. Chloroform with 1% ethanol as a preservative, UV grade.
2. Hexane, UV grade.
3. 2-Propanol, UV grade.
4. Methanol, UV grade.
5. Ethylenimine.*
6. 1,2-Naphthoquinone-4-sulfonic acid, sodium salt.
7. Deionized water.
8. NaOH solution (0.1 M). Dissolve 1 g of NaOH in water to make 250 mL of solution.
9. KH_2PO_4 solution (0.1 M). Dissolve 3.40 g of KH_2PO_4 in water to make 250 mL of solution.
10. Buffer solution (pH = 7.7). Mix 100 mL of 0.1 M KH_2PO_4 with 93.4 mL of 0.1 M NaOH.
11. Folin's reagent. Dissolve 0.40 g of 1,2-naphthoquinone-4-sulfonic acid, sodium salt, in 100 mL of buffer solution. Dilute to 500 mL with water. Wrap flask with aluminum foil and refrigerate. Solution is stable for 5 days.
12. Na_3PO_4 solution (0.5 M). Dissolve 19 g of $Na_3PO_4 \cdot 12H2O$ in water to make 100 mL of solution.
13. 4-(1-Aziridinyl)-1,2-naphthoquinone. See Appendix.
14. Calibration stock solution, 500 µg/mL. Dissolve 125 mg of 4-(1-aziridinyl)-1,2-naphthoquinone in chloroform to make 250 mL of solution.
15. Recovery stock solution, 10 mg/mL. Dissolve 2.50 g of ethylenimine in chloroform to make 250 mL of solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget bubbler, with 15 mL of Folin's reagent.
2. Personal sampling pump, 0.2 L/min, with flexible, connecting tubing.
3. High performance liquid chromatograph with column (page 1) and UV detector.
4. Syringes, 1-mL, readable to 10 µL.
5. Syringes, 100-µL, readable to 1 µL.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Volumetric flasks, low actinic glass, 500-, 250-, 100-, and 10-mL.
8. Graduated cylinders, 100- and 25-mL.
9. Separatory funnels with PTFE stopcocks.
10. Funnels, glass.
11. Beakers, 2-L and 50-mL.
12. Aluminum foil.
13. Filter paper.
14. pH paper.
15. Pipet bulb.

SPECIAL PRECAUTIONS: Ethylenimine is carcinogenic, very toxic, and extremely flammable [7]. This compound is strongly irritating to the eyes, skin, and mucous membranes. Handle only in a hood.

SAMPLING:

1. Calibrate the personal sampling pump with a representative sampler in line.
2. Sample at 0.2 L/min for a sample size of 1 to 48 L.
3. After sampling, use a pipet bulb to force air through the bubbler stem to dislodge ethylenimine derivative and recover sampling solution. Rinse the stem with 2 mL of chloroform, and add the wash to the bubbler. Seal the bubbler with a nonreactive stopper (PTFE or glass). Do not seal with rubber.
4. Protect the sample from light, and ship at 5 °C.

SAMPLE PREPARATION:

5. Transfer sample solution to a 60-mL separatory funnel.
6. Rinse bubbler with 4 mL of chloroform, and add rinse to separatory funnel.
7. Cap and shake funnel for 15 seconds. Allow the phases to separate.
8. Collect chloroform extract in a 10-mL volumetric flask.
9. Repeat steps 6 and 7, and collect chloroform extract in the same volumetric flask.
10. Dilute solution in the volumetric flask to 10 mL with chloroform.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with working standards over the range of 1.4 to 3681 μg of 4-(1-aziridinyl)-1,2-naphthoquinone per sample. Express the quantities of 4-(1-aziridinyl)-1,2-naphthoquinone in terms of the corresponding quantities of ethylenimine (1 μg of 4-(1-aziridinyl)-1,2-naphthoquinone corresponds to 0.216 μg of ethylenimine). The corresponding range is 0.3 to 795 μg of ethylenimine per sample.
    a. Dilute portions of the calibration stock solution to prepare a series of working standards in the range of 0.3 to 795 μg of ethylenimine per sample (0.03 to 79.5 μg/mL).
    b. Analyze according to steps 13 and 14.
    c. Prepare a calibration graph (peak area or peak height versus μg of ethylenimine per sample).
12. Determine recovery from bubblers.
    a. Dilute portions of recovery stock solution with chloroform to prepare a series of spiking solutions in the range of interest.
    b. Add known quantities of ethylenimine in spiking solutions to bubblers containing 15-mL quantities of Folin's reagent. Prepare five samples at each of three levels over the range of interest.
    c. Prepare sample solutions (steps 5 through 10) and analyze (steps 13 and 14).
    d. Calculate recovery, R (μg of ethylenimine found divided by μg of ethylenimine applied).
    e. Prepare a graph of recovery versus μg of ethylenimine found.

MEASUREMENT:

13. Set the liquid chromatograph according to manufacturer's instructions and to conditions on page 1.
14. Analyze sample solutions with standards.

CALCULATIONS:

15. Determine the quantities of ethylenimine in the sample corrected for Recovery, W (μg), and the average media blank, B (μg), from the calibration graph.
16. Calculate the concentration, C (mg/m^3), of ethylenimine in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method is based on Method P&CAM 300, which was evaluated with controlled atmospheres of ethylenimine [3]. Overall precision ($\hat{S}_{rT}$) was 0.069 (52 samples, pooled) for 2.6- to 39-L samples at 0.16 to 21 mg/m^3; $\hat{S}_{rT}$ includes an assumed pump error of 0.05. Independent concentrations of ethylenimine vapor in the controlled atmospheres (referred to as "taken" values) were calculated from the measured total air flow and the delivery rate of the syringe pump. Recoveries with controlled atmospheres

(recovery = average found concentration divided by the taken concentration) ranged from 91 to 105% for six sets of samples at 0.16 to 21 mg/m^3; thus, bias for sampling and analysis was not significant. Collection efficiencies of samplers at 0.15 L/min were >99% at 21 and 204 mg/m^3. Average recoveries from 15-mL quantities of Folin's reagent (fortified with ethylenimine in chloroform) were 0.93 and 0.95 at the 1.67- and 16.7-μg levels of ethylenimine, respectively; the precision ($\bar{S}_r$) was 0.024 (12 samples, pooled). Samples at the 1.67- and 16.7-μg levels were stable in Folin's reagent during storage for 14 days at 5 °C in the dark.

Methylamine, diethylamine, butylamine, ethanolamine, dihexylamine, dicyclohexylamine, benzylamine, dibenzylamine, and aniline do not interfere with measurement of ethylenimine. Propylenime and 2-bromoethylamine interfere.

REFERENCES:

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METHOD WRITTEN BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; P&CAM 300 developed under NIOSH contract.

APPENDIX

SYNTHESIS OF 4-(1-AZIRIDINYL)-1,2-NAPHTHOQUINONE

Place 2 g of 1,2-naphthoquinone-4-sulfonic acid, sodium salt, and 250 mL of water into a 1-L separatory funnel which is wrapped with aluminum foil. Add 25 mL of 0.5 M trisodium phosphate, and shake the mixture. Ascertain that the pH is between 10.5 and 11.5. Add 0.3 mL of ethylenimine and shake at intervals over 10 min. Extract the 4-(1-aziridinyl)-1,2-naphthoquinone with six 200-mL portions of chloroform. Combine extracts in a 2-L beaker wrapped with aluminum foil. Cover the beaker with aluminum foil which is punctured with three holes, and evaporate chloroform with a nitrogen purge. Transfer the dry residue to a 50-mL beaker wrapped with aluminum foil. Add 35 mL of methanol and 1 mL of chloroform to the residue. A portion of the residue will remain undissolved. Filter and cool the solution to 0 °C. Wash the crystallized product with 4 mL of chilled methanol, and dry the product with a nitrogen purge. Melting point = 173 to 175 °C.

FLUORIDE in urine 8308

F^- MW: 19.00 CAS: 16984-48-8 RTECS: LM6290000

METHOD: 8308, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to inorganic fluorides [1,2].

SYNONYMS: none.

SAMPLING		MEASUREMENT	
SPECIMEN:	urine, pre- and post-shift	**TECHNIQUE:**	ION SELECTIVE ELECTRODE (ISE)
VOLUME:	50 mL in chemically clean polyethylene bottles	**ANALYTE:**	fluoride ion (F^-)
PRESERVATIVE:	0.2 g EDTA added to bottles before collection	**DILUTION:**	mix equal volumes of urine with TISAB
SHIPMENT:	in insulated containers using bagged refrigerant	**CALIBRATION:**	solutions of sodium fluoride in water
SAMPLE STABILITY:	2 weeks @ 4 °C, longer if frozen	**QUALITY CONTROL:**	spiked urine pools; correct for creatinine content
CONTROLS:	collect 3 sets of specimens from unexposed workers (pre- and post-shift)	**RANGE:**	1 to 100 mg/L urine
		ESTIMATED LOD:	0.1 mg/L urine
		RECOVERY:	0.95 [3]
		PRECISION ($\bar{S}_r$):	0.04
		ACCURACY:	± 23.6%

APPLICABILITY: Any fluorine-containing substances that can be metabolized to fluoride (F^-) can be monitored using this procedure. Inorganic compounds of fluoride can be absorbed by the body resulting in the excretion of fluoride ions as sodium fluoride. Dietary and domestic water sources of fluoride must be considered, as well as dental treatments.

INTERFERENCES: Hydroxide, the only positive interference, is eliminated by use of the buffer. Negative interferences from complexation of fluoride by cations, such as calcium, are minimized by EDTA preservative and the high ionic strength buffer.

OTHER METHODS: This method is P&CAM 114 [4] in a revised format. Other methods that have been used are those described in the NIOSH criteria documents on inorganic fluorides [1] and hydrogen fluoride [2].

REAGENTS:

1. Distilled or deionized water.
2. Sodium citrate ($Na_3C_6H_3O_7 \cdot 2H_2O$).
3. Ethylene dinitrilotetracetic acid (EDTA), disodium salt.
4. Acetic acid, glacial.
5. Sodium chloride.
6. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in distilled water; dilute to 100 mL.
7. Sodium fluoride.
8. Calibration stock solution, 100 μg F^-/mL. Dissolve 0.2211 g dry sodium fluoride in distilled water. Make 1000 mL solution.
9. Total ionic strength activity buffer (TISAB), pH 5. Add 57 mL glacial acetic acid, 58 g sodium chloride, and 0.30 g sodium citrate to a 1-L beaker containing 500 mL distilled water. Stir to dissolve. Place beaker in waterbath for cooling. Slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature; dilute to 1 L with distilled water.

EQUIPMENT:

1. Polyethylene bottles, 125-mL, wide-mouth.
2. Fluoride ion specific electrode (ISE), with reference electrode.
3. pH/millivolt meter, reading to ± 0.5 mV.
4. Stirrer, magnetic.
5. Stirring bars, PTFE-coated.
6. Beakers, plastic, 50-mL.
7. pH electrode.
8. Pipets, appropriate sizes for standards.
9. Volumetric flasks for standards.
10. Waterbath.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect pre- and post-shift spot urine samples in polyethylene bottles containing 0.2 g EDTA.
2. Ship samples in insulated container at about 4 °C using bagged refrigerant.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of the urine (e.g., [5]).

CALIBRATION AND QUALITY CONTROL:

4. Prepare at least five working standards in the range 0.1 to 100 μg F^-/mL by appropriate dilutions of the calibration stock solution with distilled water.
5. Analyze a set of working standards together with the samples and blanks (steps 9 through 12) starting with the lowest concentration.
   NOTE: Working standards, samples, and blanks must be analyzed under the same conditions, including temperature, for accurate results.
6. Prepare a calibration graph on three-cycle semi-log paper plotting millivolts on the linear scale and fluoride concentration, μg/mL, on the log scale.
7. Maintain standardization by running a standard with every 10 specimens.

8. Run a spiked urine control specimen with every 10 specimens to maintain quality assurance.
   NOTE: Urine used for spiked controls must be analyzed before use to determine background fluoride concentration.

MEASUREMENT:

9. Add 10 mL well-mixed urine and 10 mL TISAB to a 50-mL plastic beaker.
10. Place a small stirring bar into beaker and mix continuously on a magnetic stirrer at room temperature.
11. Immerse electrodes. Allow sample to mix for 2 to 3 min and then record millivolt reading.
12. Rinse electrodes and stirring bar thoroughly with distilled water and wipe dry with tissue before next sample analysis.

CALCULATIONS:

13. Convert the millivolt readings to fluoride concentration using the calibration graph.
14. Express fluoride concentration as mg F^-/g urinary creatinine.

GUIDES TO INTERPRETATION:

Urine concentrations of fluorides in normal non-occupationally exposed workers have been reported to range from 0.2 to 3.2 mg/L depending on dietary intake [6]. Preshift levels of less than 4 mg/g creatinine and post-shift levels of less than 7 mg/g creatinine appears to protect workers against bony fluorosis [7]. NIOSH has recommended that post-shift urine specimens should not exceed 7 mg/L (corrected to a specific gravity of 1.024) and pre-shift specimens should not exceed 4 mg/L (1.024) [1,2].

The Biological Exposure Indices for fluoride are 3 mg/g creatinine prior to shift and 10 mg/g creatinine at end of shift [8].

EVALUATION OF METHOD:

No formal method evaluation has been reported; however, Tusl [3] reported recoveries of added fluoride from 94 to 100%. Precision based on analysis of 25 specimens in triplicate is estimated to be better than $\bar{S}_r = 0.04$.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Fluorides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-103 (1976).
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[3] Tusl, J. Direct determination of fluoride in human urine using fluoride electrode, Clin. Chim. Acta, 27, 216-218 (1970).
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METHOD WRITTEN BY:

William P. Tolos, NIOSH/DBBS.

FLUORIDES aerosol and gas, by IC 7906

F^- MW: 18.998 CAS: (HF) 7664-39-3 RTECS: (HF) MW7875000

METHOD: 7906, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 2.5 mg/m^3 (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m^3 (fluorides); 3 ppm (HF); STEL 6 ppm (HF)
ACGIH: 2.5 mg/m^3 (fluorides); C 3 ppm (HF)
(1 ppm HF = 0.818 mg/m^3 @ NTP)

PROPERTIES: HF: liquid; BP 19.5 °C; fluoride salts liberate HF in presence of acids

SYNONYMS: sodium fluoride (CAS #7681-49-4); hydrogen fluoride; hydrofluoric acid; cryolite; sodium hexafluoroaluminate (CAS #13775-53-6).

SAMPLING

SAMPLER: FILTER + TREATED PAD (0.8-μm cellulose ester membrane + Na_2CO_3-treated cellulose pad)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 1 L @ 3 ppm (HF)
120 L @ 2.5 mg/m^3 (water-insoluble particulate)
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY/ CONDUCTIVITY

ANALYTE: fluoride ion (F^-)

FILTER (particulate F^-): fuse in NaOH, dissolve in 100 mL water, dilute 1:40 with water

TREATED FILTER (gaseous F^-): extract in 100 mL water

INJECTION VOLUME: 50 μL

ELUENT: 5 mM $Na_2B_4O_7$, 2 mL/min

COLUMNS: IonPac-AS4A separator, IonPac-AG4A guard, anion micromembrane suppressor

CONDUCTIVITY SETTING: 10 μS full scale

CALIBRATION: standard F^- solutions in water

RANGE: 0.01 to 0.25 mg F^- per sample (gas) [1]
0.30 to 10 mg F^- per sample (particulate) [1]

ESTIMATED LOD: 3 μg F^- per sample (gas) [1]
120 μg F^- per sample (particulate) [1]

PRECISION ($\hat{S}_r$): 0.019 (gas) [1]
0.066 (particulate) [1]

APPLICABILITY: The working ranges are 0.05 to 10 ppm HF (0.04 to 8 mg/m^3) and 1.2 to 8 mg/m^3 water-insoluble fluorides for a 250-L air sample. Water soluble particulate fluorides may be extracted by the procedure for gaseous fluoride. Insoluble particles require fusion. The method applies to mining samples; aluminum reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorochemical industries. The method is applicable to ceiling limit and short-term exposure limit (STEL) monitoring.

INTERFERENCES: If other aerosols are present, gaseous fluoride may be slightly underestimated owing to adsorption onto or reaction with particles, with concurrent overestimation of particulate/gaseous fluoride ratio [2-6].

OTHER METHODS: Method 7902 (Fluorides by ISE) employs the same sampling procedure, but uses ion selective electrode for measurement. Method 7903 (Acids, Inorganic) is an alternative method for HF.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Sodium fluoride (NaF).*
4. Sodium acetate ($NaC_2H_3O_2$).
5. Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$).
6. Alkaline Fixative Solution: Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
7. Calibration Stock Solution, 100 μg/mL: Dissolve 0.2211 g NaF (dried at 105 °C for 2 h) in deionized water. Dilute to 1 L.
8. Sodium Hydroxide, 20% (w/v): Dissolve 200 g NaOH in deionized water. Dilute to 1 L.
9. Acetate Stock Solution: Dissolve 0.1389 g sodium acetate in deionized water. Dilute to 100 mL.
10. Mixed Anion Solution: Add 0.10 mL of fluoride stock solution and 0.10 mL acetate stock solution to deionized water. Dilute to 50 mL.
11. Eluent, 5 mM sodium tetraborate: dissolve 1.9079 g $Na_2B_4O_7 \cdot 10H_2O$ in deionized water. Dilute to 4 L.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 37-mm, 0.8-μm pore size, with porous plastic backup pad (Nuclepore #220800, or equivalent), treated cellulose pad (Moisten with 0.8 mL fixative solution and dry at 105 °C for 30 to 45 minutes. Discard if charred.) in a 3-piece cassette with a 1/2" extension.
   Assembly of sampler: Place treated pad in rear (outlet) piece of cassette, insert 1/2-inch extension, place porous plastic pad and membrane filter in upper part of extension, and insert top piece (inlet) of cassette. Press tightly together and seal with shrink band or tape.
   NOTE: Leak test with hand vacuum pump.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Ion chromatograph, conductivity detector, set to conditions on p. 7906-1.
4. Crucibles, nickel, zirconium, or Inconel, 20- or 30-mL.
5. Bunsen or Meeker burner.
6. Tripod.
7. Triangle, ceramic-covered.
8. Volumetric flasks, 50- and 100-mL, and 1-L.
9. Pipets, appropriate sizes for standards.
10. Specimen containers, screw caps, plastic, 150-mL.
11. Syringes, plastic, 10-mL
12. Syringe filters, 25-mm
13. Ultrasonic bath
14. Hot plate
15. Hand vacuum pump

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes. Perform all fusions in fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 1 L (gas) or 120 L (particulate) to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Pack securely for shipment.

SAMPLE PREPARATION:

4. **Cellulose ester membrane filter** (particulate fluoride).
   NOTE: Water soluble particulate fluorides may be extracted by the procedure for gaseous fluorides. Insoluble particulates require fusion, which decreases sensitivity in the measurement.
   a. Transfer the membrane filter to a crucible containing 5 mL of 20% NaOH.
   b. Evaporate to dryness on hot plate.

c. Heat residue to fusion temperature over Bunsen or Meeker burner, 1 to 2 min, and let cool.
d. Transfer crucible with sample to specimen container, add 100 mL of deionized water with a volumetric pipet, and seal with screw cap.
e. Place in an ultrasonic bath for 15 to 20 min.
f. Dilute 1:40 with deionized water and transfer by syringe fitted with filter into appropriate vial for IC analysis.

5. **Alkaline-impregnated backup pad** (gaseous fluoride).
   a. Transfer impregnated pad to specimen container, add 100 mL of deionized water with a volumetric pipet, and seal with screw cap.
   b. Place in an ultrasonic bath for 15 to 20 min.
   c. Filter into appropriate vial for IC analysis.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range of the samples.
   a. Add known amounts of mixed-anion calibration stock solution to deionized water in 50-mL volumetric flasks. Dilute to the mark with deionized water.
   b. Prepare fresh standards weekly.
   c. Analyze together with samples and blanks (steps 8 through 10).
      NOTE: Insure fluoride and acetate ion peaks are resolved. Baseline resolution is not required when using peak height for determination.
   d. Prepare a calibration graph (peak height, μS or mm, vs. μg/mL of F^-).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

8. Set ion chromatograph according to manufacturer's instructions and to conditions on p. 7906-1.
9. Inject a 50-μL sample aliquot.
   NOTE: All samples and standards must be filtered to avoid plugging the system valves or columns.
10. Measure peak height.
    NOTE: If peak height exceeds the linear calibration range, dilute, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

11. Determine the mass, μg, of fluoride found on the particulate filter, W_p, and the treated pad, W_g, and the corresponding average media blanks, B_p and B_g, using the solution volumes of the samples, V_p and V_g, and blanks, V_{pb} and V_{gb}.
12. Calculate the concentration of particulate fluoride, C_p (mg/m^3), and gaseous fluoride, C_g (mg/m^3), in the volume of air sampled, V (L):

$$C_p = \frac{W_pV_p - B_pV_{pb}}{V}, \text{ mg/m}^3 \qquad C_g = \frac{W_gV_g - B_gV_{gb}}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

With ion chromatographic analysis the following performance criteria were determined [1]. The LOD for gaseous fluoride (rear treated pad) was estimated at 3 μg fluoride per sample, with a range of 0.01 to 0.25 mg fluoride per sample. The precision ($\bar{S}_r$) was determined to be 0.019 over the range 13 to 250 μg per sample for the rear treated pad. Because the high ionic strength resulting from the fusion of the

particulate sample in NaOH required a further 1:40 dilution, the limit of detection (LOD) for particulate fluoride (front section) was estimated at 120 μg fluoride per sample, with a range of 0.30 to 10 mg fluoride per sample. The precision ($\bar{S}_r$) for the particulate filter was estimated at 0.066 at 250 μg per sample. The overall precision and bias were not determined.

REFERENCES:

[1] Lorberau, C. Determination of Gaseous and Particulate Fluorides by Ion Chromatographic Analysis. Appl. Occup. Environ. Hyg. 8(9), 775-784 (1993).

[2] Jahr, J. A New Dual Filter Method for Separate Determination of Hydrogen Fluoride and Dustlike Fluorides in the Air. Staub-Reinhalt. der Luft, 32(6) 17 (1972).

[3] Israel, G.W. Evaluation and Comparison of Three Atmospheric Fluoride Monitors under Field Conditions. Atmos. Environment, 8, 159 (1974).

[4] Pack, M.R., A.C. Hill, and G.M. Benedict. Sampling Atmospheric Fluorides with glass Fiber Filters. J. Air Pollution Control Assoc., 13 (8), 374 (1963).

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METHOD WRITTEN BY:

Charles Lorberau, NIOSH/DPSE.

FLUORIDES, aerosol and gas by ISE 7902

F^- MW: 18.998 CAS: (HF) 7664-39-3 RTECS: (HF) MW7875000

METHOD: 7902, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 2.5 mg/m^3 (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m^3 (fluorides); 3 ppm (HF); STEL 6 ppm (HF)
ACGIH: 2.5 mg/m^3 (fluorides); C 3 ppm (HF)
(1 ppm HF = 0.818 mg/m^3 @ NTP)

PROPERTIES: HF: liquid; BP 19.5 °C; fluoride salts liberate HF in presence of acids

SYNONYMS: sodium fluoride (CAS #7681-49-4); hydrogen fluoride; hydrofluoric acid; cryolite; sodium hexafluoroaluminate (CAS #13775-53-6).

SAMPLING

SAMPLER:	FILTER + TREATED PAD (0.8-μm cellulose ester membrane + Na_2CO_3-treated cellulose pad)
FLOW RATE:	1 to 2 L/min
VOL-MIN:	12 L @ 2.5 mg/m^3
-MAX:	800 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	ION-SPECIFIC ELECTRODE
ANALYTE:	fluoride ion (F^-)
FILTER (particulate F^-):	fuse in NaOH, dissolve in 50 mL water + TISAB
TREATED FILTER (gaseous F^-):	extract in 50 mL water + TISAB
CALIBRATION:	standard F^- solutions in TISAB
RANGE:	0.03 to 1.2 mg F^- per sample
ESTIMATED LOD:	3 μg F^- per sample [1]
PRECISION ($\bar{S}_r$):	0.017 @ 55 to 220 μg per sample [2]

APPLICABILITY: The working range is 0.12 to 8 mg/m^3 for a 250-L air sample. The method applies to mining samples, and samples from the aluminum reduction, ceramic, glass etching, electroplating, semi-conductor, and fluorochemical industries. If other aerosols are present, gaseous fluoride may be underestimated owing to sorption on collected particles, with concurrent overestimation of particulate/gaseous fluoride ratio [3-8].

INTERFERENCES: In samples containing cryolite, aluminum is sufficiently concentrated to give erroneous fluoride concentrations [3]. Hydroxide ion greater than 1/10 of the fluoride level will interfere positively. Fe^{3+}, Si^{4+}, and Al^{3+} give a negative interference. Concentrations >8 μg/mL of these elements cannot be suppressed [9]. The TISAB suppresses up to 500 μg/mL Fe^{3+} and up to 90 μg/mL Si^{4+}.

OTHER METHODS: This revises method 7902 [10] which was withdrawn on 5/15/89. The method was originally based on a method by Elfers and Decker [11], and NIOSH method S176 for HF [2]. Method 7903 (Acids, Inorganic) is an alternative method for HF. Method 7906 (Fluorides by IC) employs the same sampling procedure, but uses ion chromatography for measurement.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Potassium chloride (KCl).
4. Sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$).
5. Cyclohexylene diamine tetraacetic acid (CDTA).
6. Hydrochloric acid, 1:1 (v/v).
7. Sodium fluoride (NaF).*
8. Deionized water.
9. Fixative solution. Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
10. Total ionic strength activity buffer (TISAB), pH 5.5. Dissolve 37 g KCl, 68 g sodium acetate and 36 g CDTA in H_2O. Adjust to pH 5.5 ± 0.2 with 1:1 HCl. Dilute to 1 L.
11. Calibration stock solution, 100 µg/mL: Dissolve 0.2211 g NaF (dried at 105 °C for 2 h) in deionized water; dilute to 1 L.
12. Sodium hydroxide, 20% (w/v). Dissolve 200 g NaOH in deionized water to make 1 L solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 37-mm, 0.8-µm pore size, with porous plastic backup pad (Nuclepore #220800, or equivalent), treated cellulose pad (Moisten with 0.8 mL fixative solution and dry at 105 °C for 30 to 45 minutes. Discard if charred.) in a 3-piece cassette with a 1/2" extension.
   Assembly of sampler: Place treated pad in rear (outlet) piece of cassette, insert 1/2-inch extension, place porous plastic pad and membrane filter in upper part of extension, and insert top piece (inlet) of cassette. Press tightly together and seal with shrink band or tape.
   NOTE: Leak test with hand vacuum pump.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Crucibles, nickel, zirconium, or Inconel, 20- or 30-mL.
4. Bunsen or Meaker burner.
5. Tripod.
6. Triangle, ceramic-covered.
7. Volumetric flasks, 50- and 100-mL, and 1-L.
8. Pipets, appropriate sizes for standards.
9. Beakers, plastic, 100-mL or 150-mL.
10. Magnetic stirrer.
11. PTFE-coated stirring bars.
12. Fluoride ion selective electrode (ISE), NaF combination or with calomel-type reference electrode.
13. pH/ion meter with millivolt readout and pH electrode.
14. Hand vacuum pump.

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes [12]. Perform all fusions in fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 12 to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Pack securely for shipment.

SAMPLE PREPARATION:

4. **Cellulose ester membrane filter** (particulate fluoride).
   NOTE: Water-soluble particulate fluorides may be extracted by the procedure for gaseous fluorides. Insoluble particles require fusion.
   a. Transfer the membrane filter to a crucible containing 5 mL 20% NaOH.
   b. Evaporate to dryness.

c. Heat residue to fusion temperature, 1 to 2 min, cool and dissolve in ca. 5 mL deionized water.
d. Transfer sample into 100-mL plastic beakers.
e. Rinse crucible with 25 mL of TISAB then with a few drops of 1:1 HCl.
f. Adjust to pH 5.5 ± 0.2 using 1:1 HCl.
g. Transfer to 50 mL volumetric flask; dilute to volume with deionized water.

5. **Treated pad** (gaseous fluoride).
   a. Transfer treated pads to 100-mL plastic beakers.
   b. Add 25 mL TISAB and 25 mL deionized water.
   c. Soak pad for 30 min with sufficient stirring to reduce it to pulp.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 3 to 1200 μg F^- per sample.
   a. Add known amounts of calibration stock solution to 25 mL TISAB and 5 mL 20% NaOH (particulate fluoride) or 25 mL TISAB (gaseous fluoride) in 100-mL beakers.
   b. Adjust pH to 5.5 ± 0.2 with 1:1 HCl.
   c. Transfer to 50-mL volumetric flasks. Dilute to the mark with deionized water.
      NOTE: Working standards are stable at least one month in polyethylene bottles at 4 °C.
   d. Analyze together with samples and blanks (steps 7 through 10).
   e. Prepare separate calibration graphs (mV vs. log F^- concentration) for particulate and gaseous fluorides.
      NOTE: Calibration curve is not linear below 0.1 μg/mL or above 25 μg/mL.

MEASUREMENT:

7. Bring sample and standard solutions to room temperature.
   NOTE: Samples and standards must be at same temperature (within ± 2 °C) for accurate results.
8. Pour ca. 20 mL of each solution into plastic beakers.
9. Add magnetic stir bar, insert electrodes and gently stir on magnetic stirrer.
10. Record potential (mV) after 2 min.
    NOTE: If measured concentration of F^- is >25 μg/mL, dilute with appropriate matrix (step 6), reanalyze and apply dilution factor in calculations.

CALCULATIONS:

11. Using the proper calibration graph (particulate or gaseous), convert potential (mV) to solution fluoride concentration, C_s (μg/mL), in the sample solution volume, V_s (mL), and the average media blank, C_b, in the blank solution volume, V_b (mL).
12. Calculate the concentration of fluoride, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Measurement precision, $\bar{S}_r$, in the range 0.055 to 0.22 mg HF per sample averaged 0.017 with average recovery 100.0% [2]. Analytical results on field samples report detection limits of 3 μg per sample for both gaseous and particulate fluorides [1]. Reported collection ranges for gaseous fluoride and particulate fluorides were 4 to 61 μg per sample and 4 to 410 μg per sample, respectively [10].

REFERENCES:

[1] UBTL Reports, NIOSH/DPSE Analytical Sequence Nos. #2454, 2703, 3117 and 3366. Measurement Research Support Branch, NIOSH (unpublished).
[2] Documentation of the NIOSH Validation Tests, S176, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
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[6] Pack, M.R., A.C. Hill, and G.M. Benedict. Sampling Atmospheric Fluorides with glass Fiber Filters. J. Air Pollution Control Assoc., 13 (8), 374 (1963).
[7] Einfeld, W. Investigation of a Dual Filter Sampling Method for the Separate Estimation of Gaseous and Particulate Fluorides in Air. Thesis (M.S., Public Health), Univ. of Washington (1977).
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[9] Abell, M. T. Evaluation of Methods for Fluorides, Internal Technical Report, NIOSH, DPSE (1975).
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[11] Elfers, L.A. and C.E.Decker. Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode. Anal. Chem. 40, 1658 (1968).
[12] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

FLUOROTRICHLOROMETHANE 1006

CCl_3F MW: 137.37 CAS: 75-69-4 RTECS: PB6125000

METHOD: 1006, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : C 1000 ppm
NIOSH: C 1000 ppm
ACGIH: C 1000 ppm
(1 ppm = 5.62 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.53 g/mL @ 0 C; BP 23.8 C; MP -111 °C; VP 92 kPa (690 mm Hg; 91% v/v) @ 20 C; not combustible

SYNONYMS: Freon 11; trichlorofluoromethane; monofluorotrichloromethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.3 L
-MAX: 7 L

SHIPMENT: refrigerate

SAMPLE STABILITY: quantitative recovery after 8 days @ 25 C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2390 to 10500 mg/m^3 [1] (4-L samples)

BIAS: − 2.66%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.072 [1]

ACCURACY: ± 16.08%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: fluorotrichloromethane

DESORPTION: 5 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 220 °C
-COLUMN: 65 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 6 m x 3-mm OD stainless steel packed with 10 % FFAP on 100/120 Chromosorb WHP.

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 2 to 40 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.063 @ 11 to 32 mg per sample [1]

APPLICABILITY: The working range is 90 to 1800 ppm (500 to 10000 mg/m^3) for a 4-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S102 [2].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% (v/v) nonane as internal standard.
2. Fluorotrichloromethane, 99%.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg; back = 200 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1006-1).
5. Vials, glass, 10-mL, PTFE-lined septum crimp caps.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Syringes, gas-tight, 10-μL to 10-mL.
8. Syringe needle, 22-gauge.
9. Volumetric flasks, 10-mL.
10. Pipet, TD, 5-mL.
11. Balance, 0.1-mg sensitivity.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). Work with it only in a hood and away from spark sources.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.3 to 7 L.
4. Cap the sampler. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs. Seal each vial with a septum and crimp seal.
6. Insert a syringe needle through the septum to serve as a vent.
7. Add 5.0 mL eluent to each vial with a syringe. Remove the vent from the septum.
8. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 0.01 to 40 mg fluorotrichloromethane per sample. Use serial dilutions for the smallest concentrations.
   a. Add 5.0 mL eluent to each of a series of vials. Attach septum with crimp seal to each vial.
   b. Weigh each vial.
   c. Inject amounts (2 to 30 μL) of neat liquid fluorotrichloromethane (or of a standard solution in CS_2) into the vials.
   d. Reweigh the vials. Calculate the mass of fluorotrichloromethane added.
   e. Analyze with samples and blanks (steps 12 and 13).
   f. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg fluorotrichloromethane).
10. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Add 400 mg charcoal (e.g., an unused front section) to each of a series of vials.
   b. Seal each vial with a septum and crimp seal.
   c. Weigh each vial.
   d. Inject amounts (2 to 30 μL) of neat fluorotrichloromethane (or of a standard solution in CS_2) into the vials.
   e. Reweigh each vial. Calculate the mass of fluorotrichloromethane added. Allow to stand overnight.
   f. Desorb (steps 6 through 8) and analyze with freshly prepared working standards (steps 12 and 13).
   g. Prepare a graph of DE vs. mg fluorotrichloromethane recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1006-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
   NOTE 1: t_r = 3 min for fluorotrichloromethane and 4.5 min for nonane under these conditions.
   NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE), of fluorotrichloromethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
   NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of fluorotrichloromethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S102 was issued on October 29, 1976 [2], and validated with atmospheres generated by a cooled, calibrated syringe drive [1]. Average recovery was 0.98 with $\bar{S}_r$ = 0.046 (17 samples) in the range 2388 to 10520 mg/m^3 for 4-L samples. No significant difference in recovery was seen between samples (with or without backup sections) stored one or seven days at room temperature. In a separate experiment to check for migration, no significant difference in recovery was seen in samples stored for seven days, with and without backup sections, and no analyte was detectable in any of the backup sections.

Results of breakthrough (effluent concentration = 5% of test concentration) experiments were:

Charcoal, mg	Breakthrough Volume, L	Breakthrough Capacity, mg	Test Concentration, mg/m^3	Rate L/min	Humidity, % RH	Ref.
100	2	25	12502	0.05	0	[3]
400	10.5	112	10660	0.187	0	[1]
400	6.2	63	10170	0.187	90	[1]

Desorption efficiency for seventeen 400-mg samples of SKC Lot 105 charcoal spiked with 10.5 to 32 mg fluorotrichloromethane averaged 1.04 with $\bar{S}_r$ = 0.063.

REFERENCES:

[1] Backup Data Report for Fluorotrichloromethane, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB-271-712 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] Failure Report S102, prepared under Contract No. CDC (NIOSH) 99-74-45 (NIOSH, unpublished, 1977).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

FORMALDEHYDE by GC

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2541, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 3 ppm; C 5 ppm; P 10 ppm/30 min
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.067 (air = 1); BP 19.5 °C; explosive range 7 to 73% v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v HCHO); methylene oxide

SAMPLING

SAMPLER: SOLID SORBENT TUBE (10% (2-hydroxymethyl)piperdine on XAD-2, 120 mg/60 mg

FLOW RATE: 0.01 to 0.10 L/min

VOL-MIN: 1 @ 3 ppm
-MAX: 36 L

SHIPMENT: routine

SAMPLE STABILITY: 3 weeks @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 10 per sample set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of formaldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless; split vent time 30 sec

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C for 1 min; 15 °C/min; hold @ 240 °C for 10 min

CARRIER GAS: He, 1 to 2 mL/min: makeup flow 29 mL/min

COLUMN: capillary, 30 m x 0.32-mm ID, 0.5-µm film, DB-Wax or equivalent

CALIBRATION: formalin solution spiked on sorbent

RANGE: 3 to 200 µg per sample [2,3]

ESTIMATED LOD: 1 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.0052 @ 38 to 194 µg per sample [2]

APPLICABILITY: The working range is 0.24 to 16 ppm (0.3 to 20 mg/m^3) for a 10-L air sample. The method is suitable for the simultaneous determinations of acrolein and formaldehyde.

INTERFERENCES: None have been observed. Acid mists may inactivate the sorbent leading to inefficient collection of formaldehyde. A 15 m x 0.32-mm ID DB-1301 fused silica capillary column can also be used. This column will also separate the acetaldehyde and acrolein oxazolidines. A nitrogen-specific detector (NPD) can be used for improved sensitivity.

OTHER METHODS: OSHA Method 52 is similar but uses slightly larger sampling tubes [2]. This method has improved sample stability and ease of personal sampling compared to NIOSH Methods 2502 (which has been withdrawn), 3500 and 3501. However, Method 3500 (chromotropic acid) is the most sensitive.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Formalin solution, 37%*.
4. Formaldehyde* stock solution, 1 mg/mL (see Appendix A).
5. Sulfuric acid, 0.02 N.
6. Sodium hydroxide, 0.01 N.
7. Sodium sulfite (Na_2SO_3), 1.13 M. Prepare fresh immediately before use.
8. Water, deionized, distilled
9. Hydrogen, prepurified.
10. Air, filtered.
11. Helium, purified
12. Magnesium sulfate.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, with flame-sealed ends and plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX B) (front = 120 mg; back = 60 mg) retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 kPa (5.7 mm Hg). Tubes are commercially available (Supelco ORBO-23; SKC 226-118; or equivalent).
2. Personal sampling pump, 0.01 to 0.10 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2541-1).
4. Ultrasonic water bath.
5. Vials, glass, 2-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Syringes, 10-mL (readable to 0.1 mL), 25-, and 50-mL.
9. File.
10. Beakers, 50-mL.
11. pH meter.
12. Magnetic stirrer.
13. Burets, 50-mL.
14. Flasks, round-bottomed, 100-mL.
15. Soxhlet extraction apparatus.
16. Vacuum oven.
17. Distillation apparatus.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen [4,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.10 L/min for a total sample size of 1 to 36 L.
   NOTE: Formaldehyde reacts with 2-(hydroxymethyl)piperidine on the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Sampling above 0.10 L/min may cause appreciable breakthrough owing to incomplete reaction, possibly invalidating the sample. Further discussion of this reaction is included in Ref. [6].
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file in front of the first sorbent section.

6. Break sampler at score line. Remove and place front glass wool plug and front sorbent section in a vial.
7. Transfer back section with remaining glass wool plugs to a second vial.
8. Add 1.0 mL toluene to each vial. Crimp cap tightly onto each vial.
   NOTE: An appropriate internal standard, such as 1 μL/mL dimethylformamide, may be added at this point [3].
9. Agitate vials in an ultrasonic water bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards, in duplicate, covering the range of interest.
    a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from ten unused samplers (media blanks).
    b. Inject aliquots of formaldehyde stock solution into the vials at six different levels and allow to sit overnight at room temperature. Use serial dilutions of the calibration stock solutions to spike the absorbent in the range of interest.
    c. Desorb (steps 7 through 9) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (peak area or peak height) vs. μg of formaldehyde.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2541-1. Inject 1-μL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene, reanalyze, and apply the appropriate correction factor in calculations.
13. Measure peak area or peak height. For formaldehyde derivative t_r = 6.4 min and for 2-(hydroxymethyl)piperidine t_r = 9.4 min under these conditions.
    NOTE: If necessary, verify the identity of the formaldehyde oxazolidine by comparison of retention time with an authentic sample (see APPENDIX C).

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of oxazolidine derivative found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph.
    NOTE: if $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C (mg/m^3), of formaldehyde in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b)}{V}, \ mg/m^3.$$

NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary. Report field blanks as samples.

EVALUATION OF METHOD:

This method is similar to OSHA Method 52 [2]; however, the OSHA samplers contained 20% more coated sorbent than the samplers used in this method. In a study by OSHA, 5% breakthrough occurred

after 396 min at a flow rate of 0.1 L/min and a test atmosphere concentration of 5.3 mg/m^3. The relative humidity in the study was 49% at 24 °C. A storage study was done by NIOSH/MRSB [1] by spiking samplers at two concentrations, 10.0 and 61.0 μg/sample [1]. Three spikes at each concentration were stored at different temperatures for seven days. The storage conditions were as follows:

Sample set no.	Storage temp.	Storage time
1	20 °C	7 days
2 (a)	20 ° and 40 ° C	1 day
(b)	20 ° C	6 days
3	4 ° C (refrigeration)	7 days

The recovery of formaldehyde was essentially 100% for all of the storage temperatures.

REFERENCES:

[1] Williams, K. J. Methods Development Efforts, NIOSH/MRSB, (NIOSH, Unpublished, 1989).
[2] "OSHA Analytical Methods Manual, method #52", U. S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory, Salt Lake City, UT, March, 1985.
[3] User Check, DataChem Inc., NIOSH Seq. #6701-J (unpublished, June 1, 1989).
[4] NIOSH testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
[5] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U. S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[6] Kennedy, E.R., Ashley, K. Appl. Spectrosc., 46, 266-272 (1992).

METHOD WRITTEN BY:

Eugene R. Kennedy, Ph.D., and Karen J. Williams, NIOSH/DPSE.

APPENDIX A: PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0\ (N_a \cdot V_a - N_b \cdot V_b)}{V_s}.$$

where 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL)

APPENDIX B: SORBENT PREPARATION (optional if commercially-prepared tubes are used)

Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight. Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 kPa (1 mm Hg) at ambient temperature for ca. 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 12 and 13). No blank peak is expected for any aldehydes other than formaldehyde and possibly acetaldehyde.

APPENDIX C: SYNTHESIS OF FORMALDEHYDE OXAZOLIDINE

Place a solution of purified 2-(hydroxymethyl)piperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2-(hydroxymethyl) piperidine from the container used for weighing. Add magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 1 mL 37% aqueous formaldehyde in 10 mL toluene to the 2-(hydroxymethyl)piperidine solution dropwise with stirring over 1 h. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation.

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 3500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 3 ppm; C 5 ppm; P 10 ppm/30 min
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen;
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; BP −19.5 °C; vapor density 1.067 (air = 1.00); explosive range 7 to 73 % v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 60 % w/v HCHO); methylene oxide

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + IMPINGERS (1-μm PTFE membrane and 2 impingers, each with 20 mL 1% sodium bisulfite solution)	**TECHNIQUE:**	VISIBLE ABSORPTION SPECTROMETRY
		ANALYTE:	formaldehyde
FLOW RATE:	0.2 to 1 L/min	**SAMPLE WORKUP:**	note liquid volume; remove 4-mL aliquot
VOL-MIN:	1 L @ 3 ppm	**COLOR DEVELOPMENT:**	chromotropic acid + sulfuric acid; absorbance @ 580 nm
-MAX:	100 L		
SHIPMENT:	transfer samples to low-density polyethylene bottles before shipping	**CALIBRATION:**	standard solutions of formaldehyde in distilled water
SAMPLE STABILITY:	30 day @ 25 °C [1]	**RANGE:**	2 to 40 μg per sample [1,2]
BLANKS:	2 to 10 field blanks per set	**ESTIMATED LOD:**	0.5 μg per sample [2,3]
		PRECISION ($\bar{S}_r$):	0.03 @ 1 to 20 μg per sample [3]

ACCURACY

RANGE STUDIED:	1.25 to 7.5 mg/m^3 [2] (80-L samples)
BIAS:	none identified
OVERALL PRECISION ($\hat{S}_{rT}$):	0.09 [2]
ACCURACY:	± 18%

APPLICABILITY: The working range is 0.02 to 0.4 ppm (0.025 to 4.6 mg/m^3) for an 80-L air sample. This is the most sensitive formaldehyde method in the NIOSH Manual of Analytical Methods and is able to measure ceiling levels as low as 0.1 ppm (15-L sample). It is best suited for the determination of formaldehyde in area samples.

INTERFERENCES: Oxidizable organic materials may give a positive interference [2]. Phenol to formaldehyde ratios as low as 0.3 produce a - 15% bias [4]. A method for the removal of the phenol interference has been reported by Hakes et. al. [5]. Ethanol and higher M.W. alcohols, olefins, aromatic hydrocarbons [6] and cyclohexanone also produce small negative interferences [7]. Little interference is seen from other aldehydes [7].

OTHER METHODS: This method was originally adapted from the Intersociety Committee [8] and designated P&CAM 125 [4]. For personal samples or where interferences to this method are present, use Method 2541. Ref [9] is a recent review of formaldehyde methods.

REAGENTS:

1. Chromotropic acid, 1%. Dilute 0.10 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 mL with distilled water. Filter. Store in brown bottle. Prepare fresh weekly.
2. Sulfuric acid (H_2SO_4), 96%.*
3. Formaldehyde stock solution, 1 mg/mL (See APPENDIX).
4. Formalin solution, 37%.*
5. Distilled, deionized water.
6. Sulfuric acid, 0.02 N, aqueous.
7. Sodium hydroxide, 0.01 N, aqueous.
8. Sodium sulfite, 1.13 M, aqueous. Prepare fresh immediately before use.
9. Sodium bisulfite ($NaHSO_3$), 1%. Dissolve 1 g in distilled water. Dilute to 100 mL. Prepare fresh weekly.
10. Magnesium sulfate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm polytetrafluoroethylene (PTFE) membrane filter, 1- to 3-μm pore size supported by stainless steel screen or O-ring followed by two midget impingers; inert, flexible tubing for cassette-to-impinger connection.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Bottles, screw-cap low-density polyethylene (Nalgene CPE or equivalent), 50-mL.
   NOTE: Do not use bottles with "polycone" liners (see step 4)
4. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm.
5. Volumetric pipettes, 0.1-, 0.5-, 1-, 4-, 5-, 6- and 10-mL; 1-, 2- and 5-m, graduated in 0.1-mL units, with pipet bulb.
6. Volumetric flasks, 10- and 100-mL, and 1-L.
7. Burets, 50-mL.
8. pH meter.
9. Flasks, glass-stoppered, 25-mL.
10. Graduated cylinder, 25-mL.
11. Waterbath at 95 °C.
12. Magnetic stirrer.
13. Beaker, 50-mL.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles. Formaldehyde is viewed as a potential carcinogen [9,10] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the two impingers for each sample with 20 mL, 1% sodium bisulfite solution. Make cassette-to-impinger and impinger-to-sampling pump connections with flexible, inert tubing. Insert a second filter/cassette assembly in line between the sampler and sampling pump to trap any liquid which might splash over from the impingers during sampling.
   NOTE: The PTFE filter is necessary when sampling is to be conducted in a dusty environment, which could contribute either a positive or negative interferences to the method [1]. The use of dual impingers in series is recommended to ensure efficient collection of formaldehyde.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 1 to 100 L.
4. Transfer the contents of the impingers to separate low-density polyethylene bottles for shipping.
   Note: Sample contamination may occur if glass scintillation vials with "polycone" plastic lined caps are used [11].

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Record volume of solution from front impinger, V_f (mL) and backup impinger, V_b (mL).

6. Pipette 4-mL aliquots from each sample solution into 25-mL glass-stoppered flasks.
   NOTE: Adjust aliquot size to contain between 2 and 20 μg formaldehyde for optimum absorbance. The calibration graph between becomes non-linear above an absorbance of ca. 1.0. A.U.
7. Add 0.1 mL 1% chromotropic acid to the flask and mix.
   NOTE: This amount of chromotropic acid can react with ca. 40 μg of formaldehyde. Due to this fact, the range of the calibration curve should not exceed 36 μg (90% of theoretical).
8. Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution to mix.
   CAUTION: Mixing of the sample solution with concentrated sulfuric acid is highly exothermic.
9. Heat the solution to 95 °C for 15 min. Allow the solution to cool at room temperature for 2 to 3 hours.
   NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure buildup within the flask.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    a. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL 1% sodium bisulfite solution.
    b. Pipet, e.g., 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 mL calibration stock solution into 25-mL glass-stoppered flasks.
    c. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL. Also prepare a reagent blank.
    d. Analyze together with samples and blanks (steps 12 through 15).
    e. Prepare calibration graph (absorbance vs. μg formaldehyde/mL).

MEASUREMENT:

11. Set spectrophotometer according to manufacturer's recommendations and to conditions given on p. 3500-1. Fill 1-cm cuvette with sample.
12. Read sample absorbance at 580 nm.
    NOTE: If absorbance is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 4 mL with 1% sodium bisulfite solution, and analyze. (Steps 11 and 12). For optimum results, all samples containing over 20 μg formaldehyde should be diluted and reanalyzed.

CALCULATIONS:

13. Calculate the mass, μg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and average reagent blank (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot from step 6) and the total sample volume noted in step 5.
    NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass found in the front impinger. Collection efficiency is ca. 95% for each impinger [15], but may be reduced due to chipped or mismatched impinger parts, or by carryover from the front impinger.
14. Calculate the concentration, C, of formaldehyde in the air volume sampled, V (L):

$$C = \frac{M_f + M_b - 2M_B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard samples containing between 1 and 20 μg formaldehyde. The results agreed within ± 5% [8]. This method was independently compared with the 2,4,-dinitrophenylhydrazine-coated silica gel method of Beasley et al. [12] over the range of 0.8 to 2.2 ppm formaldehyde and was found to give approximately 25% lower concentrations.

In another study comparing this method and the method of Beasley, et al., all three methods were found to be statistically equivalent for loadings from 8.2 to 22.4 μg per sample [13]. The method of Septon and Ku [14] was compared with this method. The slope of the correlation line was 1.09. The concentration range of the comparison was not given.

In a study comparing the pararosaniline method [4] and NIOSH P&CAM 125 over the range of 0.021 to 0.5 ppm, the NIOSH method gave better collection efficiency and accuracy [15]. Precision for both methods was equivalent.

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METHOD WRITTEN BY:

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APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 6.6 mg/mL)

Dilute 17.8 mL 37% formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde solution. The pH should now be about 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sulfuric hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0\ (\ N_a \cdot V_a - N_b \cdot V_b\ )}{V_s}.$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL).

FORMALDEHYDE ON DUST (TEXTILE OR WOOD) 5700

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: 36172

METHOD: 5700, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 3 ppm; C 5 ppm; P 10 ppm/30 min
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; BP −19.5 °C; vapor density 1.067 (air = 1); explosive range 7 to 73 % in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v formaldehyde), methylene oxide

SAMPLING

SAMPLER: Institute of Occupational Medicine inhalable dust sampler or equivalent containing a 25-mm PVC filter, 5 μm pore size

FLOW RATE: 2.0 L/min

VOL-MIN: 240 L @ 0.002 mg/m^3
-MAX: 1050 L

SHIPMENT: Place cassette with filter in 30-mL screw-cap low density polyethylene (LDPE) bottle; keep upright. Ship cold.

SAMPLE STABILITY: 21 days (matrix dependent) (cold storage advised)

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.007 to 0.16 mg/m^3 [1] (1050-L sample)

BIAS: − 4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.093 [1]

ACCURACY: ± 22%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone derivative of formaldehyde

EXTRACTION: 10 mL distilled water @ 37 °C, 4 h; 1 mL to 3 mL 2,4-dinitrophenylhydrazine/acetonitrile (1.3 mg/mL DNP/ACN)

INJECTION VOLUME: 15 μL

MOBILE PHASE: 34% acetonitrile/66% methanol/water (1:1, v/v), 1.0 mL/min

COLUMN: Radial Compression Module C_{18} column, 5-μm particle size, 10 cm x 8-mm ID (with a C_{18} guard column) or equivalent

DETECTOR: UV @ 365 nm

CALIBRATION: Standard solutions of formaldehyde in 1.3 mg/mL DNPH/ACN

RANGE: 0.40 to 4000 μg per sample [1]
ESTIMATED LOD: 0.08 μg per sample [1]
PRECISION ($\hat{S}_r$): 0.078 @ 7 to 174 μg per sample [1]

APPLICABILITY: The working range is 0.0004 to 3.8 mg/m^3 for a 1050-L air sample. This method has been used for the determination of formaldehyde in both textile dusts and wood dusts.[1] Caution should be exercised in the way that data collected with this method are interpreted. These results should be reported separately from vapor-phase formaldehyde exposure data until sufficient data has been collected to allow appropriate epidemiological interpretation of formaldehyde-containing particulate exposures.

INTERFERENCES: None identified.

OTHER METHODS: In the absence of phenol or other substances known to interfere with the chromotropic acid analysis of formaldehyde, the analysis procedure described in NIOSH method #3500 [2] can also be used with this extraction technique (See Appendix). The analysis procedure used in this method has also been used for the determination of formaldehyde in automobile exhaust [3]. An alternate analysis [4] may be used in conjunction with this method to determine the amount of "released" formaldehyde from the collected particulate material. NMAM 5700 determines both "released" formaldehyde and formaldehyde equivalents (e.g., small oligomeric pieces of formaldehyde-containing resin) present in the hydrolysis solutions. The use of these two analytical approaches may differentiate between the two forms of formaldehyde present in the sample by the difference in results.

REAGENTS:

1. 2,4-dinitrophenylhydrazine (2,4-DNP) (1.3 g.) in 1 L. acetonitrile; 1.3 mg/mL solution.
2. Formaldehyde stock solution, 1 mg/mL (see Appendix).
3. Methanol, distilled in glass.
4. Acetonitrile, distilled in glass.
5. Water, deionized and distilled.
6. Perchloric acid solution, 1 N.*

* See Special Precautions

EQUIPMENT:

1. Sampler: 25-mm PVC filter (5.0-μm pore size) in a 25-mm Institute of Occupational Medicine inhalable (dust) sampler (Air Quality Research, Berkeley, CA, or equivalent). The sampler should meet the American Conference of Governmental Industrial Hygienists definition for collection of the inhalable fraction of particulate mass. [5]
2. Personal sampling pump, 2.0 L/min, with flexible polyethylene or PTFE tubing.
3. Bottles, screw-cap, low-density polyethylene (Nalgene LDPE or equivalent), 30-mL.
   Note: Do NOT use bottles with 'polycone' liners (source of high formaldehyde blank).
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5700-1).
5. Tweezers.
6. Syringes, 10-, 25-, 50-, and 100-μL.
7. Volumetric flasks, 10-, 100-mL and 1 L.
8. Pipets, 0.1-, 0.5-, 1.0-, and 3-mL glass, delivery, with pipet bulb.
9. Graduated cylinders, glass, 25-mL.
10. Cotton gloves.
11. Equipment for standardizing formaldehyde stock solution, Burets, 50-mL.
12. pH meter.
13. Magnetic stirrer.
14. Beaker, 50-mL.
15. Vials, 5-mL.
16. Filters, 0.45 μm.
17. Scintillation vials, 20-mL.

SPECIAL PRECAUTIONS: Perchloric acid is a strong oxidizing agent, toxic by ingestion and inhalation and is a strong irritant. Use only in a hood. Formaldehyde is a suspect carcinogen [1,6] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. If gravimetric measurements are needed, handle the I. O. M. cassettes only while wearing cotton gloves. Follow NMAM 0500 [7] for pre- and post-collection weighing procedure. Place the cassette containing a 25-mm PVC 5-μm pore filter in the filter holder.
3. Attach outlet of filter holder to the sampling pump.
4. Sample 240 to 1050 L of air at 2.0 L/min flow rate.
5. Transfer cassette from filter holder carefully to a 30-mL LDPE screw-cap bottle while wearing cotton gloves and seal the bottle. Ship in a suitable container in order to prevent damage during transit and keep bottles upright.
6. Collect a bulk sample (ca. 1 g) of the dust/fiber in a glass vial and ship separately.

SAMPLE PREPARATION:

7. If gravimetric weighing is done, post-weigh the entire cassette (see NMAM 0500 [7]) then return the cassette to the screw-cap bottle.

8. Transfer 8-mL distilled water to the LDPE screw-cap bottle containing the cassette. Use tweezers (two) to disassemble cassette which is immersed in water, remove all cassette pieces (shake off excess water) leaving the filter and dust in the bottle. Transfer the resulting solution to a 20-mL scintillation vial and rinse the screw-cap bottle with an additional 2 mL of distilled water. Replace the cap on the vial and then place the vial in a 37 °C water bath for four hours. Remove from the bath and allow to cool 1/2 hour. Filter through a 0.45 μm pore size filter into another bottle.

CALIBRATION AND QUALITY CONTROL:

9. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL with distilled water.
10. Pipet aliquots of calibration stock solution (e.g., 40, 200, 750, 2000, 5000, and 10000 μL) into 10-mL volumetric flasks to prepare working standards. Higher level standards, if needed, can be prepared by using different dilutions of the formaldehyde stock solution.
11. Add distilled water to bring the volume of each working standard to 10 mL.
12. Analyze working standards together with samples and blanks (steps 14 through 17).
13. Prepare calibration graph of area vs. amount (μg) of formaldehyde per sample (10-mL total volume).

MEASUREMENT:

14. Transfer a 1-mL aliquot of the solution from step 8. to a 5-mL vial containing 3-mL of an 2,4-dinitrophenylhydrazine/acetonitrile solution (1.3 mg/mL). Add one drop 1 N perchloric acid (to catalyze the reaction to form the corresponding hydrazone), cap the vial and shake it gently for several seconds.
15. Set liquid chromatograph to conditions given on page 1.
16. Inject 15-μL sample aliquot.
17. Measure peak area.

    NOTE 1: If peak area is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 1 mL with distilled water and analyze (steps 14 through 17) and apply appropriate dilution factor in the calculations.

    NOTE 2: For optimum results, all samples containing over 400 μg/mL should be diluted and reanalyzed, since the maximum amount of formaldehyde that can react with 3.9 mg of 2,4-dinitrophenylhydrazine is 590 μg.

CALCULATIONS:

18. Determine mass, μg, of formaldehyde (W) found in the sample and the average media blank (B) from the calibration graph. Use the appropriate aliquot factor (e. g., 1 mL aliquot/original volume from step 14) and the total sample volume (10-mL) unless corrected for in calibration plot (step 13).
    NOTE: Include dilution factor for any sample which exceeded the highest calibration standard.
19. Calculate concentration, C, of formaldehyde from dust in the air volume, V (L).

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range of 7 to 174 μg/sample at 24 °C and pressure of 761 mm Hg [1] using the chromotropic analysis procedure. Overall measurement precision, $\hat{S}_{rT}$, was 0.093 including a 5% pump error factor. Similar precision was observed with the 2,4-dinitrophenylhydrazine analysis procedure. Sample stability during storage was evaluated at 7 μg formaldehyde/2 mg of wood dust treated with a urea/formaldehyde resin. Samples showed 101% recovery after 21 days of storage at ambient conditions compared to one-day old samples. However, studies with a different matrix (urea-formaldehyde treated wood fibers) indicated that samples may be unstable when stored at room temperature.

Comparison of results from 2,4-DNP analyses with those from acetylacetone analyses [4] indicated that there was a significant difference between the two methods. The acetylacetone analyses used much milder conditions and appears to be reacting only with released formaldehyde, whereas the 2,4-DNP analysis required the addition of perchloric acid and may be breaking up oligomeric pieces of the partially hydrolyzed resin in the sample. By analyzing samples with the two methods, a further characterization of the sample matrix and potential exposure may be obtained. In matrices where materials that can form complexes with formaldehyde are present, such as sulfites, the acetylacetone analysis may be biased low, since it is unable to break up these complexes [8].

Two comparisons of the I.O.M. samplers with closed-face cassette samplers were conducted in field situations [1]. The I.O.M. samplers, on average, collected more dust/fibers measured gravimetrically than the closed-face cassette samplers in both studies. Formaldehyde levels in the dust/fibers on a μg/mg basis measured with the extraction procedure used in this method were comparable for both the I.O.M. and closed-face cassette samplers. On the average, the I.O.M. sampler tended to collect more dust that the closed-face cassette sampler.

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METHOD WRITTEN BY:

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APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg formaldehyde; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0\ (N_s\ V_s - N_b\ V_b)}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL)

ALTERNATE ANALYSIS PROCEDURE FOR THE DETERMINATION OF FORMALDEHYDE LIBERATED FROM DUST/FIBER SAMPLES

Note: This analysis procedure should only be used where interferences to the chromotropic acid analysis are not present. These interferences include phenol, oxidizable organic material, other aldehydes and alcohols.

For formaldehyde determination by the chromotropic acid method, a 4-mL aliquot of the solution resulting from the desorption and incubation of the filter (step 8.) was analyzed by the procedure described in NIOSH Method 3500.[2] The amount of chromotropic acid added to the sample could react with a maximum of 42 μg of formaldehyde per sample aliquot. (Whenever the amount of formaldehyde approached 30 μg per aliquot, the sample was diluted and reanalyzed.) The absorbance of samples at 580 nm was then compared to a calibration curve constructed from results obtained from analysis of calibration standards containing known amounts of formaldehyde. The amount of formaldehyde present in each sample was determined based on the calibration curve.

Calibration standards were prepared by dilution of a standard solution of formalin in distilled water (1 mg/mL) and analyzed in the same manner as the samples. The calibration range usually covered 1 to 25 μg of formaldehyde/4-mL aliquot. A limit of detection of 0.44 μg formaldehyde/filter sampler was determined in laboratory evaluation of this analysis procedure.

FORMIC ACID 2011

HCOOH MW: 46.03 CAS: 64-18-6 RTECS: LQ4900000

METHOD: 2011, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA: 5 ppm
NIOSH: 5 ppm
ACGIH: 5 ppm
(1 ppm = 1.882 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 107 °C; d 1.22 g/mL (90% solution) @ 20 °C; VP 4.7 kPa (33 mm Hg); vapor density (air = 1) 1.6; colorless; pungent odor

SYNONYMS: hydrogencarboxylic acid; methanoic acid

SAMPLING

SAMPLER: FILTER + SOLID SORBENT TUBE (PTFE membrane, 5-μm + washed, silica gel, 400 mg/200 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: formate ion

DESORPTION: 10 mL deionized water; stand 5 minutes

INJECTION VOLUME: 50 μL

ELUENT: 2.5 mM $Na_2B_4O_7 \cdot 10\ H_2O$, 2.0 mL/min

COLUMN: Dionex HPIC-AG4 guard, HPIC-AS4 anion separator, anion micromembrane suppressor

DETECTOR: conductivity, 10 μS full scale

CALIBRATION: standard solutions of formate spiked onto sample media

RANGE: 6 to 100 μg formate per sample [1]

ESTIMATED LOD: 2 μg formate per sample [2,3]

PRECISION($\bar{S}_r$): 0.026 @ 106 to 426 μg per sample [2]
0.097 @ 10 to 80 μg per sample [3]

APPLICABILITY: The working range is 0.13 to 12 ppm (0.25 to 22 mg/m^3) for a 24-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is a modification of Method 7903 (Acids, inorganic) and revises Method S173 [1,3].

REAGENTS:

1. Acetone, ACS reagent grade.
2. Water, deionized.
3. Eluent: 2.5 mM $Na_2B_4O_7 \cdot 10\ H_2O$. Dissolve 3.82 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 4 liters high purity water. Filter if necessary to remove any particulate matter.
4. Suppressor regenerant, 25 mN H_2SO_4.*
5. Calibration stock solution, 1 mg formate anion per mL. Dissolve 1.511 g sodium formate (dried @ 110 °C for 4 h, stored in desiccator) in 100 mL deionized water.
6. Formic acid, 88% or 95% (Optional; see Appendix A).
7. Dioxane (Optional; see Appendix A).
8. 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$. Dissolve 145 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 4 liters deionized water. Filter if necessary to remove particles > 1 μm.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 7-mm OD, 4-mm ID, flamed-sealed ends with plastic 20/40 caps, containing 20/40 mesh washed silica gel (front = 400 mg, back = 200 mg) separated by a 4-mm urethane foam plug. A thick glass fiber filter plug precedes the front section and a 5-mm urethane foam plug follows the back section. Tubes are commercially available (ORBO-53, Supelco, or equivalent) or prepare according to APPENDIX B. Prefilter, PTFE, 25-mm, with porous plastic support pad. Pressure drop across the sampler at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. Ion chromatograph, with a conductivity detector, chart recorder, integrator, and column.
4. Vials, polyethylene, 20-mL, with plastic caps.
5. Micropipettes, with disposable plastic tips.
6. Volumetric flasks, 100-mL.
7. Pipet, 10-mL, graduated in 0.1-mL intervals.
8. Pipet, volumetric, 20-mL.
9. Syringes, 10-mL, plastic, with luer tip.
10. Filters, luer tip, with membrane filter, 13-mm, 0.45-μm pore size.

SPECIAL PRECAUTIONS: Users of this method should be acquainted with the degree of hazard of each chemical and take the proper precautions. Handle all hazardous chemicals in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach a sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for total volume of 1 to 24 L.
4. Cap the tubes with plastic (not rubber) caps, plug filter cassettes, and pack securely for shipment.
   NOTE: Prefilters may be analyzed for particulate formates, or may be discarded.

SAMPLE PREPARATION:

5. Place the front with glass fiber filter plug and back sorbent sections of the sampler tube (and prefilter, optional) in separate 20-mL plastic vials. A glass rod may be used to push the contents out of the tube. Discard the foam plugs.
6. Add 10 mL deionized water to each plastic vial. Loosely cap.
7. Heat in boiling water for 10 min, cool, and analyze the same day the formic acid is desorbed.
8. Transfer a portion of sample to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the range of 2 to 100 μg formate per sample.
   a. Spike appropriate amounts of calibration stock solution or a dilution thereof, onto sorbent tubes.
   b. Desorb in the same manner as field samples.
   c. Analyze working standards together with samples and blanks (steps 12 through 14).
   d. Prepare a calibration graph of peak height vs. amount (μg) of formic acid per 10 mL of sample.
      NOTE: Apply the conversion 1 μg formate = 1.022 μg formic acid.
10. (Optional) Determine recovery for each lot of silica gel used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus three media blanks.
    a. Add a known amount of DE stock solution, or a dilution thereof, onto sorbent tube (see Appendix A).
    b. Analyze in the same manner as field samples.
    c. Prepare graph of recovery vs. μg formic acid.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 2011-1.
13. Inject 50-μL sample aliquot. For manual operation inject 2 to 3 mL of sample from the syringe (through inline filter) to ensure complete rinse of sample loop.
    NOTE: Flushing the column between injections with 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$ for one minute removes the later eluting ions quickly.
14. Measure peak height.
    NOTE: If peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

15. Read mass, μg of formic acid found on the front (W_f) and back (W_b) sections and the average media blank front (B_f) and (B_b) sections from the calibration graph.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration C of formic acid (mg/m^3) in the actual air volume, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 4.4 to 21.6 mg/m^3 at 23 °C and pressure of 759 mm Hg using 24-L samples [1]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.073, with average recovery of 96% in the range 4 to 22 mg/m^3 per sample [1]. Sample stability during storage was evaluated at 11 mg/m^3 per sample. Samples showed 91.5% recovery after one week of storage at ambient conditions compared to one-day old samples [1]. Breakthrough did not occur when a 25 mg/m^3 test atmosphere (85% relative humidity) was sampled at 0.18 liter/minute for 300 minutes. This modification of NMAM 7903, which uses 2.5 mM $Na_2B_4O_7 \cdot 10\ H_2O$ eluent, resulted in a LOD of 2 μg/sample and a range 7 to 100 μg per sample. Samples were collected on silica gel, desorbed in 10 mL eluent, heated 10 minutes in boiling water, then analyzed.[3]

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., Vol. 5, S173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[2] Backup Data Report for Formic Acid, prepared under NIOSH Contract No. 210-76-0123.
[3] User Check of OSHA ID112/NIOSH modification of NIOSH Method #7903, NIOSH Sequences #7077-J, 7078-K, (unpublished October, 1990).

METHOD REVISED BY:

George Y. Williamson, MRSB, DPSE.

APPENDIX A: DESORPTION EFFICIENCY STOCK SOLUTION, 51.5 mg FORMIC ACID/mL

Pipet 6 mL of 88% formic acid into a 125-mL volumetric flask. Make to volume with dioxane. For standardization, appropriate aliquots are withdrawn, diluted with deionized water, and analyzed as in steps 9 through 15.

NOTE: The solution must be prepared fresh daily. Loss of formic acid was observed after 24 h. Pipetting below the liquid level of the standard will minimize loss of formic acid from evaporation.

APPENDIX B: SAMPLING TUBE PREPARATION

Silica gel cleaning procedure: Add 500 to 600 mL deionized water, slowly and with stirring, to ca. 200 mL volume of silica gel in 1-L beaker. When exothermal reaction has subsided, heat in boiling waterbath for ca. 30 min with occasional stirring. Decant and rinse four to five times with deionized water. Repeat cleaning procedure and dry overnight in 100 °C oven until free flowing. If blank of silica gel shows impurities, repeat cleaning procedure.

Silica gel tubes: Pack glass tubes, 7-mm OD, 4.8-mm ID, 11 cm long, with 400 mg of 20/40 mesh washed silica gel in front section and 200 mg backup section. Use urethane foam plugs between sorbent sections and at back end. Hold front section in place with 6-mm diameter, 1-mm thick glass fiber filter plug (Gelman 66088).

FURFURAL

$C_5H_4O_2$ MW: 96.09 CAS: 98-01-1 RTECS: LT7000000

METHOD: 2529, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: no recommended standard
ACGIH: 2 ppm (skin)
(1 ppm = 3.93 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.160 g/mL @ 20 °C; BP 162 °C; MP - 36 °C; VP 0.26 kPa (2 mm Hg; 2600 ppm) @ 20 °C; explosive range 2.1 to 19.3% v/v in air

SYNONYMS: 2-furaldehyde; 2-furancarboxaldehyde

SAMPLING

SAMPLER: SOLID SORBENT TUBE (10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set
MEDIA BLANKS: 18 per set (for DE)

ACCURACY

RANGE STUDIED: 2.6 to 40 mg/m^3 [1] (15-L samples)

BIAS: - 7.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 21.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of furfural

DESORPTION: 2 mL toluene; 30 min ultrasonic

INJECTION VOLUME: 1 µL; splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 20 °C/min; hold 2 min @ 290 °C

CARRIER GAS: He, 20 cm/sec

COLUMN: 10 m x 0.25-mm, 1 µm DB5

CALIBRATION: furfural standards spiked on sampler

RANGE: 16 to 640 µg per sample [1]

ESTIMATED LOD: 5 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.057 [1]

APPLICABILITY: The working range is 0.3 to 5.5 ppm (1.3 to 22 mg/m^3) for a 12-L air sample. The method is suitable for the simultaneous determination of furfural and glutaraldehyde [1].

INTERFERENCES: None have been observed.

OTHER METHODS: Method S17 [2] is an alternate, less sensitive method for furfural which uses bubbler collection and derivatization with Girard T reagent.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas) or equivalent. Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Furfural,* freshly distilled under N_2 to remove impurities. Store at 0 °C.
5. Calibration stock solution, 100 μg/μL. Add 1 g furfural to toluene and dilute to 10 mL. Prepare in duplicate.
6. Furfural oxazolidine (see APPENDIX) stock solution, 2.5 mg/mL. Add 25 mg to toluene and dilute to 10 mL.
7. Water, deionized, then distilled.
8. Hydrogen, prepurified.
9. Air, filtered.
10. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm x 4-mm ID, flame-sealed, with plastic caps, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl)piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 756 kPa. Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2529-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-μL (readable to 0.1 μL), 25-, and 50-μL.
10. File.
11. Beakers, 50-mL.
12. Magnetic stirrer.
13. Flasks, round-bottomed, 100-mL.
14. Soxhlet extraction apparatus.
15. Vacuum oven.
16. Distillation apparatus.

SPECIAL PRECAUTIONS: Furfural can irritate the mucous membranes and act on the central nervous system [3,4]. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 12 L.

   NOTE: Furfural reacts with 2-(hydroxymethyl)piperidine to form a derivative during sampling. Sampling rate is limited by the speed of this reaction; rates above 0.05 L/min may cause breakthrough owing to incomplete reaction.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place rear glass wool plug and rear sorbent section in a vial.

6. Transfer front section with remaining glass wool plugs to a second vial.
7. Add 2.0 mL toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Prepare oxazolidine standard solutions.
   a. Add known amounts of furfural oxazolidine stock solution (equivalent to the range of the samples) to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with at least six working standards covering the range of the samples.
   a. Weigh 120-mg portions of unused sorbent into vials.
   b. Add aliquots of calibration stock solution or dilutions thereof. Cap vials and allow them to stand overnight at room temperature.
   c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
   d. Prepare calibration graph (peak area vs. μg furfural).
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.
11. Analyze three quality control blind spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2529-1. Inject 1-μL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene and apply the appropriate dilution factor in calculations.
13. Measure total peak area of the two analyte peaks.
    NOTE: On the DB-5 column, the oxazolidine derivative of furfural gives two peaks, since the diastereoisomers are resolved. t_r for the furfural derivative = 5.0 and 5.3 min; glutaraldehyde derivative = 9.4 and 9.7 min; and t_r for 2-(hydroxymethyl)piperidine = 2.6 min for these conditions.

CALCULATIONS:

14. Determine the mass, μg of furfural found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of furfural in the air volume sampled, V (L):

$$C = \frac{W_f + W_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Atmospheres were generated by flash vaporization of an aqueous furfural solution into a stream of air flowing at a fixed rate [1]. Relative humidity during generation was 80% ±5%. The generator and sampling manifold system have been described previously [5]. Concentration of furfural vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [6]. The method was studied over the range of 2.6 to 40 mg/m^3 using 15-L samples. Desorption efficiencies on statically-spiked samples averaged 94% in the range 16 to 640 $-\mu$g per sample. Recovery of dynamically-generated samples was 93%, owing to breakthrough of furfural at the highest level studied (40 mg/m^3). Recovery was quantitative at lower levels.

REFERENCES:

[1] E. R. Kennedy, Y. T. Gagnon, J. R. Okenfuss and A. W. Teass, "The determination in air of selected low-molecular weight aldehydes as their oxazolidines by capillary gas chromatography." Appl. Ind. Hyg., 3, 274-279 (1988).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S17, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[4] The Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
[5] Kennedy, E. R. and R. H. Hill, Jr. "Determination of Formaldehyde in Air as an Oxazolidine Derivative by Capillary Gas Chromatography," Anal. Chem., 54, 1739-1741 (1982).
[6] Lipari, F. and S. J. Swarin. "Determination of Formaldehyde and other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method", J. Chromatog., 247, 297-306, (1982).

METHOD REVISED BY:

Julie R. Okenfuss and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

SORBENT PREPARATION (optional if commercially prepared tubes are used):
Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 hr. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for furfural.

SYNTHESIS OF FURFURAL OXAZOLIDINE [1]:
Place a solution of 0.58 g (0.5 mL; 6 mmol) freshly distilled furfural in 10 mL toluene in a 50-mL round-bottomed flask. Add 2.5 g magnesium sulfate to the flask to remove water which forms during the reaction. Add a solution of 0.61 g (5.3 mmol) purified 2-hydroxymethylpiperidine in 10 mL toluene dropwise with stirring over 1 hr. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation. The product is a yellow viscous oil.

DESORPTION EFFICIENCY:
The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10. If desired, the following procedure can be used to determine DE:
a. Prepare and analyze a set of oxazolidine standard solutions (step 9.a) and a set of working standards (step 10) including media blanks.
b. Treating the working standards as unknowns, read the mass (mg) of oxazolidine found in each working standard (W), and in the average media blank (B).
c. Using the mass of furfural, mg, spiked onto the working standard (W_o) and the stoichiometric conversion factor between furfural and furfural oxazolidine (2.01), calculate the desorption efficiency:

$$DE = \frac{W - B}{W_o \cdot 2.01}.$$

d. Prepare a graph of DE vs. μg furfural recovered per sample [(W - B)/2.01].

FURFURYL ALCOHOL

$C_4H_3OCH_2OH$ MW: 98.10 CAS: 98-00-0 RTECS: LU9100000

METHOD: 2505, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin); STEL 15 ppm
NIOSH: 10 ppm (skin); STEL 15 ppm
ACGIH: 10 ppm (skin); STEL 15 ppm
(1 ppm = 4.01 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.13 g/mL @ 20 °C; BP 170 °C; VP 0.13 kPa (1 mm Hg) @ 31.8 °C; explosive range 1.8% to 16.3% (v/v) in air

SYNONYMS: 2-furyl carbinol; 2-(hydroxymethyl)furan; 2-furylmethanol

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Porapak Q, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 3L @ 10 ppm
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 118 to 478 mg/m^3 [1] (6-L samples)

BIAS: − 1.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.072 [1]

ACCURACY: ± 14.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: furfuryl alcohol

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5.0 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 225 °C
-COLUMN: 200 °C

CARRIER GAS: He or N_2, 50 mL/min

COLUMN: stainless steel, 1 m x 3-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of furfuryl alcohol in acetone

RANGE: 0.12 to 3.6 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.031 @ 0.6 to 2.4 mg per sample [1]

APPLICABILITY: The working range is 4 to 150 ppm (20 to 600 mg/m^3) for a 6-L air sample.

INTERFERENCES: None identified. The method was used in epoxy spray paint operations with no apparent interference from ethylene chloride, toluene, xylene, perchloroethylene and Freon 113 [2]. Alternative columns for this method are 5% FFAP on Chromosorb T (40/60 mesh) packed on stainless steel [2] and a WCOT OV-101 (0.25 µm film thickness) glass capillary [3].

OTHER METHODS: This revises NIOSH Method S365 [4].

REAGENTS:

1. Furfuryl alcohol* (purify as in APPENDIX).
2. Acetone, distilled in glass.
3. Benzene,* distilled in glass.
4. DE stock solution, 0.1 mg/μL. Dilute 1.0 g furfuryl alcohol to 10 mL with benzene.
   NOTE: Acetone may be substituted for benzene if desorption efficiency is adequate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, flame-sealed with plastic caps, 8.5 cm long, 6-mm OD, 4-mm ID; two sections of 50/80 mesh pre-extracted Porapak Q (front = 150 mg; back = 75 mg) separated by a 2-mm section of urethane foam and held in place with plugs of silanized glass wool. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2505-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10- to 50-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL and other convenient sizes.
7. Pipets, TD, 1.0-mL and other convenient sizes.

SPECIAL PRECAUTIONS: Furfuryl alcohol is toxic and reacts violently with acids [5]. Benzene is a suspected human carcinogen [5]. Perform all work with this solvent in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 3 to 25 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Cap each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 3.6 mg furfuryl alcohol per sample.
   a. Add known amounts of pure furfuryl alcohol to acetone or benzene in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions to prepare the lower concentrations.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg furfuryl alcohol).
9. Determine desorption efficiency (DE) at least once for each lot of Porapak Q used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of DE stock solution or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.

d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg furfuryl alcohol recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2505-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of furfuryl alcohol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of furfuryl alcohol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 118 to 478 mg/m^3 on February 18, 1977 using test atmospheres generated dynamically by the vapor pressure saturation/air dilution technique at 765 torr and 22 °C [1,4,6]. At a challenge concentration of 105 ppm (418 mg/m^3), furfuryl alcohol in humidified air (RH>80%) and a flowrate of 0.044 L/min, there was no breakthrough of the front sorbent bed after sampling for 7 hours. The mean desorption efficiency over the range 0.59 to 2.36 mg per sample was 0.96. Recovery of analyte collected (in a 6-L sample) from synthetic atmospheres over the range 118 to 478 mg/m^3 averaged 98.4%. The recovery of the collected analyte (1.2 mg per sample), stored at ambient temperatures for 1 week, was 97%.

REFERENCES:

[1] Backup Data Report for Furfuryl Alcohol, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB-271-464 from NTIS, Springfield, VA 22161.
[2] NIOSH Health Hazard Evaluation Report HHE 80-154-1027, (unpublished, 1981).
[3] Holt, J. UBTL Inc., personal communication to NIOSH (1983).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S365, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[5] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[6] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Robert Glaser, NIOSH/DPSE; S365 originally validated under NIOSH Contract 210-76-0123.

APPENDIX:

PURIFICATION OF NEAT STANDARD:
Pure furfuryl alcohol is a clear viscous liquid; however, it decomposes upon standing for extended periods. If the furfuryl alcohol as received is a dark-colored, distill it at 170 °C prior to use. Store the purified material in a dark bottle in a refrigerator at 0 °C.

GLUTARALDEHYDE 2532

$O=CH(CH_2)_3CH=O$ MW: 100.12 CAS: 111-30-8 RTECS: MA2450000

METHOD: 2532, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : no PEL
NIOSH: C 0.2 ppm
ACGIH: C 0.2 ppm
(1 ppm = 4.09 mg/m^3 @ NTP)

PROPERTIES: oil; d 0.72 g/mL @ 20 °C; BP 188 °C; MP −14 °C; VP 2.2 kPa (17 mm Hg) @ 20 °C

SYNONYMS: glutaric dialdehyde; 1,5-pentanedial; glutaral; 1,3-diformylpropane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel coated with 2,4-dinitrophenylhydrazine HCl, 300 mg/150 mg)

FLOW RATE: 0.05 to 0.5 L/min

VOL-MIN: 1 L @ 0.2 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: at least 30 days @ 25 °C

BLANKS: 2 to 10 field blanks per set; 10 to 20 media blanks per set

ACCURACY

RANGE STUDIED: none

ACCURACY: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: glutaraldehyde dinitrophenylhydrazone

EXTRACTION: 3 mL acetonitrile; shaken 2 h

INJECTION VOLUME: 25 µL

MOBILE PHASE: 65% acetonitrile/35% water

FLOWRATE: 1.5 mL/min

COLUMN: reverse phase C8, 5-µm particle size (Alltech Altima C8, 5-µm or equivalent)

DETECTOR: UV at 365 nm

CALIBRATION: standard solutions spiked onto sampler tubes

RANGE: 0.8 to 24 µg per sample

ESTIMATED LOD: 0.3 µg per sample

PRECISION ($\bar{S}_r$): 0.007 @ 12 µg per sample; 0.025 @ 1.2 µg per sample

APPLICABILITY: The working range is 0.01 to 0.3 ppm (0.04 to 1.2 mg/m^3) for a 20-L air sample.

INTERFERENCES: Other aldehydes and ketones react with 2,4-dinitrophenylhydrazine but can be resolved using proper HPLC parameters.

OTHER METHODS: OSHA Method 64 [1] uses a glass fiber filter coated with 2,4-dinitrophenylhydrazine and phosphoric acid for collection, with HPLC analysis.

REAGENTS:

1. Glutaraldehyde, 25% (w/v) solution in water (Aldrich D19,930-3 or equivalent).*
2. Water, distilled, deionized.
3. Acetonitrile, HPLC grade.
4. Sodium sulfite, 1.13 M. Prepare fresh immediately before use.
5. Sulfuric acid, 0.02 N.
6. Sodium hydroxide, 0.01 N.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass tube, 110 mm long, 6-mm OD, flame-sealed ends and plastic caps containing two sections of silica gel coated with 2,4-dinitrophenylhydrazine HCl. The front section contains 300 mg, the back 150 mg, and sections are retained and separated by small plugs of silanized glass wool. (SKC 226-119 or equivalent).
2. Personal sampling pump, 0.05 to 0.5 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC), UV detector (365 nm), column, and integrator (page 2532-1).
4. Shaker, mechanical.
5. Syringe, 10-mL, disposable.
6. Vials, glass, scintillation, 20-mL, with PTFE-lined caps.
7. Syringes, microliter, readable to 0.1-μL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.
10. Burets, 50-mL.
11. Stirrer, magnetic.
12. pH meter.
13. Beakers, 50-mL.
14. File.

SPECIAL PRECAUTIONS: Glutaraldehyde can irritate the mucous membrane and act on the central nervous system [2]. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.5 L/min for a total sample size of 1 to 30 L.
   NOTE: Glutaraldehyde reacts with the 2,4-dinitrophenylhydrazine to form a hydrazone derivative which provides sample stability and UV chromophores for analysis.
4. Immediately after sampling, cap the sample tubes, including blanks, and pack securely for shipment, include 10-20 unused tubes from the same lot to be used for standard preparation.

SAMPLE PREPARATION:

5. Score each sampler with a file in front of the front sorbent section and break the tube at the score line.
6. Remove and place front glass wool plug and front sorbent section (300 mg) in a vial.
7. Transfer back section (150 mg) with remaining glass wool plugs to a second vial.
8. Add 3.0 mL of acetonitrile to each vial. Screw cap tightly onto each vial.
9. Agitate vials in a mechanical shaker for at least 2 h.
   NOTE: The use of ultrasonic bath yields incomplete recovery.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of interest.
    a. Prepare and standardize glutaraldehyde stock solution. (See APPENDIX.) Make serial dilutions of the stock solution with water.
    b. Using a microliter syringe, add known amounts of glutaraldehyde directly onto the DNPH-coated silica gel tubes over the range of interest. Allow the tubes to stand overnight for solvent evaporation and equilibration.
    c. Prepare the standards as described in Steps 5 through 9 and analyze with samples and blanks.
    d. Prepare a calibration graph (peak area or height vs. concentration).
    NOTE: Because the working standards are prepared on media blanks, no additional blank correction or extraction efficiency correction is necessary. Check extraction efficiency occasionally in the range of interest.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

12. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 5512-1.
13. Inject 25-μL sample aliquot.
14. Measure peak area or height for each UV response. The two isomers of glutaraldehyde are separated using these chromatographic conditions. Sum the peak area or height of both isomers to obtain the total area of height.

CALCULATIONS:

15. Determine the mass, μg, of glutaraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE 1: Corrections for extraction efficiency and blanks are incorporated into the method by using spiked media as standards.
    NOTE 2: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration (C) of glutaraldehyde in the air volume sampled in liters (V):

$$C = \frac{(W_f + W_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The pressure drop at 0.2 L/min across representative tubes was 6" H_2O, at 0.5 L/min about 14" H_2O, but at 1 L/min it was about 46" H_2O. This method incorporates the use of spiked media as standards eliminating recovery bias. Mechanical agitation gave better recovery and linearity of the calibration curve ranging from 0.6 to 24 μg per sample. Recoveries from tubes agitated by sonic bath decreased as the concentration increased. Recoveries of glutaraldehyde from the DNPH-coated tubes were determined by spiking 6 tubes each at concentrations of 1.2, 2.4, and 12 μg per sample. After standing overnight to allow the solvent to evaporate, the sorbent was transferred to a vial, 3 mL of acetonitrile was added, and the sample was agitated in a mechanical shaker for at least 1 h.

At the same time, 6 more tubes were spiked at each of these concentrations and stored in the laboratory at ambient conditions for 42 days. The data are shown in Table 1.

Table 1. Recovery and Stability Study of Glutaraldehyde

Concentration (μg/sample)	Day Analyzed	Recovery (%)	S_r
1.2	1	95	.028
	42*	100	.014
2.4	1	97	.027
	42	98	.034
12	1	96	.034
	42	98	.023

* Samples stored at 25 °C for 42 days.

A 20-point, 4-concentration curve was used to determine a LOD of 0.24 μg/sample and a LOQ of 0.78 μg/sample. No air samples were generated during this evaluation. Audit samples were prepared with liquid spikes of glutaraldehyde in water added directly onto the DNPH-coated silica gel tube. These audit samples were shipped, stored, and analyzed by an independent laboratory using this method. The results were acceptable with recoveries of about 100% at 1.2 μg per tube, 94% at 2.4 μg per tube, 85% at 12 μg per tube, and <0.3 μg per tube for the blanks [3].

REFERENCES:

[1] OSHA Analytical Methods Manual, Glutaraldehyde, Method 64. OSHA Technical Center, Salt Lake City, UT. U.S. Dept. of Labor (1985).
[2] The Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).
[3] User Check, DataChem Labs, Sequence #7958-J (unpublished, 3/14/94).

METHOD WRITTEN BY:

Charles E. Neumeister, NIOSH/DPSE, and Gordon Hill, DataChem Laboratories, Salt Lake City, UT.

APPENDIX: PREPARATION AND STANDARDIZATION OF GLUTARALDEHYDE STOCK SOLUTION (ca. 10 μg/μL).

Dilute 1 mL 25% aqueous glutaraldehyde to 25 mL with distilled, deionized water. Place 10.0 mL 1.13 M sodium sulfite solution in a beaker and stir magnetically. With a pH meter, adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 1.0 mL glutaraldehyde stock solution. The pH should be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, Cs (μg/μL) of the glutaraldehyde stock solution.

$$C_s = 50.06 \cdot \frac{(N_a \cdot V_a) - (N_b \cdot V_b)}{V_s}.$$

where: 50.06 = equivalent weight of glutaraldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of sodium hydroxide
V_b = volume of sodium hydroxide (mL) used for back titration
V_s = volume of glutaraldehyde stock solution (1.0 mL).

GLYCIDOL 1608

$C_3H_6O_2$ MW : 74.08 CAS: 556-52-5 RTECS: UB4375000

METHOD: 1608, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 50 ppm
NIOSH: 25 ppm
ACGIH: 25 ppm
(1 ppm = 3.03 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.117 g/mL @ 20 °C; BP 167 °C (decomposes); MP - 45 °C; VP 0.12 kPa (0.9 mm Hg); 0.12% v/v) @ 20 °C

SYNONYMS: 2,3-epoxy-1-propanol; 2-(hydroxymethyl)oxirane; oxiranemethanol

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 5 L @ 150 mg/m^3
-MAX: 100 L

SHIPMENT: at 4 °C

SAMPLE STABILITY: at least 7 days @ 4 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 73 to 310 mg/m^3 [2] (50-L samples)

BIAS: − 2.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.080 [1]

ACCURACY: ± 13.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: glycidol

DESORPTION: 0.5-mL tetrahydrofuran; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 260 °C
-COLUMN: 155 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: 3 m x 2-mm ID stainless steel; 10% FFAP on 100/120 mesh Chromosorb W-HP

CALIBRATION: glycidol in tetrahydrofuran

RANGE: 0.8 to 22 mg per sample

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.016 [1]

APPLICABILITY: The working range is 16 to 450 mg/m^3 (5 to 150 ppm) for a 50-L air sample. During sampling, high humidity may greatly decrease the breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S70 [2] in a revised format.

REAGENTS:

1. Tetrahydrofuran, chromatographic quality.
2. Glycidol, reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("blue ice" or equivalent).
4. Gas chromatograph, flame ionization detector, integrator and column (page 1608-1).
5. Vials, 1-mL, PTFE-lined caps.
6. Syringes, 10-μL, and other convenient sizes for preparing standards, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipet, 0.5-mL.

SPECIAL PRECAUTIONS: Glycidol is irritating to the upper respiratory tract, skin, and mucous membranes and will attack some forms of plastics, rubber and coatings [3]. It is absorbed through skin [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 5 to 100 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment at 4 °C.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 0.5 mL tetrahydrofuran to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 22 mg glycidol per sample.
   a. Add known amounts of glycidol to tetrahydrofuran in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (peak area vs. mg glycidol).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of glycidol directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight in refrigerator at 4 °C.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg glycidol recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1608-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with tetrahydrofuran, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of glycidol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of glycidol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S70 was issued on February 14, 1975 [2], and validated over the range 73 to 310 mg/m^3 at 21 °C and 768 mm Hg using a 50-L sample [1]. Overall precision, $\hat{S}_{rT}$ was 0.080 with an average recovery of 0.953, representing a non-significant bias. The concentration of glycidol was independently verified using a total hydrocarbon analyzer calibrated with gas mixtures of glycidol in air. Desorption efficiency was 0.92 in the range 3.8 to 15.0 mg per sample. Desorption efficiencies using carbon disulfide or methylene chloride were much lower. Samples appeared unstable at room temperature. The breakthrough volume (where the concentration of glycidol in the effluent from the 100-mg charcoal bed was 5% of that in the influent) was 152 L; this was determined by sampling dry air containing 300 mg/m^3 glycidol at 0.93 L/min.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S70, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from the Superintendent of Documents, Washington, DC 20402.

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S70, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] Occupational Health Guidelines for Chemical Hazards, Glycidol, U.S. Department of Health and

Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from the Superintendent of Documents, Washington, DC 20402.

[4] The Merck Index, 9th ed., Merck & Co., Rahway, NJ (1976).

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S70 originally validated under NIOSH Contract CDC-99-74-45.

n-HEPTANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

HEXACHLOROBUTADIENE

$Cl_2C{:}CClCCl{:}CCl_2$ MW: 260.74 CAS: 87-68-3 RTECS: EJ0700000

METHOD: 2543, Issue 2 **EVALUATION: FULL** **Issue 1: 28 June 1979**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: 0.02 ppm (skin); carcinogen
ACGIH: 0.02 ppm (skin); carcinogen
(1 ppm = 10.67 mg/m^3 @ NTP)

PROPERTIES: clear, colorless liquid with a mild odor; d = 1.675 (15.5 °C); VP 2.9 kPa (22 mm Hg) @ 100 C°; B.P. 220 °C

SYNONYMS: 1,3-hexachlorobutadiene; HCBD; perchlorobutadiene; DOLEN-PUR

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2; 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 100 L @ 0.2 L/min

SHIPMENT: routine, but store in dark

SAMPLE STABILITY: 7 days @ 25 °C; 28 days @ 0 °C in dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.01 to 2 mg/m^3 [1] (100-L samples)

BIAS: + 0.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [1]

ACCURACY: ± 18.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY/ECD

ANALYTE: hexachlorobutadiene (HCBD)

EXTRACTION: 2 mL hexane; ultrasonic bath 1 h

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 150 °C
-DETECTOR: 250 °C
-COLUMN: 135 °C

COLUMN: Nukol or Stabilwax-DA

CARRIER GAS: Ar, 30 mL/min

DETECTOR: ECD

PURGE GAS: He or N_2, 80 mL/min

CALIBRATION: standard solutions of hexachlorobutadiene in hexane

RANGE: 0.06 µg to 6 µg per sample [1]

ESTIMATED LOD: 0.02 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.03 [1]

APPLICABILITY: The working range is 0.01 to 2.0 mg/m^3 for a 100-L sample [1]. An alternate column, DB-210, may be used with appropriate changes in instrumental conditions.

INTERFERENCES: Conditions of high humidity (>90%) may reduce capacity. Any compound with overlapping or similar retention times, or any sample containing chloroform may interfere[2].

OTHER METHODS: This revises method P&CAM 307 [1].

REAGENTS:

1. Hexane (spectrographic grade).
2. Hexachlorobutadiene, 98+ purity.
3. Argon, high purity.
4. Methane, high purity.
5. Hexachlorobutadiene calibration stock solution (16.7 mg/mL): Dilute 1 mL (1.67 g) hexachlorobutadiene to 100 mL with hexane.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 (front = 150 mg; back = 75 mg) separated and held in place by plugs of silylated glass wool. Pressure drop across the tube must be <3.4 kPa (2.5 cm Hg) at 1 L/min airflow.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph with 63 Ni ECD.
4. Capillary column (Nukol, or equivalent)
5. Vials, glass, 4 mL, with PTFE-lined caps.
6. Microliter syringes (10-μL, 25-μL, etc.)
7. Pipettes (1-mL, 2-mL, etc.)
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Hexachlorobutadiene is a toxic material. Exercise all appropriate safety precautions.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break open the ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurate flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 100 L.
4. Cap the samplers with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sections of the sorbent tube in separate 4 mL vials. Discard glass wool plugs.
6. Add 2.0 mL hexane to the vials containing the front sections and 1.0 mL hexane to vials containing the backup sections. Desorb each vial for 1 h in an ultrasonic bath.
7. Transfer 1 mL aliquots to 13-mm autosampler vials for analysis.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.02 μg to 6 μg per sample.
   a. Add appropriate aliquots of calibration stock solution to hexane in 10-mL volumetric flasks and dilute to mark.
   b. Analyze working standards together with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph of peak area vs. μg of hexachlorobutadiene per sample.
9. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the concentration range of interest. Prepare three tubes at each of five levels, plus three media blanks.
   a. Remove and discard the back sorbent section of a sampler.
   b. Inject a known amount (e.g., 1 to 20 μL) of calibration stock solution, or a dilution thereof in hexane, directly onto the front section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.

d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare graphs of DE vs. μg hexachlorobutadiene recovered.

10. Analyze three quality control blind spikes and three analyst spikes with each subsequent set from the same lot to ensure that the calibration graph and DE graph are in control

MEASUREMENT:

11. Set gas chromatograph to conditions given on p. 2543-1. Inject a 1 μL sample aliquot.
12. Measure and record peak area.
    NOTE: If peak area is above linear range of the working standards, dilute, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of HCBD found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank, front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate the concentration of HCBD in the actual air volume, V (L), at the sampling site:

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 0.01 to 2 mg/m^3 at 25 °C to 28 °C at a relative humidity of 90% or greater using a 3-L sample [1]. Generation samples at four concentration levels gave an average mean recovery of 100.5% with an overall precision, $\hat{S}_{rT}$, of 0.09 [3]. Desorption efficiency (DE) of HCBD from XAD-2 tubes was 100% at a loading of 0.0167 μg per sample [3]. Samples showed good storage stability for 28 days if stored @ 0 °C after the seventh day [3].

REFERENCES:

[1] Hexachlorobutadiene, NIOSH Method P&CAM 307, 1979.
[2] Imagawa, T. and Miyazaki, A., Formation of hexachlorobutadiene and related compounds from chloroform in a flame ionization detector, Bunski Kagaku, 36(2), 118-120, 1987.
[3] Backup Data Report for Hexachlorobutadiene, NIOSH Contract 210-78-0012.

METHOD REVISED BY:

S.M. Pendergrass, NIOSH/DPSE/MRSB; P&CAM 307 originally validated under NIOSH Contract 210-78-0012.

HEXACHLORO-1,3-CYCLOPENTADIENE 2518

C_5Cl_6 MW: 272.77 CAS: 77-47-4 RTECS: GY1225000

METHOD: 2518, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: 0.01 ppm; Group II Pesticide
ACGIH: 0.01 ppm
(1 ppm = 11.15 mg/m^3 @ NTP)

PROPERTIES: liquid; MP 10 °C; BP 239 °C; d 1.714 g/mL @ 15.5 °C; VP 13 Pa (0.1 mm Hg; 132 ppm) @ 25 °C

SYNONYMS: perchlorocyclopentadiene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (2 tubes, Porapak T, 75 mg and 25 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 0.01 ppm
-MAX: 90 L

SHIPMENT: separate tubes, seal, ship @ 25 °C; store @ 0 °C in the dark

SAMPLE STABILITY: ≥7 days @ 25 °C; ≥28 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 13 to 873 μg/m^3 [1] (3-L samples)

BIAS: − 0.3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.082 [2]

ACCURACY: ± 16.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: hexachloro-1,3-cyclopentadiene

DESORPTION: 1 mL hexane; ultrasonic bath 1 h

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 250 °C
-COLUMN: 135 °C

CARRIER GAS: 5% CH_4/95% Ar, 30 mL/min

COLUMN: glass, 2 m x 4-mm ID; 3% OV-1 on 100/120 Gas Chrom Q

CALIBRATION: hexachloro-1,3-cyclopentadiene in hexane

RANGE: 25 to 140 ng per sample

ESTIMATED LOD: 5 ng per sample

PRECISION ($\bar{S}_r$): 0.030 [1]

APPLICABILITY: The working range is 0.005 to 0.2 ppm (5 to 2400 mg/m^3) for a 5-L air sample. Area samples from a municipal wastewater treatment plant were analyzed by a variation of this method [2].

INTERFERENCES: None identified.

OTHER METHODS: This revises P&CAM 308 [3] which was evaluated with a reference method which involved sampling with impingers of hexane and gas chromatography with electron capture detection [1].

REAGENTS:

1. Porapak T (optional if commercial tubes are used), 80/100 mesh (Waters Associates, Inc.), cleaned as follows:
   a. Soxhlet extract 4 h with 80/20 acetone/methanol (v/v).
   b. Soxhlet extract 4 h with hexane.
   c. Dry in vacuo 12 h at 50 to 75 °C.
2. Hexane, spectral quality.*
3. Hexachloro-1,3-cyclopentadiene, 98% or purer.
4. Acetone, spectral quality.*
5. Methanol, spectral quality.*
6. Stock solution, 20 mg/mL. Dissolve 2.00 g hexachloro-1,3-cyclopentadiene in hexane to make 100 mL solution. Store at 0 °C, protect from light and discard after 60 days.
7. Calibration stock solution, 10 μg/mL. Dilute 50 μL stock solution with hexane to make 100 mL solution. Store at 0 °C, protect from light and discard after 14 days.
8. Mixture of 5% methane and 95% argon.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes connected in series with 1.8-cm piece of plastic tubing; each tube, 5 cm long, 6-mm OD, 4-mm ID, contains one section of 80/100 mesh Porapak T held in place with two plugs of silylated glass wool (front tube = 75 mg; back tube = 25 mg) with plastic caps. Pressure drop <2.3 kPa (<17 mm Hg) at flow rate of 0.2 L/min. Samplers are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tape.
4. Gas chromatograph, ^{63}Ni ECD, integrator and column (page 2518-1).
5. Volumetric flasks, 10- and 100-mL.
6. Vials, 1-mL, with PTFE-lined caps.
7. Syringes, 10-μL, readable to 0.1 μL.
8. Syringes, 100-μL, readable to 1 μL.
9. Syringes, 1-mL, readable to 10 μL.
10. Pipet, 1-mL.
11. Ultrasonic bath.

SPECIAL PRECAUTIONS: Hexane, acetone and methanol are flammable. Hexachloro-1,3-cyclopentadiene is highly toxic and can be absorbed through the skin. Wear gloves, avoid inhalation of vapors and protect solvents from sparks and flames.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 90 L. Do not sample for longer than 8 h.
4. Separate the two tubes of the sampler. Cap the ends of each tube with PTFE tape and plastic caps. Pack securely for shipment.

SAMPLE PREPARATION:

NOTE: If the tubes have been refrigerated, allow the tubes to stand at room temperature before removal of the caps and tape to prevent condensation of water on the sorbent.

5. Place the front and back sorbent sections with their respective glass wool plugs, in separate vials.
6. Add 1.0 mL hexane to each vial. Attach cap to each vial.
7. Allow to stand 60 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 5 to 140 ng hexachloro-1,3-cyclopentadiene per sample.

a. Add known amounts (5 to 140 μL) of calibration stock solution to hexane in 10-mL volumetric flasks and dilute to the mark.
b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area or height vs. ng hexachloro-1,3-cyclopentadiene).

9. Determine desorption efficiency (DE) at least once for each lot of Porapak T used for sampling in the range 25 to 12,500 ng hexachloro-1,3-cyclopentadiene per sample. Prepare three tubes at each of five levels plus three media blanks.
   a. Prepare five DE standard solutions in the range 5 to 2500 μg/mL by diluting aliquots of 20 mg/mL stock solution with hexane.
   b. Inject 5 μL of a DE standard solution directly into a media blank front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand 12 hrs at room temperature.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. ng hexachloro-1,3-cyclopentadiene recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2518-1. Prior to analyzing samples, condition the column by making three 5-μL injections of a 1-μg/mL solution of hexachloro-1,3-cyclopentadiene in hexane. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 7 min for these conditions.
    NOTE: If peak area is above the useful range of the working standards, dilute with hexane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or height.

CALCULATIONS:

13. Determine the mass, ng (corrected for DE) of hexachloro-1,3-cyclopentadiene found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of hexachloro-1,3-cyclopentadiene in the air volume sampled, V (L):

$$C \frac{(W_f + W_b - B_f - B_b)}{V}, \mu g/m^3.$$

EVALUATION OF METHOD:

A variation of this method employed single 100- or 50-mg sections of Porapak T per sampler. This variation was tested with controlled atmospheres and verified with impingers containing hexane and with gas chromatographic analysis for 13.1 to 873 $\mu g/m^3$ [1]. Overall precision ($\hat{S}_{rT}$) was 0.082 (18 samples, pooled) for 2.9-L samples; the temperature of each atmosphere was 25 to 28 °C, and the relative humidity was at least 90%. Mean recovery for three concentration levels was 99.7%. The average concentration found at each level was not significantly different from the corresponding reference concentration at 95% confidence level. Breakthrough (1 mg/m^3, 0.2 L/min, 27 °C, RH 90%) = 55 L for a 50-mg section of Porapak T. Values of DE from 50 mg of Porapak T with 1 mL of hexane were 1.01, 0.99, and 1.01 for 24.5, 352, and 3670 ng per sample, respectively; $\bar{S}_r$ = 0.030 (18 samples, pooled). Hexachloro-1,3-cyclopentadiene (about 30 ng per sample) was stable for 28 days inside each tube which contained 100- and 50-mg sections of Porapak T (samples were stored at room temperature for the first seven days and at 0 °C for the next 21 days). However, hexachloro-1,3-cyclopentadiene did migrate from front sections of sorbent to backup sections. Area samples from a municipal wastewater treatment

plant were collected and analyzed by a variation of this method [2]. Differences in the method included sampling with 150 mg of 80/100 Chromosorb 102 and desorption with petroleum ether. Concentrations of hexachloro-1,3-cyclopentadiene ranged from 0.03 to 39 $\mu g/m^3$.

REFERENCES:

[1] Dillon, H. K. Research Report for Hexachlorocyclopentadiene, Southern Research Institute, Birmingham, AL, NIOSH Contract 210-78-0012 (1980).

[2] Elia, V. J., C. S. Clark, V. A. Majeti, P. S. Gartside, T. MacDonald, N. Richdale, C. R. Meyer, G. L. Van Meer and K. Hunninen. Environ. Res., 32, 360-371 (1983).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 308, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; P&CAM 308 originally validated under NIOSH Contract 210-78-0012.

HEXACHLOROETHANE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

n-HEXANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

2-HEXANONE

See KETONES I (Method 1300) for procedure

HIPPURIC ACID in urine 8300

$C_6H_5CONHCH_2COOH$ MW: 179.18 CAS: 495-69-2 RTECS: MR8150000

METHOD: 8300, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to toluene.

SYNONYMS: N-benzoylglycine

SAMPLING		MEASUREMENT	
SPECIMEN:	urine, end of shift after 2 days exposure	**TECHNIQUE:**	VISIBLE ABSORPTION SPECTROPHOTOMETRY
VOLUME:	50 to 100 mL in 125-mL plastic bottle	**ANALYTE:**	complex of hippuric acid and benzenesulfonyl chloride
PRESERVATIVE:	a few crystals of thymol; keep at about 4 °C	**WAVELENGTH:**	410 nm
SHIPMENT:	pack in insulated shipper with bagged refrigerant; ship by air express	**PATH LENGTH:**	1 cm
SAMPLE STABILITY:	stable 1 day @ 20 °C; 1 week @ 4 °C; and 2 months @ −20 °C	**CALIBRATION:**	aqueous hippuric acid standards
CONTROLS:	collect pre-shift urines as well as urines from non-exposed controls	**QUALITY CONTROLS:**	frozen pooled urine; correct for creatinine content
		RANGE:	0.005 to 0.5 g/L (1:5 urine dilution)
		ESTIMATED LOD:	0.002 g/L
		PRECISION ($\bar{S}_r$):	0.06
		ACCURACY:	not determined

APPLICABILITY: Toluene is metabolized by the body and is excreted in the urine as hippuric acid, the glycine congugate of benzoic acid. This method is useful in screening workers exposed to toluene in the absence of xylene or styrene. The latter 2 compounds produce metabolites that are measured as "hippuric acid."

INTERFERENCES: In addition to positive interferences from styrene and xylene in the workplace, the ingestion of sodium benzoate in food, salicylic acid, or aspirin by the worker will produce a positive interference. A careful work history/questionnaire is suggested.

OTHER METHODS: This method replaces P&CAM 327 [1] with minor revisions. Method 8301 (Hippuric and Methyl Hippuric Acids in urine) is a specific HPLC method and can be used in the presence of xylene, styrene, salicylic acid and aspirin. Other biological monitoring methods include measurement of blood toluene and alveolar air toluene [2].

REAGENTS:

1. Calibration stock solution, 0.5 g/L. Dissolve 50 mg hippuric acid in 100 mL distilled water. Stable one month at 25 °C.
2. Benzenesulfonyl chloride.*
3. Pyridine, reagent.*
4. Thymol, USP.
5. Ethanol, absolute.

* See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125-mL.
2. Spectrophotometer, 1-cm light path, to read at 410 nm, band width $\leq$ 10 nm, with 1-cm cuvettes.
3. Centrifuge, clinical, table top.
4. Centrifuge tubes, 15-mL, conical.
5. Pipets, serological, 0.5-, 1.0-, and 5.0-mL
6. Pipet bulb.
7. Mixer, vibration.
8. Volumetric flasks, 10- and 100-mL.
9. Graduated cylinder, 10-mL.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. Work with pyridine and benzenesulfonyl chloride only in a fume hood.

SAMPLING:

1. Collect a spot urine sample of 50 to 100 mL in a 125-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Take the sample at the end of the second day of suspected exposure to toluene. Also take pre-exposure samples and samples from non-exposed workers as controls.
2. Pack the samples in an insulated shipper with bagged refrigerant.

SAMPLE PREPARATION:

3. Thaw the urine samples, if frozen.
4. Perform a creatinine determination on an aliquot of the urine (e.g., [3]).
5. Dilute 1 volume urine with 4 volumes distilled water.

CALIBRATION AND QUALITY CONTROL:

6. Prepare working standards over the range of 0.005 to 0.5 g/L by dilution of calibration stock solution. Working standards are stable for one week at room temperature.
7. Analyze the working standards (steps 10 through 15).
8. Include a frozen pooled urine control with each measurement run.
9. Plot the absorbance at 410 nm against hippuric acid concentration (g/L) in the working standard to prepare the calibration graph.

MEASUREMENT:

10. Mix 0.5 mL diluted urine and 0.5 mL pyridine in a conical centrifuge tube.
11. Add 0.2 mL benzenesulfonyl chloride and mix for about 5 sec on a vibration mixer.
12. Let stand for 30 min at 20 to 30 °C.

13. Stop the reaction by adding 5.0 mL ethanol, followed by mixing on a vibration mixer.
14. Centrifuge at 1500 to 2000 RPM (full speed) for 5 min to reduce turbidity.
15. Remove supernatant with pipet and place in a 1-cm cuvette. Read absorbance at 410 nm using ethanol to zero the instrument.
    NOTE: If absorbance is above the calibration range, discard the sample and start a new sample (beginning at step 5) with greater dilution.

CALCULATIONS:

16. Determine the concentration, C_s (g/L), of hippuric acid corresponding to the absorbance of the sample from the calibration graph.
17. Calculate the concentration of hippuric acid/g creatinine in the urine sample, C (g/g creatinine), using the dilution factor, D (usually 5), from step 5 and the creatinine value, C_r (g creatinine/L urine), from step 4:

$$C = \frac{C_s \times D}{C_r}, \text{ g hippuric acid/g creatinine.}$$

GUIDES TO INTERPRETATION:

1. Tomukuni, et al. [4] reported a normal range in 20 non-exposed adults as 0.44 ± 0.20 g/L (equivalent to approximately 0.7 g/g creatinine).
2. Lauwreys [2] reported a normal range of 1.5 g/g creatinine and a "tentative maximum permissible value" of 2.5 g/g creatinine.
3. Pagnotto, et al. [5] reported that exposure to 100 ppm toluene would produce end-of-shift urinary hippuric acid levels of 4 g/L (equivalent to about 5 g/g creatinine).
4. Urine from non-exposed workers should be collected, as well as pre-shift specimens from exposed workers because levels of hippuric acid in urine vary widely.

EVALUATION OF METHOD:

Precision (s_r) for within-run and day-to-day runs over the analytical range was found to average 0.06. No method comparison studies have been conducted.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 6, Method P&CAM 327, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[2] Lauwerys, R.R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, California, 57-65 (1983).
[3] Tietz, N.W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-999, W.B. Saunders Co., Philadelphia, PA (1976).
[4] Tomokuni, K. and M. Ogata. Direct Colorimetric Determination of Hippuric Acid in Urine, Clin. Chem. 18, 349-351 (1972).
[5] Pagnotto, L.D. and L.M. Lieberman. Am. Ind. Hyg. Assoc. J., 28, 129-134 (1967).

METHOD REVISED BY:

Frederick C. Phipps, NIOSH/DBBS.

HIPPURIC and METHYL HIPPURIC ACIDS in urine 8301

$C_6H_5CONHCH_2CO_2H$ MW: 179.18 CAS: 495-69-2 RTECS: MR8150000
$CH_3C_6H_4CONHCH_2CO_2H$ 193.20 o-42013-20-7
m-27115-49-7
p-27115-50-0

METHOD: 8301, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to toluene and xylene.

SYNONYMS: hippuric acid: N-benzoylglycine.

SAMPLING		MEASUREMENT	
SPECIMEN:	urine, end of shift after 2 days exposure	**TECHNIQUE:**	HPLC-UV DETECTION
VOLUME:	complete spot voiding	**ANALYTE:**	(1) hippuric acid and (2) methyl hippuric acid
PRESERVATIVE:	a few crystals of thymol; keep @ 4 °C	**EXTRACTANT:**	ethyl acetate
SHIPMENT:	pack in styrofoam shipper with bagged refrigerant, ship by air express	**WAVELENGTH:**	254 nm
SAMPLE STABILITY:	stable 1 week @ 4 °C and 2 months @ −20 °C	**COLUMN:**	reverse phase (C_{18})
CONTROLS:	collect samples from unexposed, matched population as well as pre-shift urines from exposed workers	**MOBILE PHASE:**	90/10/0.02% (v/v/v) water/acetonitrile/glacial acetic acid; 3 mL/min
		CALIBRATION:	aqueous solutions of analyte
		QUALITY CONTROL:	frozen pooled urine; normalize to creatinine
		RANGE:	0.2 to 1.0 mg/mL
		ESTIMATED LOD:	(1) 0.015 μg/mL; (2) 0.030 μg/mL
		RECOVERY:	98%
		PRECISION ($\bar{S}_r$):	0.04

APPLICABILITY: Hippuric acid and m-methyl hippuric acid are the principal metabolites of toluene and xylene, respectively. An occupational exposure to either of these organic solvents may be monitored by following the pattern of excretion of these metabolites in urine.

INTERFERENCES: None known; however, para- and meta- isomers elute together in this system. There are other sources of hippuric acid such as food preservatives, ethylbenzene, and styrene.

OTHER METHODS: This is based on the method of Matsui, et al [1]. Method 8300 can be used for screening. Isotachophoresis has also been used [2]. Newer HPLC methodologies do a better job of resolving these compounds [3].

REAGENTS:

1. Thymol, USP.
2. Sodium chloride.
3. Hydrochloric acid, conc. (36% w/w).
4. Ethyl acetate, HPLC quality.
5. Hippuric acid stock solution, 1 mg/mL. Dissolve 100.0 mg hippuric acid in 75 mL distilled water. Dilute to 100 mL. Stable one month.
6. o-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
7. m-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
8. p-Methyl hippuric acid, 1 mg/mL. Prepare as described for hippuric acid.
9. Mobile phase. Add 900 mL distilled water to 100 mL acetonitrile (HPLC grade) and 200 μL glacial acetic acid. Mix and filter.
10. Prepurified nitrogen, 99.9%.

EQUIPMENT:

1. Bottles, polyethylene, 250-mL.
2. Refrigerant, bagged ("Blue Ice," or equivalent).
3. HPLC system consisting of sample injector, pump, column, ultraviolet detector at 254 nm, strip chart recorder, integrator, and column; plastic, 14 x 155-mm, packed with 10-μm irregularly-shaped reversed phase (C_{18}) packing.
4. Radial compression module capable of delivering constant, uniform pressure to the entire longitudinal surface of the column.
5. Concentrator-evaporator with heated waterbath.
6. Centrifuge.
7. Analytical balance.
8. Pipettes, serological, 10-mL, with pipet bulb.
9. Centrifuge tubes, glass-stoppered, graduated, 15-mL.
10. Culture tubes, 12-mm x 75 mm, disposable.
11. Micropipettes, 40-, 100- and 200-μL.
12. Microsyringe, 10-μL.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect a spot sample of urine in a 250-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Take the sample at the end of the second day of suspected exposure to toluene or xylene. Also take pre-exposure samples and samples from non-exposed workers as controls.
2. Pack bottles in styrofoam shipper with bagged refrigerant and ship by air express.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of urine (e.g., [4]).
4. Pipette 1.0 mL of well-mixed urine into a 15-mL graduated centrifuge tube.
5. Add 40 μL conc. HCl, mix, and add 0.3 g sodium chloride (enough to saturate).
6. Add 4 mL ethyl acetate. Shake for 2 min.
7. Centrifuge at 100 x gravity for 5 min. Transfer 200 μL of the organic layer to a culture tube and evaporate to dryness using a heated waterbath and a gentle stream of nitrogen.
8. Redissolve the residue in 200 μL distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards over the range 0.2 to 1 mg/mL by dilution of hippuric acid stock solution and methyl hippuric acid stock solutions with distilled water. Working standards are stable for 1 week at room temperature.
10. Prepare and analyze the working standards together with samples, blanks and controls (steps 4 through 8 and 14 and 15).
11. Determine the peak height to concentration ratio (H/C) using the mean peak height of three injections for each working standard. Calculate the response factor, F, for each compound by dividing the respective peak height to concentration ratio by the peak height to concentration ratio for hippuric acid.
12. Include a batch of replicate standards with each batch of samples.
13. Include aliquots of previously analyzed frozen urine pool.

MEASUREMENT:

14. Set up the HPLC according to manufacturer's recommendations and to conditions on page 8301-1.
15. Inject 5 μL of the test solution from step 8 into the HPLC. Determine peak heights.

CALCULATIONS:

16. Calculate the concentration of analyte in the urine sample, C_u (mg/mL), using the concentration of a standard, C_s (mg/mL), the peak height of the analyte, H, and the peak height of the respective standard, H_s:

$$C_u = \frac{C_s \cdot H}{F \cdot H_s}.$$

17. Calculate the concentration of analyte/g creatinine in the urine sample, C (g/g creatinine), using the concentration of creatinine in urine determined in step 3, C_r (g creatinine/L urine):

$$C = \frac{C_u}{C_r}.$$

GUIDES TO INTERPRETATION:

1. The upper limit of the range for hippuric acid in non-exposed NIOSH employees was 0.6 mg/mL (0.6 g/L). Meta-methyl hippuric acid is not found in non-exposed humans.
2. Lauwerys [5] reports an upper limit of normal for hippuric acid of 1.5 g/g creatinine using a specific gas chromatographic method. He reports a "tentative maximum permissible value" of 2.5 g/g creatinine.
3. Lauwerys [5] reports a "tentative maximum permissible value" of 1.5 g/g creatinine for methyl hippuric acid collected at the end of a work shift.

EVALUATION OF METHOD:

Within-run precision ($\bar{S}_r$) averaged 0.04 over the analytical range. No further evaluation of the method was performed except as reported by Matsui, et al. [1].

REFERENCES:

[1] Matsui, H., M. Kasao, and S. Imamura. High Performance Liquid Chromatographic Determination of Hippuric Acid in Human Urine, J. Chromatog., 45, 231 (1978).

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[3] Tardif and Brodeur, J. Anal. Tox., 13, 313 (1985).

[4] Tietz, N.W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-999, W.B. Saunders Co., Philadelphia, PA (1976).

[5] Lauwerys, R.R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA, pp. 57-69 (1983).

METHOD WRITTEN BY:

Frederick C. Phipps, NIOSH/DBBS.

HYDRAZINE

H_2NNH_2 MW: 32.05 CAS: 302-01-2 RTECS: MU7175000

METHOD: 3503, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1 ppm (skin)
NIOSH: C 0.03 ppm/120 min(suspect carcinogen)
ACGIH: 0.1 ppm (skin; suspect carcinogen)
(1 ppm = 1.31 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.004 g/mL @ 25 °C; BP 113.5 °C; MP 2 °C; VP 1.92 kPa (14.4 mm Hg; 18,900 ppm) @ 25 °C)

SYNONYMS: diamide; diamine

SAMPLING

SAMPLER: BUBBLER (15 mL 0.1 M HCl)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 7 L @ 1 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 6 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.59 to 3.4 mg/m^3 [1] (91-L samples)
BIAS:	− 0.3%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.094 [1]
ACCURACY:	± 17.1%

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: quinoid derivative of p-dimethylaminobenzaldazine [2]

COMPLEXATION: p-dimethylaminobenzaldehyde; stand 30 min; acetic acid

FINAL VOLUME: 625 mL

WAVELENGTH: 480 nm

CALIBRATION: hydrazine in methanol

RANGE: 9 to 400 μg per sample

ESTIMATED LOD: 0.9 μg per sample

PRECISION ($\bar{S}_r$): 0.031 [1]

APPLICABILITY: The working ranges are 0.07 to 3 ppm (0.09 to 4 mg/m^3) for 100-L air samples and 0.45 to 21 ppm (0.6 to 27 mg/m^3) for 15-L air samples. This method is applicable to hydrazine vapor. It has not been tested with aerosol forms. The free base cannot be distinguished from salts, such as hydrazine monohydrochloride and hydrazine sulfate, which are aerosols.

INTERFERENCES: Methylhydrazine is an interference. Other hydrazines may interfere.

OTHER METHODS: This method is a modification of and replaces Method S237 [2]. Method P&CAM 248 is a gas chromatographic method which can be used for quantitation of hydrazine or substituted hydrazines [3]. Methods S143, S149 and S160 utilize a non-specific colorimetric method for substituted hydrazines [4].

REAGENTS:

1. Hydrochloric acid, 0.1 M. Dilute 8.6 mL conc. HCl to 1 L with distilled water.
2. Methanol, reagent grade.*
3. Calibration stock solution, 1.0 mg/mL. Dissolve 0.10 mL hydrazine* in methanol to make 100 mL solution.
4. Solution of p-dimethylaminobenzaldehyde in methanol, 0.168 M. Dissolve 12.5 g p-dimethylaminobenzaldehyde in methanol to make 500 mL solution.
5. Glacial acetic acid.*
6. Sodium hydroxide solution, 1.8 M. Dissolve 7.2 g NaOH in distilled water to make 100 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget bubbler, glass, with 15 mL 0.1 M HCl.
2. Glass tube, 5 cm x 6-mm ID, packed loosely with glass wool.
3. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
4. Vials, 20-mL, with PTFE-lined screw caps.
5. Spectrophotometer set at 480 nm, with matched cuvettes, glass, 1-cm path length.
6. Volumetric flasks, 25-, 50-, 100- and 500-mL and 1 L.
7. Pipets, 1-, 2-, 10- and 15-mL, with pipet bulb.
8. Syringe, 10-μL, readable to 0.1 μL.
9. Syringe, 50-μL, readable to 1 μL.
10. pH paper.

SPECIAL PRECAUTIONS: Hydrazine is carcinogenic, toxic, and flammable, and can be absorbed through the skin [5].

Acetic acid and methanol are flammable. Wear gloves, handle compounds in a well-ventilated fume cabinet, avoid inhalation of vapors, and protect compounds from sparks and flames.

SAMPLING:

1. Connect the outlet of the sampler and the inlet of the pump to a tube packed with glass wool to protect the pump from splashover.
2. Calibrate the personal sampling pump with sampler in line.
3. Sample at 0.2 to 1.0 L/min for a sample size of 7 to 100 L.
4. Transfer the solution from the bubbler to a glass vial, rinsing both the bubbler stem and body with 1-mL portions of 0.1 M HCl. Cap the vial securely for shipment.

SAMPLE PREPARATION:

5. Transfer bubbler solution to a 50-mL volumetric flask.
6. Rinse vial with 1 mL 0.1 M HCl, and add rinse to the flask.
7. Add 1.8 M NaOH (ca. 1 mL) to make the solution neutral or slightly alkaline to pH paper.
8. Immediately add 10 mL 0.168 M p-dimethylaminobenzaldehyde solution. Agitate the mixture and allow to stand 30 min.
9. Bring volume of solution to 50 mL with glacial acetic acid.
10. Dilute 2 mL of the solution to 25 mL with glacial acetic acid.
11. Prepare field blanks and media blanks according to steps 4 through 10.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with a blank and six working standards over the range 1 to 400 μg hydrazine per sample.
    a. Add aliquots of calibration stock solution to 15 mL 0.1 M HCl in 50-mL volumetric flasks and dilute to the mark. Designate one flask as a blank and do not add hydrazine to that flask.

b. Process the working standards according to steps 7 through 10.
c. Determine absorbance for each solution (steps 13 and 14).
d. Prepare calibration graph (absorbance vs. μg hydrazine).

MEASUREMENT:

13. Set up the spectrophotometer according to manufacturer's instructions. Place blank solution (from step 12.a) into reference cuvette.
14. Determine absorbance of solution at 480 nm.

CALCULATIONS:

15. Determine the quantities of hydrazine in the sample, W (μg), and average media blank, B (μg), from the calibration graph.
16. Calculate the concentration, C (mg/m^3), of hydrazine in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method is based on Method S237 using 15 mL of 0.1 M HCl for sampling instead of 10 mL. Method S237 was validated with controlled atmospheres of hydrazine [1]. Overall precision ($\hat{S}_{rT}$) was 0.094 (18 samples, pooled) for 91-L samples at 0.59 to 3.4 mg/m^3. Concentrations of hydrazine in controlled atmospheres were not verified by an independent method. Average collection efficiency at 0.9 L/min for six bubblers was 0.997 at 3.4 mg/m^3. Average recoveries from HCl solution were 1.03, 0.98 and 1.01 at the 60.7-, 121- and 243-μg levels of hydrazine, respectively. The $\bar{S}_r$ for analysis = 0.031 (18 samples, pooled). Samples at the 121-μg level were stable during storage in 0.1 M HCl for six days at room temperature.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S237, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S237, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Ibid. V. 1, P&CAM 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid. S143, S149, S160.
[5] Criteria for a Recommended Standard...Occupational Exposure to Hydrazine, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-172 (1978).
[6] Dambrauskas, T., and H. H. Cornish. Am. Ind. Hyg. Assoc. J., 23, 151-156 (1962).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; S237 developed under NIOSH Contract CDC-99-74-45.

HYDROBROMIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure

HYDROCARBONS, BP 36 - 126 °C

FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:	benzene	n-heptane	n-octane
(Synonyms	cyclohexane	n-hexane	n-pentane
in Table 1)	cyclohexene	methylcyclohexane	toluene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 250 °C
-COLUMN: see step 11

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass, 3.0 m x 2-mm, 20% SP-2100 on 80/100 mesh Supelcoport

CALIBRATION: analytes in CS_2

RANGE AND PRECISION: Table 4

ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]

APPLICABILITY: This method is intended for determining the OSHA-regulated hydrocarbons included within the boiling point range of n-pentane through n-octane. It may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and change desorption efficiencies.

INTERFERENCES: At high humidity, breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are likely interferences. If interference is suspected, use a more polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene and toluene [2]; S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S311, benzene [4]; S343, toluene [4]; S378, octane [4]; and S379, pentane [4]. For benzene or toluene in complex mixture of alkanes ($\leq C_{10}$), Method 1501 (aromatic hydrocarbons) is more selective.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality with (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1500-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Syringes, 5-, 10-, 25- and 100-μL.
7. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = − 30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11, 12 and 13).
   c. Prepare calibration graph (peak area of analyte vs. mg analyte per sample).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1500-1. Select appropriate column temperature:

	Approximate Retention Time (min), at Indicated Column Temperature			
Substance	40 °C	70 °C	100 °C	Programmed[a]
n-pentane	2.2	1.2		1.8
solvent (CS_2)	3.0	1.6		2.4
n-hexane	5.1	2.2		3.5
benzene[b]	7.7	3.2		4.5
cyclohexane[b]	8.4	3.4		4.7
cyclohexene	9.5	3.8		4.9
n-heptane	12	4.3		5.4
methylcyclohexane	14	5.2	2.2	5.9
toluene	17	6.5	2.6	6.5
n-octane	19	8.7	3.2	7.1

[a] Temperature program: 50 °C for 2 min, then 15 °C/min to 150 °C, 2-min final hold.
[b] Not completely resolved.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

REFERENCES:

[1] User check, UBTL, NIOSH Sequence #4213-L (unpublished, January 31, 1984).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S28, S82, S89, S90, S94, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] R. D. Driesbach, "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
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[7] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1989); 29 CFR 1910.1000.
[8] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 92-100 (1992).
[9] 1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati, OH (1993).
[10] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., based on results of NIOSH Contract CDC-99-74-45.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES.

Name Synonyms	CAS# RTECS	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)
benzene[a] benzol; cyclohexatriene	71-42-2 CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
cyclohexane[a] hexahydrobenzene hexamethylene	110-82-7 GU6300000	C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene[a] tetrahydrobenzene benzene tetrahydride	110-83-8 GW2500000	C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-heptane[b]	142-82-5 MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane[b] hexyl-hydride	110-54-3 MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane[a] cyclohexylmethane	108-87-2 GV6125000	C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-octane[b]	111-65-9 RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane[b]	109-66-0 RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	0.626
toluene[a] methylbenzene; toluol	108-88-3 XS5250000	C_7H_8	92.14	110.6	28.4	3.8	0.867

[a] Properties from [5].
[b] Properties from [6].

TABLE 2. EXPOSURE LIMITS, PPM [7-9].

Substance	OSHA TWA	OSHA C	OSHA Peak	NIOSH TWA	NIOSH C	ACGIH TLV	ACGIH STEL	mg/m³ per ppm @ NTP
benzene*	10	25	50[b]	0.1[d]	1	10[d]		3.19
cyclohexane	300			300		300		3.44
cyclohexene	300			300		300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane[a]	500			50		50		3.52
methylcyclohexane	500			400		400		4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500[b]	100	150[c]	100	150	3.77

[a] The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.
[b] Maximum duration 10 min in 8 h.
[c] STEL
[d] Suspect carcinogen

TABLE 3. SAMPLING FLOWRATE[a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [2-4, 10].

Substance	Sampling Flowrate (L/min)	Sampling Volume (L) MIN	Sampling Volume (L) MAX[b]	Breakthrough Volume at Concentration (L)	Breakthrough Volume at Concentration (mg/m³)	Range at VOL-NOM (mg/m³)	Overall Bias (%)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)
benzene	≤0.20	2[c]	30	>45	149.1	41.5-165	0.4	0.059	±11.4
cyclohexane	≤0.20	2.5	5	7.6	1650	510-2010	1.1	0.060[d]	±11.5
cyclohexene	≤0.20	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-heptane	≤0.20	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-hexane	≤0.20	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
methylcyclohexane	≤0.20	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-octane	≤0.20	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-pentane	≤0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6
toluene	≤0.20	2[c]	8	11.9	2294	548-2190	1.6	0.052	±10.9

[a] Minimum recommended flow is 0.01 L/min.
[b] Approximately two-thirds the breakthrough volume.
[c] 10-min sample.
[d] Corrected value, calculated from data in [10].

TABLE 4. MEASUREMENT RANGE, PRECISION, AND CHROMATOGRAPHIC CONDITIONS [2-4,10].

	Measurement[a]		Carrier		Column Parameters[b]			
Substance	Range (mg)	Precision ($\bar{S}_r$)	Gas	Flow (mL/min)	t (°C)	Length (m)	Dia-meter (mm)	Packing[c]
benzene	0.09-0.35	0.036	N_2	50	115	0.9	3.2	A
cyclohexane	1.3 - 5.3[d]	0.024	N_2	50	210	1.2	6.4	B
cyclohexene	2.4 - 9.7[d]	0.021	N_2	50	205	1.2	6.4	B
n-heptane	4.08-16.3	0.016	He	30	80	3.0	3.2	C
n-hexane	3.56-14.5	0.014	He	30	52	6.1	3.2	D
methylcyclohexane	3.98-16.1	0.012	He	30	55	6.1	3.2	D
n-octane	4.75-18.9	0.009	He	30	52	6.1	3.2	D
n-pentane	2.98-11.8	0.014	He	30	52	6.1	3.2	D
toluene	1.13-4.51	0.011	N_2	50	155	0.9	3.2	B

[a] Injection volume, 5.0 μL; desorption volume, 1.0 mL, except cyclohexane and cyclohexene, 0.5 mL.

[b] All columns stainless steel. Diameter is outside dimension.

[c] A, 50/80 mesh Porapak P; B, 50/80 mesh Porapak Q; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

[d] Corrected value, calculated from data in [10].

FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1501, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1) benzene; cumene; α-methylstyrene; styrene; vinyltoluene; p-tert-butyltoluene; ethylbenzene; naphthalene; toluene; xylene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE, VOLUME: Table 3

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 225 °C
-COLUMN: see step 11

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass, 3.0 m x 2-mm, 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent (Table 4)

CALIBRATION: analytes in CS_2

RANGE AND PRECISION ($\bar{S}_r$): Table 4

ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]

APPLICABILITY: This method is for peak, ceiling and TWA determinations of aromatic hydrocarbons. It may be used for simultaneous measurements, though there is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies.

INTERFERENCES: Use of the recommended column will prevent interference by alkanes ($\leq C_{10}$). Under conditions of high humidity, the breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are possible interferences. If interference is suspected, use a less polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene, styrene, toluene and xylene [2]; S311, benzene [4]; S22, p-tert-butyltoluene [3]; S23, cumene [3]; S29, ethylbenzene [3]; S26, α-methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinyltoluene [3]; S318, xylene [4].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Naphthalene calibration stock solution, 0.40 g/mL in CS_2.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pumps, 0.01 to 1 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1501-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, and pipet bulb.
6. Syringes, 5-, 10-, 25- and 100-μL.
7. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = −30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (to 1 L/min for naphthalene or styrene) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
   a. Add known amounts of analyte (calibration stock solution for naphthalene) to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 through 13).
   c. Prepare calibration graph (peak area of analyte vs. mg analyte per sample).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte (calibration stock solution for naphthalene) directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 through 13).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Select appropriate column temperature:

	Approximate Retention Time (min), at Indicated Column Temperature			
Substance[a]	50 °C	100 °C	150 °C	Programmed[b]
benzene	2.5			2.5
toluene	4.3	1.1		4.2
xylene (para)	7.0	1.4		5.2
ethylbenzene	7.0	1.4		5.5
xylene (meta)	7.2	1.5		5.6
cumene	8.3	1.6		6.0
xylene (ortho)	10	1.9		6.5
styrene	16	2.6		7.6
α-methylstyrene		3.2	1.0	8.1
vinyltoluene (meta)		3.8	1.2	8.5
naphthalene		25	4.3	12

[a] Data not available for p-tert-butyltoluene and p-vinyltoluene.
[b] Temperature program: 50 °C for 3 min, then 15 °C/min to 200 °C.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions given in Table 4 were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [9] provides more specific information.

REFERENCES:

[1] User check, UBTL, NIOSH Sequence #4121-S (unpublished, December 7, 1983).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 2, S22, S23, S25, S26, S29, S30, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
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METHOD REVISED BY:

R. Alan Lunsford, Ph.D., based on results of NIOSH Contract CDC-99-74-45.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES [5].

Name/Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	(kPa)	Density @ 20 °C (g/mL)
benzene CAS #71-43-2 RTECS CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 1-tert-butyl-4-methylbenzene RTECS XS8400000	$C_{11}H_{16}$	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 isopropylbenzene RTECS GR8575000	C_9H_{12}	120.20	152.4	4.7	0.63	0.862
ethylbenzene CAS #100-41-4 RTECS DA0700000	C_8H_{10}	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 isopropenylbenzene (1-methylethenyl)-benzene RTECS WL5075300	C_9H_{10}	118.18	165.4	2.5	0.33	0.911
naphthalene CAS #91-20-3 RTECS QJ0525000	$C_{10}H_8$	128.18	80.2[a]	0.2	0.03	1.025
styrene CAS #100-42-5 vinylbenzene RTECS WL3675000	C_8H_8	104.15	145.2	6.1	0.81	0.906
toluene CAS #108-88-3 methylbenzene RTECS XS5250000	C_7H_8	92.14	110.6	28.4	3.79	0.867
vinyltoluene[b]	C_9H_{10}	118.18	167.7	1.6	0.22	0.898
CAS #25013-15-4	(meta)		171.6	1.9	0.26	0.911
methylstyrene (p-vinyltoluene)	(para)		172.8	1.8	0.24	0.911
methylvinylbenzene	(ortho)		169.8	1.8	0.24	0.904
RTECS WL5075000						
xylene[c]	C_8H_{10}	106.17				
CAS #1330-20-7	(ortho)		144.4	6.7	0.89	0.880
dimethylbenzene (p-xylene)	(meta)		139.1	8.4	1.12	0.864
RTECS ZE2100000	(para)		138.4	8.8	1.18	0.861

[a] Melting point.
[b] Commercial mixture of meta and para isomers.
[c] Mixture of isomers.

TABLE 2. PERMISSIBLE EXPOSURE LIMITS, PPM [6-8].

Substance	OSHA TWA	NIOSH TWA	NIOSH C	NIOSH STEL	ACGIH TLV	ACGIH STEL	mg/m³ per ppm
benzene	1	0.1[c]	1		10[f]		3.19
p-tert-butyltoluene	10	10		20	1		6.06
cumene	50 (skin)	50 (skin)			50 (skin)		4.91
ethylbenzene	100	100		125	100	125	4.34
α-methylstyrene	100	50		100	50	100	4.83
naphthalene	10	10[d]		15	10	15	5.24
styrene	100	50		100	50**	100 (skin)	4.26
toluene	200	100		150	50 (skin)		3.77
vinyltoluene	100	100			50	100	4.83
xylene	100	100[e]		150	100	150	4.34

[a] Maximum duration 10 min in 8 h.
[b] Maximum duration 5 min in any 3 h.
[c] Potential carcinogen
[d] Group III Pesticide
[e] Group I Pesticide
[f] Suspect carcinogen

TABLE 3. SAMPLING FLOWRATE[a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [3,4,9].

Substance	Sampling Flowrate (L/min)	Sampling Volume[b] (L) MIN	Sampling Volume[b] (L) MAX	Breakthrough Volume @ Concentration (L)	Breakthrough Volume @ Concentration (mg/m³)	Range at VOL-MIN (mg/m³)	Overall Bias (%)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (±%)
benzene	≤0.20	5	30	>45	149	42- 165	−0.4	0.059	11.4
p-tert-butyltoluene	≤0.20	1	29	44	112	29- 119	−10.3	0.071[d]	20.7
cumene	≤0.20	1	30	>45	480	120- 480	5.6	0.059	15.2
ethylbenzene	≤0.20	1	24	35	917	222- 884	−7.6	0.089[d]	17.1
α-methylstyrene	≤0.20	1	30	>45	940	236- 943	−7.6	0.061[d]	16.9
naphthalene[e]	≤1.0	100	200	>240	81	19- 83	−2.6	0.055	11.5
styrene	≤1.0	1	14	21	1710	426-1710	−7.9	0.058[d]	16.7
toluene	≤0.20	1	8	12	2294	548-2190	1.6	0.052	10.9
vinyltoluene	≤0.20	1	24	36	952	256- 970	−7.0	0.061[d]	16.3
xylene	≤0.20	2	23	35	870	218- 870	−1.2	0.060	12.2

[a] Minimum recommended flow is 0.01 L/min.
[b] V_{Min} = minimum sample volume @ OSHA TWA;
V_{Max} = maximum sample volume @ OSHA TWA
[c] 10-min sample.
[d] Corrected value, calculated from data in Reference 9.
[e] Naphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.
[f] 15-min sample.
[g] 5-min sample.

TABLE 4. MEASUREMENT RANGE, PRECISION AND CONDITIONS[a] [3,4,9].

Substance	Desorption Volume (mL)	Measurement Range (mg)	Measurement Precision ($\bar{S}_r$)	Carrier Flow (mL/min)	Column Parameters[b] t (°C)	Column Parameters[b] Length (m)	Column Parameters[b] Packing[c]
benzene	1.0	0.09- 0.35	0.036	50	115	0.9	A
p-tert-butyltoluene	0.5	0.27- 1.09	0.021[d]	50	115	3.0	B
cumene	0.5	0.86- 3.46	0.010	50	99	3.0	B
ethylbenzene	0.5	2.17- 8.67	0.010	50	85	3.0	B
α-methylstyrene	0.5	0.69- 3.57	0.011	50	115	3.0	B
naphthalene	1.0	4.96-19.7	0.019	30	125	3.0	C
styrene	0.5	2.17- 8.49	0.013[d]	50	109	3.0	B
toluene	1.0	1.13- 4.51	0.011	50	155	0.9	D
vinyltoluene	0.5	2.41- 9.64	0.008	50	120	3.0	B
xylene	1.0	2.60-10.4	0.010	50	180	0.9	D

[a] Injection volume, 5.0 μL; nitrogen carrier gas.
[b] All columns stainless steel, 3.2-mm outside diameter.
[c] A, 50/80 mesh Porapak P; B, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS; C, 10% OV-101 on 100/120 mesh Supelcoport; D, 50/80 mesh Porapak Q.
[d] Corrected value, calculated from data in [9].

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1003, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : See TABLE 1
NIOSH: See TABLE 1
ACGIH: See TABLE 1

PROPERTIES: See TABLE 2

COMPOUNDS:	benzyl chloride	chlorobromomethane	1,1-dichloroethane	1,1,1-trichloroethane
(synonyms	bromoform	chloroform	1,2-dichloroethylene	tetrachloroethylene
in Table 1)	carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	1,1,2-trichloroethane
	chlorobenzene	p-dichlorobenzene	hexachloroethane	1,2,3-trichloropropane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: see EVALUATION OF METHOD [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD [1]

ACCURACY: see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 4

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 3; alternates are SP-2100, Sp-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: standard solutions of analyte in CS_2

RANGE: Table 4

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\hat{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: See Table 2 for working ranges. This method can be used for simultaneous determination of two or more substances suspected to be present by changing gas chromatographic conditions (i.e., temperature program). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interferences.

OTHER METHODS: This method combines and replaces P&CAM 127 [3], S101 [4], S110 [5], S113 [6], S114 [7], S115 [8], S122 [9], S123 [10], S126 [11], S133 [12], S134 [13], S135 [14], S281 [15], S314 [16], S328 [17], S335 [18], S351 [19], and Method 1003 (dated 2/15/84).

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Analyte, reagent grade.
3. Calibration stock solutions:
   a. benzyl chloride, 10 mg/mL in n-heptane.
   b. bromoform, 10 mg/mL in n-hexane.
   c. o-dichlorobenzene, 200 mg/mL in acetone.
   d. p-dichlorobenzene, 300 mg/mL in acetone.
   e. hexachloroethane, 25 mg/mL in toluene.
4. Decane, n-undecane, octane or other internal standards (see step 6).
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (e.g., SKC #226-01).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (see Table 3).
4. Vials, 2-mL, glass, PTFE-lined septum crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Pipet, TD, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). Work with it only in a hood. Several of the analytes are suspect carcinogens (Table 1). n-Heptane, n-hexane, and acetone are fire hazards.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size between the limits shown in Table 2.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as decane [16], n-undecane [6,19], or octane [9,13,17] at 0.1% (v/v) may be added at this step and step 8.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (Table 3).
   a. Add known amounts of neat analyte or calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of pure analyte, or calibration stock solution (see REAGENTS, 3.), directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1 and in Table 3. Inject sample aliquot either manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Laboratory testing was performed with spiked samples and generated atmospheres using SKC Lot 105 coconut shell charcoal [1]. Results were:

Compound	Range mg/m³	Sample Size	Bias %	Precision Overall	Precision Measurement	Accuracy ±%	Desorption Efficiency	Ref.
Benzyl chloride	2-8	10 L	−8.4	0.096	0.031	25.6	0.90 @ 0.03-0.1 mg	[8]
Bromoform	3-10	10 L	−1.3	0.071	0.043	14.0	0.80 @ 0.025 mg	[7]
Carbon tetrachloride	65-299	15 L	−1.6	0.092	0.037	18.0	0.96 @ 1.3-4.8 mg	[16]
Chlorobenzene	183-736	10 L	0.3	0.056	0.025	11.0	0.91 @ 1.8-7.1 mg	[12]
Chlorobromomethane	640-2655	5 L	3.4	0.061	0.051	14.0	0.94 @ 3.3-13 mg	[6]
Chloroform	100-416	15 L	1.3	0.057	0.047	11.6	0.97 @ 1.8-7.4 mg	[19]
o-Dichlorobenzene	150-629	3 L	−1.9	0.068	0.013	13.7	0.86 @ 0.5-1.9 mg	[14]
p-Dichlorobenzene	183-777	3 L	−4.3	0.052	0.022	12.5	0.91 @ 0.7-2.7 mg	[15]
1,1-Dichloroethane	212-838	10 L	2.6	0.057	0.011	12.4	1.01 @ 1.9-8 mg	[10]
1,2-Dichloroethylene*	475-1915	3 L	−2.9	0.052	0.017	11.3	1.00 @ 2.4-9.5 mg	[5]
Ethylene dichloride	195-819	3 L	−2.0	0.079	0.012	15.7	0.96 @ 0.6-2.5 mg	[9]
Hexachloroethane	5-25	10 L	−6.6	0.121	0.014	25.4	0.98 @ 0.05-0.2 mg	[4]
1,1,1-Trichloroethane	904-3790	3 L	−0.6	0.054	0.018	10.6	0.99 @ 2.9-11 mg	[17]
Tetrachloroethylene	655-2749	3 L	−7.2	0.052	0.013	15.1	0.96 @ 2.1-8 mg	[18]
1,1,2-Trichloroethane	26-111	10 L	−9.0	0.057	0.010	17.5	0.97 @ 0.3-1.2 mg	[13]
1,2,3-Trichloropropane	163-629	10 L	2.1	0.068	0.027	14.2	0.95 @ 1.5-6 mg	[11]

*isomer used (i.e., cis- or trans-) in evaluation unknown.

REFERENCES:

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[2] User check, UBTL, NIOSH Sequences #3990-T, 3990-U and 3990-W (NIOSH, unpublished, November 3, 1983) and 4304-J (NIOSH, unpublished, April 3, 1984).
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[5] Ibid., S110.
[6] Ibid., S113.
[7] Ibid., S114.
[8] Ibid., S115.
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[10] Ibid., S123.
[11] Ibid., S126.
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[28] Criteria for a Recommended Standard...Occupational Exposure to Tetrachloroethylene (Perchloroethylene), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-185 (1976).

METHOD REVISED BY:

G. David Foley and Yvonne T. Gagnon, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

TABLE 1. GENERAL INFORMATION.

Compound RTECS	Synonyms	OSHA/NIOSH/ACGIH (ppm)
Benzyl chloride[a] ($C_6H_5CH_2Cl$); XS8925000	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1/C 1.0/1
Bromoform ($CHBr_3$); PB5600000	tribromomethane; CAS #75-25-2	0.5 (skin)/0.5 (skin)/0.5 (skin)
Carbon tetrachloride[ab] (CCl_4); FG4900000	tetrachloromethane; CAS #56-23-5	10, C 25/STEL 2 (1 h)/5 (skin)
Chlorobenzene (C_6H_5Cl); CZ0175000	monochlorobenzene; phenyl chloride; CAS #108-90-7	75/--/10
Chlorobromomethane (CH_2BrCl); PA5250000	bromochloromethane; Halon 1011; CAS #74-97-5	200/200/200
Chloroform[ab] ($CHCl_3$); FS9100000	trichloromethane; CAS #67-66-3	C 50/STEL 2/10
o-Dichlorobenzene[c] (1,2-$C_6H_4Cl_2$); CZ4500000	1,2-dichlorobenzene; CAS #95-50-1	50/C 50/25 (skin); STEL 50
p-Dichlorobenzene[ac] (1,4-$C_6H_4Cl_2$); CZ45500000	1,4-dichlorobenzene; CAS #106-46-7	75/1.7 (LOQ)/75, STEL 110
1,1-Dichloroethane (CH_3CHCl_2); KI0175000	ethylidene chloride; CAS #75-34-3	100/100/100
1,2-Dichloroethylene (ClCH=CHCl); KV9360000	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200/200/200
Ethylene dichloride[ab] ($ClCH_2CH_2Cl$); KI0525000	1,2-dichloroethane; CAS #107-06-2	50, C 100/1, STEL 2/10
Hexachloroethane[ac] (CCl_3CCl_3); KI4025000	perchloroethane; CAS #67-72-1	1 (skin)/1/1 (skin)
1,1,1-trichloroethane (CH_3CCl_3); KJ2975000	methyl chloroform; CAS #71-55-6	350/C 350/350, STEL 450
Tetrachloroethylene[ab] ($Cl_2C=CCl_2$); KX3850000	perchloroethylene; CAS #127-18-4	100, C 200, P 300/0.4 (LOQ)/ 25, STEL 100
1,1,2-Trichloroethane[ad] (Cl_2CHCH_2Cl); KJ3150000	vinyl trichloride; CAS #79-00-5	10 (skin)/10 (skin)/10 (skin)
1,2,3-Trichloropropane[a] ($CH_2ClCHClCH_2Cl$); TZ9275000	allyl trichloride; glycerol trichlorohydrin; CAS #96-18-4	50/10 (skin)/10 (skin)

[a]Suspect carcinogen [20,21,22]; [b]Group I Pesticide; [c]Group II Pesticide; [d]Group III Pesticide

TABLE 2. PHYSICAL PROPERTIES

Compound RTECS	M.W.	mg/m^3 = 1 ppm @ NTP	Synonyms	Properties
Benzyl chloride ($C_6H_5CH_2Cl$)	126.58	5.17	(chloromethyl) benzene; -chlorotoluene	liquid; BP 179 °C; MP −48 to −43 °C; d 1.100 @ 20 °C; flash pt. 67 °C
Bromoform ($CHBr_3$)	252.75	10.33	tribromomethane	liquid, d 2.887; BP 148 °C; nonflammable
Carbon tetrachloride (CCl_4)	153.84	6.29	tetrachloromethane	liquid; d 1.585; BP 76.7 °C; FP −23.0 °C; VP 91.3 mm @ 20 °C; vapor density (air = 1) 5.3
Chlorobenzene (C_6H_5Cl)	112.56	4.60	monochlorobenzene; phenyl chloride	liquid; d 1.105 @ 25 °C; BP 131.6 °C; MP −45 °C; flash pt. 29.4 °C (CC)
Chlorobromomethane (CH_2BrCl)	129.39	5.29	bromochloromethane; Halon 1011	liquid; d 1.93 @ 20 °C; BP 68 °C; MP −88 °C; nonflammable
Chloroform ($CHCl_3$)	119.39	4.88	trichloromethane	liquid, d 1.485 @ 20 °C; BP 61.2 °C; FP -63.5 °C
o-Dichlorobenzene (1,2-$C_6H_4Cl_2$)	147.00	6.01	1,2-dichlorobenzene	liquid; d 1.284; BP 172 to 179 °C; FP −17 °C; flash pt. 65.5 °C
p-Dichlorobenzene (1,4-$C_6H_4Cl_2$)	147.00	6.01	1,4-dichlorobenzene	solid crystals; d 1.458; BP 173.7 °C; MP 53 °C; sublimes; flash pt. 65.5 °C
1,1-Dichloroethane (CH_3CHCl_2)	98.95	4.05	ethylidene chloride	liquid, d 1.174 @ 20 °C; BP 57 to 59 °C; FP −98 °C
1,2-Dichloroethylene (ClCH=CHCl)	96.94	3.96	acetylene dichloride; 1,2-dichloroethene	liquid; transisomer; d 1.257; BP 47 to 49 °C; MP −57°C; cis-isomer; d 1.282; BP 58 to 60 °C; flash pt. 3.9 °C; FP −80 °C
Ethylene dichloride ($ClCH_2CH_2Cl$)	98.96	4.05	1,2-dichloroethane	liquid; d 1.2554 @ 20 °C; BP 83.5 °C; FP −35.5 °C; flash pt. 13 °C; explosive limits in air 6 to 16%
Hexachloroethane (CCl_3CCl_3)	236.74	9.66	perchloroethane	solid; d 2.091; MP 185 °C; BP sublimes at 187 °C
1,1,1-trichloroethane (CH_3CCl_3)	133.42	5.45	methyl chloroform	liquid; d 1.325; BP 75 °C; FP −30.4 °C; nonflammable
Tetrachloroethylene ($Cl_2C=CCl_2$)	165.83	6.78	perchloroethylene	liquid; d 1.625 @ 20 °C; BP 121 °C; FP −22.4 °C
1,1,2-Trichloroethane (Cl_2CHCH_2Cl)	133.41	5.45	vinyl trichloride	liquid; d 1.4432 @ 20 °C; BP 113.7 °C; FP −36.4 °C; VP 19 mm Hg @ 20 °C
1,2,3-Trichloropropane ($CH_2ClCHClCH_2Cl$)	147.43	6.03	allyl trichloride; glycerol trichlorohydrin	liquid; d 1.3888 @ 20 °C; BP 156.2 °C; FP −15 °C; flash pt. 82.2 °C (OC)

TABLE 3. SAMPLING LIMITS.

Compound	Air Sample Volume (L)			Working Range, ppm, at Max Sample Volume
	Min	Max	Target	
Benzyl chloride	6 @ 1 ppm	50	10	0.6 to 5.8
Bromoform	4 @ 0.5 ppm	70	10	0.2 to 4
Carbon tetrachloride	3 @ 10 ppm	150	15	2 to 105
Chlorobenzene	1.5 @ 75 ppm	40	10	10 to 430
Chlorobromomethane	0.5 @ 200 ppm	8	5	18 to 450
Chloroform	1 @ 50 ppm	50	15	2 to 190
o-Dichlorobenzene	1 @ 50 ppm	60	3	16 to 1100
p-Dichlorobenzene	1 @ 75 ppm	10	3	27 to 330
1,1-Dichloroethane	0.5 @ 100 ppm	15	10	4 to 250
1,2-Dichloroethylene	0.2 @ 200 ppm	5	3	16 to 560
Ethylene dichloride	1 @ 50 ppm	50	3	16 to 1320
Hexachloroethane	3 @ 1 ppm	70	10	0.3 to 8.3
1,1,1-Trichloroethane	0.1 @ 350 ppm	8	3	18 to 1450
Tetrachloroethylene	0.2 @ 100 ppm	40	3	9 to 1900
1,1,2-Trichloroethane	2 @ 10 ppm	60	10	1.8 to 64
1,2,3-Trichloropropane	0.6 @ 50 ppm	60	10	3 to 310

TABLE 4. MEASUREMENT PARAMETERS.

Compound	Column*	Temp. (°C) Column/Injector/Detector	Range (mg per sample)
Benzyl chloride	A	160/170/210	0.02 to 0.15
Bromoform	A	130/170/210	0.02 to 0.15
Carbon tetrachloride	B	60/155/200	0.2 to 7
Chlorobenzene	A	105/190/250	0.4 to 10
Chlorobromomethane	A	80/170/210	0.5 to 15
Chloroform	B	75/155/200	0.4 to 11
o-Dichlorobenzene	C	140/225/250	0.1 to 3
p-Dichlorobenzene	A	140/225/275	0.2 to 4
1,1-Dichloroethane	A	50/100/175	0.4 to 12
1,2-Dichloroethylene	A	60/170/210	0.2 to 7
Ethylene dichloride	C	70/225/250	0.1 to 4
Hexachloroethane	D	110/170/210	0.02 to 0.3
1,1,1-Trichloroethane	C	70/225/250	0.6 to 17
Tetrachloroethylene	C	90/225/250	0.4 to 12
1,1,2-Trichloroethane	C	70/250/225	0.05 to 2
1,2,3-Trichloropropane	E	160/180/230	0.3 to 9

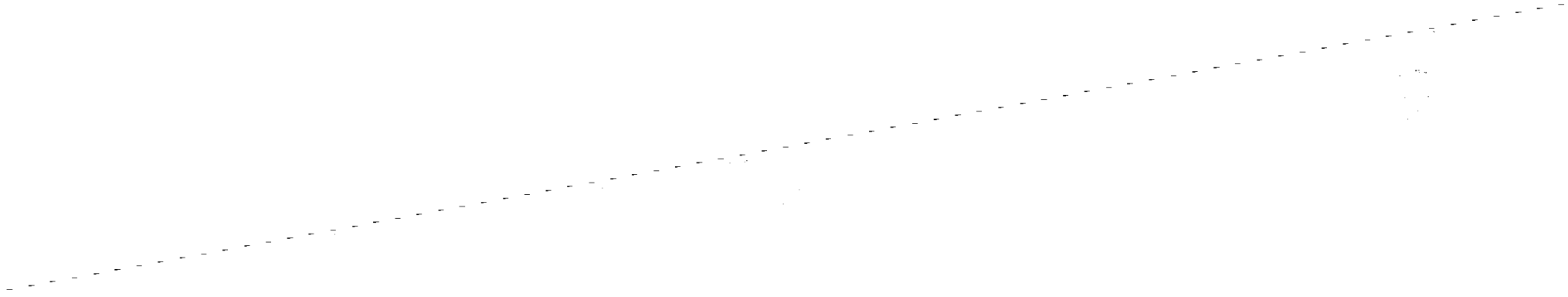
*A = 3 m x 3-mm OD stainless steel, 10% SP-1000 on 80/100 mesh Chromosorb WHP.
B = 6 m x 3-mm OD, otherwise same as A.
C = 3 m x 3-mm OD stainless steel, 10% OV-101 on 100/120 mesh Chromosorb WHP.
D = 3 m x 6-mm OD glass, 3% SP-2250 on 80/100 mesh Chromosorb WHP.
E = 3 m x 3-mm OD stainless steel, 10% FFAP on 80/100 mesh Chromosorb WHP.

HYDROCHLORIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure

HYDROFLUORIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure



HYDROGEN CYANIDE 6010

HCN MW: 27.03 CAS: 74-90-8 RTECS: MW6825000

METHOD: 6010, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: STEL 4.7 ppm
ACGIH: C 10 ppm (skin)
(1 ppm = 1.105 mg/m^3 @ NTP)

PROPERTIES: gas; BP 26 °C; vapor density 0.93 (air = 1.00); d(liq) 0.69 g/mL @ 20 °C; VP 82.7 kPa (620 mm Hg) @ 20 °C; explosive range 5 to 40% v/v in air

SYNONYMS: hydrocyanic acid, prussic acid, formonitrile

SAMPLING

SAMPLER: SOLID SORBENT TUBE (soda lime, 600 mg/200 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 2 L @ 5 ppm
-MAX: 90 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 15 mg/m^3 [1] (3-L samples)

BIAS: Not significant

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 15.0%

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: cyanide ion complex

DESORPTION: 10 mL deionized water; stand 60 min

COLOR DEVELOPMENT: N-chlorosuccinimide/ succinimide oxidizing agent and barbituric acid/pyridine coupling agent; absorption @ 580 nm in 1-cm cuvette

CALIBRATION: standard solutions of KCN in 0.1 N NaOH

RANGE: 10 to 300 µg CN^- per sample [1]

ESTIMATED LOD: 1 µg CN^- per sample [1]

PRECISION ($\bar{S}_r$): 0.041 @ 10 to 50 mg per sample [1]

APPLICABILITY: The working range is 0.3 to 235 ppm (3 to 260 mg/m^3) for a 3-L air sample. This method is applicable to STEL measurements. Particulate cyanides are trapped by the initial glass fiber membrane disk. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904, which uses ion specific electrode analysis. The method was used to determine HCN in firefighting environments [2].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference.

OTHER METHODS: This is based on the method of Lambert, et al. [3]. NIOSH Method 7904 uses an ion specific electrode for measurement. The method has been adapted for use with a Technicon Autoanalyzer [4].

REAGENTS:

1. Potassium cyanide*, reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectrophotometric quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, concentrated, reagent grade.
8. Sodium hydroxide (NaOH), reagent grade.*
9. Sodium lime (CaO + 5-20% NaOH), reagent grade (Aldrich #26,643-4 or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
10. Water deionized-distilled.
11. Sodium hydroxide solution, 0.1 N.*
12. Calibration stock solution. 1 mg /mL CN^-. Dissolve 0.125 g KCN in 0.1 N NaOH in a 50-mL volumetric flask. Dilute to mark with 0.1 N NaOH. Standardize by titration with standard $AgNO_3$ solution.
13. Hydrochloric acid solution, 0.15 N.
14. N-Chlorosuccinimide/succinimide oxidizing reagent. Dissolve 10.0 g succinimide in about 200 mL distilled water. Add 1.00 g N-chlorosuccinimide. Stir to dissolve. Adjust volume to 1 liter with distilled water. Stable 6 months when refrigerated.
15. Barbituric acid/Pyridine reagent. Add about 30 mL distilled water to 6.0 g barbituric acid in a 100-mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust the volume to 100 mL with water. Stable 2 months when refrigerated.

EQUIPMENT:

1. Sampler, glass tube, 9 cm long, 7-mm OD, 5-mm ID, with plastic caps, containing two sections (front = 600 mg; back = 200 mg) granular soda lime 10/35 mesh, separated and contained with silanized glass wool plugs, with a 5-mm diameter glass fiber filter disk placed before the plug on inlet side. Tubes are commerically available. (SKC, Inc. 226-28 or equivalent.)
2. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm light path.
3. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
4. Pipets, volumetric 0.1-, 0.5-, 1.0-, 2.0-, 10.0-mL.
5. Vials, glass or plastic, 15-mL with PTFE-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Syringes, 10-μL, readable to 0.1 μL.
9. Flask, Erlenmeyer, 100-mL.
10. Syringes, 10-mL, polyethylene with luer tip.
11. Filter cassette, with membrane filter, 13-mm diameter, 0.45-μm pore size, with luer fitting.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [5]. Soda lime and NaOH are very caustic [5]. Use gloves and a fume hood for handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
4. Cap tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
6. Transfer front and back sorbent sections to separate vials. Discard glass wool plugs separating and retaining sorbent sections.
   NOTE: An estimate of particulate cyanide may be obtained by analyzing the initial glass fiber filter disk as follows; however, no evaluation data are available for particulate cyanides determined in this manner.
   (i) Transfer the glass wool plug at the tube inlet and the glass fiber filter disk immediately behind it to a third vial.
   (ii) Add 10.0 mL 0.1 N NaOH to each vial.
   (iii) Proceed with step 8.
7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section. Cap each vial.
8. Allow to stand 60 minutes, with occasional agitation. Transfer to a 10-mL plastic syringe fitted with an in-line 0.45-μm filter. Collect the filtrate in a clean vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 1 to 300 μg CN^- per sample.
   a. Prepare a working standard solution, 1.00 μg /mL CN^-, by diluting 100 μL of calibration stock solution to 100 mL with 0.1 N NaOH.
   b. Pipet 0.5-, 1.00-, 1.50-, 2.00- and 2.50-mL of the working standard solution into 25-mL volumetric flasks to make 0.50-, 1.00-, 1.50-, 2.00- and 2.50- μg CN^- standards.
   c. Analyze together with field samples and blanks (steps 12 through 19).
   d. Prepare calibration graph (absorbance vs. μg CN^-).
10. Determine desorption efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a blank sampler.
   b. Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
   c. Cap, and allow to stand overnight.
   d. Desorb (steps 5 through 8) and analyze together with working standards and blanks (steps 12 through 19).
   e. Prepare a graph of DE vs. μg CN^- recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set spectrophotometer according to manufacturer's recommendations and to conditions on p. 6010-1.
13. Pipet a sample aliquot estimated to contain 0.5 to 2.5 μg CN^- into a 25-mL volumetric flask. Alternately, to cover an unknown sample concentration range, pipet 0.5-, 1.00-, and 3.00-mL aliquots into separate 25-mL vol. flasks for each field sample. Larger or smaller aliquots may be taken, based on prior knowledge of expected analyte level.
14. Pipet 0.5 mL 0.1 N NaOH into a 25-mL volumetric flask for reagent blank.
15. Add one drop phenolphthalein solution to each standard or sample.
   NOTE: Add a little deionized-distilled water to increase volume for easier mixing. All solutions should be alkaline (pink) at this point.
16. Starting with the reagent blank, add dropwise 0.15 N HCl, with mixing, until pink color just disappears. CAUTION: HCN may be produced. Work in hood. Immediately add 1.0 mL N-chlorosuccinimide/succinimide oxidizing reagent. Mix and let stand.

NOTE 1: To avoid possible loss of HCN, add the oxidizing agent before proceeding to the next sample.

NOTE 2: Do not prepare more samples than can be analyzed within the 30-minute maximum time for color development.

17. After at least 5 min. standing (but not longer than 15 min), starting with the reagent blank, add 1.0-mL barbituric acid-pyridine coupling reagent. Mix.
18. Adjust sample volume to 25 mL with deionized-distilled water and allow to stand at least 12 min (but not longer than 30 min) for color development.
19. Read absorbance at 580 nm in a 1-cm light path cuvette on a spectrophotometer. If sample absorbance is outside the range of the calibration standards, take an aliquot, re-analyze (steps 12 through 19), and apply the appropriate aliquot factor in calculations.

CALCULATIONS:

20. Calculate the mass, μg, of CN^- in aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, μg, of CN^- in the original 10-mL solution.
21. Determine the mass, μg CN^- (corrected for DE), found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections. If $W_b > W_f/10$, report breakthrough and possible sample loss.
22. Calculate concentration, C, of HCN in the air volume sampled, V(L).

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.039}{V}, \text{ mg/m}^3.$$

where 1.039 = conversion factor, CN^- to HCN

EVALUATION OF METHOD:

The method was evaluated by sampling the test atmospheres of HCN generated from a compressed mixture of HCN in nitrogen [1]. The range of HCN concentration was equivalent to 2 to 15 mg/m^3 for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision $\hat{S}_{rT}$ of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at the flow rate of 0.2 L/min at an HCN concentration of 148 mg/m^3. Sample tubes spiked with solutions of KCN and analyzed after storage, indicated that the samples of cyanide ions were stable on the tube for at least 2 weeks. Analysis of 22 tubes which were spiked with KCN standard solutions in the range 10 to 50 μg indicated a recovery of nearly 100% with a pooled precision of 0.041. Desorption efficiency may be poor below 10 μg CN^- [6].

REFERENCES:

[1] Williamson, George. "Method Development Protocol and Backup Data Report on Hydrogen Cyanide" Internal NIOSH/MRSB Report, Unpubl. NIOSH (1988).
[2] Williamson, George. "Analysis of Air Samples on Project 166 (Firesmoke) on HCN; Sequence NIOSH/MRSB-6366A, Unpubl. NIOSH, (1988).
[3] Lambert, J. L., Ramasamy, J., and J. V. Paukstelis, "Stable Reagents for the Colorimetric Determination of Cyanide by Modified Konig Reactions," Analyt. Chem., 47, 916-918 (1975).
[4] DataChem Laboratories, NIOSH Sequence #6837-K (unpublished, March 21, 1990).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services. Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 form NTIS, Springfield, VA 22161.
[6] DataChem Laboratories, User Check, NIOSH Sequence #6837-J (unpublished, March 19, 1990).

METHOD WRITTEN BY: George Williamson, NIOSH/DPSE.

HYDROGEN SULFIDE 6013

H_2S MW: 34.08 CAS: 7783-06-4 RTECS: MX1225000

METHOD: 6013, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 20 ppm; P 50 ppm/10 min
NIOSH: C 10 ppm/10 min
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 1.39 mg/m^3 @ NTP)

PROPERTIES: gas; d (liq) 1.54 g/mL @ 0 °C; BP - 60 °C; VP 20 atm @ 25 °C; vapor density (air=1) 1.19; explosive range 4.3 to 46% v/v in air

SYNONYMS: sulfuretted hydrogen; hydrosulfuric acid; hepatic gas; stink damp

SAMPLING	
SAMPLER:	FILTER + SOLID SORBENT TUBE (Zefluor, 0.5 μm; coconut shell charcoal, 400 mg/200 mg)
FLOW RATE-RANGE:	0.1 to 1.5 L/min
-RECOMMENDED:	0.2 L/min
VOL-MIN:	1.2 L @ 10 ppm
-MAX:	40 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 30 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY	
RANGE STUDIED:	1.4 to 22.0 mg/m^3 [1] (20-L samples)
BIAS:	− 0.17% [1]
OVERALL PRECISION ($\bar{S}_{rT}$):	0.059 [1]
ACCURACY:	± 11.6%

MEASUREMENT	
TECHNIQUE:	ION CHROMATOGRAPHY, CONDUCTIVITY
ANALYTE:	sulfate ion
DESORPTION:	2 mL 0.2 M NH_4OH + 5 mL 30% H_2O_2
INJECTION VOLUME:	50 μL
ELUENT:	40 mM NaOH, 1.5 mL/min
COLUMN:	Ion-Pac AS4A separator, AG4A guard
CALIBRATION:	SO_4^{2-} in deionized water
RANGE:	17 to 200 μg per sample
ESTIMATED LOD:	11 μg per sample
PRECISION ($\bar{S}_r$):	0.031 [1]

APPLICABILITY: The working range is 0.6 to 14 ppm (0.9 to 20 mg/m^3) for a 20-L air sample [1]. The method is applicable to 15-min samples taken at 1 L/min and 10-min samples taken at 1.5 L/min. The upper limit of loading depends on the concentrations of hydrogen sulfide and other substances in the air, including water vapor. High relative humidity (80%) increases the capacity of the sampler four-fold, relative to dry air.

INTERFERENCES: SO_2 is a positive interference, equivalent to H_2S by approximately twice the SO_2 concentration by weight. Methyl and ethyl mercaptans do not interfere [1].

OTHER METHODS: Alternate methods are S4 [2] which uses impinger collection, and P&CAM 296 [3] which uses a molecular sieve sampler but has poor stability.

REAGENTS:

1. Ammonium hydroxide solution, 25%.
2. Hydrogen peroxide, 30%.*
3. Sodium hydroxide, 50% (w/v).*
4. Extraction soln: 0.2 M NH_4OH.
5. Eluent: 40 mM NaOH. Dilute 4.16 mL of 50% NaOH to 2 L with deionized water (degassed).
6. Suppressor regenerant: 0.025 N H_2SO_4. Dilute 1.4 mL concentrated H_2SO_4 to 2 L with deionized water.*
7. Calibration Stock solution: 1 mg/mL (as anion). Dissolve 0.1814 g K_2SO_4 in 100 mL deionized water.
8. H_2S, calibration gas mixture, or permeation device.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg, back = 200 mg) separated by a 6-mm urethane foam plug. A silanized glass wool plug precedes the front section and a 6-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. Zefluor PTFE prefilter, 0.45-μm, 25-mm, with porous plastic support pad in 25-mm cassette.
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, conductivity detector, integrator and columns (page 6013-1).
4. Centrifuge tubes, 15-mL, plastic with screw caps.
5. Syringes, 10-mL, polyethylene with luer tip.
6. Syringe filters, 13-mm, 0.45-μm pore size.
7. Vials, autosampler, 4-mL, PTFE-lined caps.
8. Micropipettes, disposable tips.
9. Pipettes, 2-, 3-, 5-mL.
10. Volumetric flasks, 10-, 25-mL.
11. Vortex mixer (optional).

SPECIAL PRECAUTIONS: Hydrogen peroxide is a strong oxidizer causing burns to skin and mucous membranes. Sulfuric acid and sodium hydroxide are extremely corrosive to all body tissue. Wear protective clothing and eye protection. All work should be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler and attach prefilter with a small piece of flexible tubing immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 1.5 L/min for a total sample size of 15 to 40 L.
4. Cap the sorbent tubes with plastic caps and plug prefilter cassettes. Pack securely for shipment.

NOTE: The prefilters may be discarded or analyzed for particulate sulfates by, e.g., Method 6004.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate screw-top centrifuge tubes. Discard the glass wool and foam plugs.
6. Add 2.0 mL of 0.2 M NH_4OH and 5.0 mL H_2O_2 to each centrifuge tube. Attach screw cap and loosen 1/4 turn.
7. Allow to react at least 10 min. Tighten cap and shake for 30 s or vortex 10 s.
8. Dilute to 10 mL with 3 mL of deionized water. Cap and shake vigorously.
9. Transfer sample to 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.1 to 20 μg sulfate ion per mL of sample (1 to 200 μg per 10 mL).
    a. Add known amounts of calibration stock solution to deionized water in 10- or 25-mL volumetric flasks and dilute to the mark. Prepare fresh working standards biweekly.
    b. Analyze together with samples and blanks (steps 14 and 15).
    c. Prepare calibration graph (peak height vs. μg SO_4^{2-} per sample).
11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 10). Prepare four tubes at each of three levels plus three media blanks.
    a. Generate concentrations of H_2S from a calibration gas mixture or a permeation device. Mix with dilution air as necessary.
    b. Collect samples at a flow rate of 1 L/min for 30 min.
    c. Cap the tubes and allow to stand overnight.
    d. Desorb (steps 5 through 9) and analyze together with working standards (steps 14 and 15).
    e. Prepare a graph of DE vs. μg sulfate recovered.
12. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6013-1.
14. Inject a 50-μL sample aliquot manually or with autosampler.
15. Measure peak height.
    NOTE: If peak height is above the linear range of the working standards, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, μg (corrected for DE) of sulfate ion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of hydrogen sulfide in the air volume sampled, V (L), applying the factor 0.3548 (MW H_2S/MW SO_4^{2-}) for the conversion of SO_4^{2-} to H_2S:

$$C = \frac{0.3548\ (W_f + W_b - B_f - B_b)}{V},\ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated test atmospheres of H_2S in air [1]. Time-weighted average samples were taken at four concentration levels over a range of 1.4 to 22 mg/m^3 (1 to 16 ppm). For ceiling concentrations or short-term exposure limits, 15-L samples were collected at 1 L/min. Breakthrough was determined for coconut charcoal from a generated atmosphere at a concentration of 20 ppm (2 x PEL) and at both low (~20%) and high (~80%) relative humidity (RH). Breakthrough volumes for low and high RH were 21 L and 84 L, respectively, corresponding to capacities of 588 μg of H_2S (low RH) and 2352 μg of H_2S (high RH). At 1 x PEL, the equivalent breakthrough volume is 42 L (low RH) and 164 L (high RH). Large coconut charcoal tubes have sufficient capacity to collect a 4-h sample at the PEL of 10 ppm, as well as STEL samples (15 ppm for 15 min). H_2S samples are stable for at least 30 days. Recoveries, based on mass of H_2S found on samples analyzed on day 1, were 97.2% for ambient storage and 98.9% for refrigerated storage. The overall method for H_2S has a limit of detection of 11 μg per sample and a limit of quantitation of 17 μg per sample. A mean bias of -0.17%

was determined from the recoveries of six samples generated at each of four concentration levels (0.1, 0.5, 1 and 2 x PEL) with a precision ($\bar{S}_r$) of 0.031. The method had a total precision including pump error ($\bar{S}_{rT}$) of 0.059, and an estimate of overall error of ±11.6%.

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[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S4, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 296, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

HYDROQUINONE 5004

HOC_6H_4OH MW: 110.11 CAS: 123-31-9 RTECS: MX3500000

METHOD: 5004, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 mg/m^3
NIOSH: C 2 mg/m^3/15 min
ACGIH: 2 mg/m^3

PROPERTIES: solid; MP 170 °C; BP 285 °C @ 730 mm; VP 0.0024 Pa (1.8 x 10^{-5} mm Hg; 0.11 mg/m^3) @ 25 °C

SYNONYMS: 1,4-benzenediol; hydroquinol; quinol; 1,4-dihydroxybenzene.

SAMPLING

SAMPLER:	FILTER (0.8-μm cellulose ester membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	30 L @ 2 mg/m^3
-MAX:	180 L
FIELD TREATMENT:	transfer filter immediately to jar with 10 mL 1% acetic acid
SHIPMENT:	ship sample solutions
SAMPLE STABILITY:	at least 7 days @ 25 °C
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.8 to 4 mg/m^3 [1] (90-L samples)
BIAS:	4.4%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.061
ACCURACY:	± 15.0%

MEASUREMENT

TECHNIQUE:	HPLC, UV DETECTION
ANALYTE:	hydroquinone
EXTRACTION:	1% acetic acid, 10 mL
INJECTION VOLUME:	100 μL
MOBILE PHASE:	1% acetic acid in H_2O; 1 mL/min
COLUMN:	25 cm x 4.6-mm ID Partisil 10-ODS, μ-Bondapack C_{18} or equivalent; ambient temperature, 400 to 600 psi (2800-4100 kPa)
DETECTOR:	UV @ 290 nm
CALIBRATION:	solutions of hydroquinone in 1% aqueous acetic acid
RANGE:	0.06 to 0.8 mg per sample [2]
ESTIMATED LOD:	0.01 mg per sample [3]
PRECISION ($\bar{S}_r$):	0.030 [1]

APPLICABILITY: The working range is 0.7 to 8 mg/m^3 for a 90-L air sample or 2 to 25 mg/m^3 for a 30-L air sample. This method can be used when significant concentrations of hydroquinone vapor are not present.

INTERFERENCES: None known. Hydroquinone is unstable on the collection media and must be stabilized immediately after collection by dissolution in 1% acetic acid.

OTHER METHODS: This is Method S57 [2] in a revised format. The method also appears in a NIOSH recommended standard [4].

REAGENTS:

1. Hydroquinone, reagent grade.
2. Distilled water.
3. Acetic acid, glacial.
4. Acetic acid, 1%. Dilute 10 mL acetic acid to 1 L with distilled water.
   NOTE: This solution is needed at the sampling site for field treatment of samples.
5. Calibration stock solution, 3.6 mg/mL. Dissolve 0.0900 g hydroquinone in 25 mL 1% acetic acid. Prepare fresh daily, in duplicate.

EQUIPMENT:

1. Sampler: 37-mm cassette containing 0.8-μm cellulose ester membrane filter and cellulose backup pad.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with UV detector at 290 nm, integrator and column (page 5004-1).
4. Jars, 60-mL, ointment, low form, with PTFE film gaskets and screw caps.
5. Syringe, 100-μL, or autosampler for sample injection.
6. Microliter syringes for standard preparation.
7. Volumetic flasks, 10- and 25-mL, and 1-L.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 30 to 180 L.
   NOTE: This method will collect hydroquinone aerosol only. The equilibrium vapor pressure is equivalent to 0.11 mg/m^3 at 25 °C and may be a significant factor at elevated temperatures.
3. Immediately after sampling, transfer the filter (do not include backup pad) with tweezers to a 60-mL ointment jar. Add 10 mL 1% acetic acid. Process field blanks similarly.
4. Ship the filters in the ointment jars.

SAMPLE PREPARATION:

5. Transfer the sample solution from the ointment jar to a 25-mL volumetric flask.
6. Rinse the ointment jar twice with 5 mL 1% acetic acid. Add the washings to the volumetric flask. Make up to volume with 1% acetic acid.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.01 to 0.8 mg hydroquinone per sample.
   a. Add known amounts of calibration stock solution to 1% acetic acid in 25-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg hydroquinone).
8. Check recovery with at least three spiked media blanks per sample set.
   a. Add aliquot of calibration stock solution with a microliter syringe directly to a representative filter. Transfer filter to 60-mL ointment jar, add 10 mL 1% acetic acid, and allow to stand overnight.
   b. Prepare and analyze together with working standards (steps 5, 6, 9 and 10).
   c. Calculate recovery [(mg recovered - mg blank)/mg added)].

MEASUREMENT:

9. Set HPLC to conditions given on page 5004-1. Inject 100-mL sample aliquot.
10. Measure peak area. Retention time is ca. 5.2 min under these conditions.

CALCULATIONS:

11. Determine the mass, mg (corrected for recovery) of hydroquinone, found in the sample (W) and in the average media blank (B).
12. Calculate concentration of hydroquinone, C, in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{(V)}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S57 [2] was issued on November 26, 1976, and validated over the range 0.8 to 4 mg/m^3 at 20 °C and 762 mm Hg using 90-L air samples [1,5]. Overall precision, $\hat{S}_{rT}$, was 0.061 with average recovery 105%, representing a non-significant bias. The atmospheres were generated by atomization of an aqueous solution of hydroquinone into dry air; aerosol concentrations were independently verified by direct UV spectrophotometry on filter samples. Average collection efficiency was 100% at 4 mg/m^3. No loss of hydroquinone was seen from filters spiked with 720 μg hydroquinone, and then used to sample 180 L clean air, indicating the hydroquinone vapor pressure is not significant at these conditions. At elevated temperature, however, contribution from vapor may be significant. Storage studies were conducted by storing exposed filters in 1% acetic acid at ambient temperature for seven days. No change in hydroquinone concentration was seen.

REFERENCES:

[1] Backup Data Report No. S57, NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S57, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] User check, A. D. Little, Inc., NIOSH Sequence #4121Q (unpublished, October 25, 1983).
[4] Criteria For A Recommended Standard-Occupational Exposure to Hydroquinone, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-155 (1978).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

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IODINE

I_2 MW: 253.81 CAS: 7553-56-2 RTECS: NN1575000

METHOD: 6005, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : C 0.1 ppm
NIOSH: C 0.1 ppm; Group I Pesticide
ACGIH: C 0.1ppm
(1 ppm = 10.38 mg/m^3 @ NTP)

PROPERTIES: Solid; d (solid @ 25 °C) 4.93 g/mL;MP 113.6 °C; BP 185.2 °C; VP 40 kPa (0.305 mm Hg; 395 ppm) @ 25 °C; not combustible

SYNONYMS: None

SAMPLING

SAMPLER: SOLID SORBENT TUBE (alkali-treated charcoal, 100 mg/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 15 L @ 0.05 ppm
-MAX: 225 L

SHIPMENT: routine

SAMPLE STABILITY: 8 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 per sample set + 15 per lot of charcoal

ACCURACY

RANGE STUDIED: 0.74 to 2.1 mg/m^3 [1] (15-L air samples)

BIAS: − 5.7%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.085 [2]

ACCURACY: ± 22.4%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: iodide ion (I^-)

DESORPTION: 3 mL 10 mM Na_2CO_3

INJECTION LOOP VOLUME: 50 µL

ELUENT: 10 mM Na_2CO_3; 3 mL/min

COLUMNS: HPIC-AS4A anion separator; HPIC-AG4A anion guard; micromembrane suppressor

CONDUCTIVITY SETTING: 3 µS full scale

CALIBRATION: standard solutions of KI in eluent

RANGE: 8 to 200 µg I_2 per sample [1]

ESTIMATED LOD: 1 µg I_2 per sample [1]

PRECISION ($\hat{S}_r$): 0.071 @ 10 to 30 µg I_2 per sample [1]

APPLICABILITY: The working range is 0.05 to 5 ppm (0.5 to 50 mg/m^3) for a 15-L air sample. The method is applicable to 15-min ceiling measurements.

INTERFERENCES: Particulate iodide salts, HI, or organic iodides may give positive interferences, but collection of these compounds on treated charcoal has not been investigated. Iodate, other halogens, nitrate, phosphate, and sulfate do not interfere.

OTHER METHODS: Better sensitivity (ppb range) has been found using amperometric detection (AS1 column [2] or AG2 and AS2 columns [3]). An AS5 column using 6 mM Na_2CO_3/0.8 mM paracyanophenol in 2% acetonitrile as eluent and either conductometric or amperometric detection yielded the best sensitivity [2].

REAGENTS:

1. Deionized, filtered water with specific conductance ≤ 10 μS/cm.
2. Sodium carbonate (Na_2CO_3), reagent grade.
3. Potassium iodide (KI), reagent grade.
4. Iodine (I_2), reagent grade.*
5. Toluene, distilled in glass.
6. Eluent: 10 mM Na_2CO_3. Dissolve 4.240 g Na_2CO_3 in 4 L filtered, deionized water.
7. Calibration stock solution, 1000 μg/mL of I^-. Dissolve 0.1308 g KI in filtered, deionized water to make 100 mL solution.
8. Desorption Efficiency (DE) stock solution, 50 μg/μL. Dissolve 500 mg I_2 in toluene to make 10 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends and plastic caps, containing two sections of 20/40 mesh alkali-treated charcoal (Barnebey-Cheney Type 580-19) (front = 100 mg; back = 50 mg) separated by 2-mm urethane foam plug. A glass wool plug and metal retaining spring precede the front section and a 3-mm foam plug follows the back section. Pressure drop ≤ 2.1 kPa across the tube at 1.2 L/min airflow. Tubes are commercially available (SKC No. 226-67, SKC, Inc., Eighty-Four, PA, or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separator and guard columns, anion suppressor (page 6005-1), conductivity detector, integrator (optional) and strip chart recorder.
4. File, triangular.
5. Ultrasonic bath.
6. Vials, 20-mL, glass, with PTFE-lined screw caps.
7. Syringes, 3-mL, polyethylene with luer tip.
8. Filters, luer tip, with PTFE filter, 13-mm diameter, 5-μm pore size.
9. Volumetric flasks, 10-, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipets, 0.05- to 3-mL.
12. Syringe, 5-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Iodine is a severe irritant to the eyes and respiratory system and, to a lesser extent, the skin [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.0 L/min for a total sample size of 15 to 225 L.
4. Cap samplers. Pack securely for shipment.
   NOTE: Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate at room temperature.
6. Score sampler with a file in front of primary sorbent section. Break sampler at score line.
7. Transfer front sorbent section with glass wool plug to vial.
8. Place back sorbent section with foam plugs in separate vial.
9. Add 3.0 mL eluent to each vial. Cap immediately.

10. Agitate vials in ultrasonic bath for 2 min at room temperature.
11. Draw sample extract through 13-mm PTFE filter attached to 3-mL syringe.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging the system valves or columns.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least six working standards.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to prepare solutions containing 1 to 60 μg/mL of I^- (equivalent to 1.2 to 72 μg/mL of I_2). Store in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    b. Analyze working standards with samples and blanks (steps 15 through 17).
    c. Prepare calibration graph [peak height (mm or μS) vs. μg].
13. Determine desorption efficiency (DE) for each lot of charcoal used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place treated charcoal from unused front sorbent section in vial. Discard glass wool and backup section.
    b. Inject a known amount (2 to 5 μL) of DE stock solution, or a serial dilution thereof, onto charcoal with microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 9 through 11) and analyze together with standards (steps 15 through 17).
    e. Prepare a graph of DE vs. μg I_2 recovered.
14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

15. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6005-1.
16. Inject sample aliquot. For manual operation, inject 1 to 2 mL of sample to ensure complete rinse of sample loop, or use autosampler.
17. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply appropriate dilution factor in calculations.

CALCULATIONS:

18. Determine mass, μg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
19. Calculate concentration, C, of iodine in the air volume sampled, V (L):

$$C = \frac{1.2 \cdot (W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

where 1.2 = The stoichiometric factor arising from conversion of iodine to iodide on the sampler ($3\ I_2 + 6\ OH^- \rightarrow 3\ H_2O + 5\ I^- + IO_3^-$).

EVALUATION OF METHOD:

This method was optimized and evaluated by Southern Research Institute [1] and is based on a method developed by Kim et al. [5]. The method was evaluated over the range 0.74 to 2.11 mg/m^3 iodine in

15-L air samples with a pooled sampling and measurement precision, $\bar{S}_r$, of 0.062. The capacity of the 100-mg charcoal front section was at least 6 mg of iodine vapor. The total variance, $\hat{S}_{rT}$, including pump error, was 0.085. Overall average recovery based on 18 samples, six at each of three levels, was 90.8%. When corrected for desorption efficiency (0.962 in the range 0.0088 to 0.03 mg I_2 per sample), the recovery was 94.3%, representing an insignificant bias. Samples stored at ambient temperature for eight days were stable with recovery of 101.6% and a precision, S_r, of 0.103 based on samples analyzed on day one.

REFERENCES:

[1] Dillon, H. K., M. L. Bryant and W. K. Fowler. Methods Development for Sampling and Analysis of Chlorine, Chlorine Dioxide, Bromine and Iodine: Research Report for Iodine, Contract 210-80-0067, Southern Research Institute, Birmingham, AL, (1983), available as PB83-246595 from NTIS, Springfield, VA 22161 .

[2] The Determination of Iodide by Ion Chromatography, Application Note 37, Dionex Corporation, Sunnyvale, CA (February, 1982).

[3] Han, K., W. F. Koch and K. W. Pratt. Improved Procedure for the Determination of Iodide by Ion Chromatography with Electrochemical Detection, Anal. Chem. 59, 731-736(1987).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[5] Kim, W. S., J. D. McGlothlin and R. E. Kupel. Sampling and Analysis of Iodine in the Industrial Atmosphere, Am. Ind. Hyg. Assoc. J., 43, 187-190 (1981).

METHOD REVISED BY:

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IRON

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

ISOAMYL ACETATE

See ESTERS I (Method 1450) for procedure

ISOAMYL ALCOHOL

See ALCOHOLS III (METHOD 1402) for procedure

ISOBUTYL ACETATE

See ESTERS I (Method 1450) for procedure

ISOBUTYL ALCOHOL

See ALCOHOLS II (Method 1401) for procedure

		MW:	CAS:	RTECS:
2,4-TDI:	$CH_3C_6H_3(NCO)_2$	174.16	584-84-9	CZ6300000
2,6-TDI:	$CH_3C_6H_3(NCO)_2$	174.16	91-08-7	CZ6310000
MDI:	$CH_2(C_6H_4NCO)_2$	250.26	101-68-8	NQ9350000
HDI:	$OCN(CH_2)_6NCO$	168.20	822-06-0	MO1740000
NDI:	$C_{10}H_6(NCO)_2$	210.20	25551-28-4	NQ9600000

METHOD: 5521, Issue 2 **EVALUATION:** UNRATED **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA: Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

SAMPLER: IMPINGER (solution of 1-(2-methoxyphenyl)-piperazine in toluene)

FLOW RATE: 1 L/min

VOL-MIN: 5 L @ 35 μg TDI/m^3
-MAX: 500 L

SHIPMENT: ship in screw-cap vial refrigerated @ 4 °C or lower

SAMPLE STABILITY: may be unstable; perform steps 7 & 8 as soon as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not known
OVERALL PRECISION ($\hat{S}_{rT}$):	not known
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE: HPLC, ELECTROCHEMICAL AND UV DETECTION

ANALYTE: urea derivatives of isocyanates

SAMPLE PREP: acetylate excess reagent, evaporate toluene, redissolve in 5 mL CH_3OH

INJECTION VOLUME: 10 μL

MOBILE PHASE: acetonitrile (20% to 40%)/pH 6.0 methanolic buffer (80% to 60%) 1 mL/min; ambient temperature

COLUMN: Supelcosil, LC-8-DB, 3-μm particle size, 7.5 cm x 4.6-mm; 2-cm guard column, 10-μm particle size

DETECTOR: 242 nm; ECHD, + 0.80 V vs. Ag/AgCl

CALIBRATION: standard solutions of ureas in methanol

RANGE: 2,4-TDI: 0.5 to 8 μg per sample [1]
2,6-TDI: 0.7 to 10 μg per sample [1]
MDI: 0.3 to 4 μg per sample [1]
HDI: 1 to 15 μg per sample [1]
NDI: 0.2 to 13 μg per sample

ESTIMATED LOD: ca. 0.1 μg diisocyanate per sample [1]

PRECISION ($\hat{S}_r$): not determined

APPLICABILITY: The working range is from 5 μg/m^3 2,4-TDI, 7 μg/m^3 2,6-TDI, 3 μg/m^3 MDI, 1 μg/m^3 HDI, and 2 μg/m^3 NDI to more than 1 mg/m^3 for 100-L air samples. This method determines the air concentration of specific diisocyanates. The method has been applied to samples from general foaming, spray- or dip-painting industries [1].

INTERFERENCES: Any substance which elutes with the ureas and is electroactive will interfere with the analysis. Mobile phase conditions can be adjusted to separate most co-eluting peaks, however, ureas of HDI and TDI are difficult to separate.

OTHER METHODS: This method is a modification of Method MDHS 25 published by the Health and Safety Executive of Great Britain [2,3]. Method 2535 is an alternate method for TDI vapor, employing collection on glass wool impregnated with N-(4-nitrophenylmethyl)propylamine.

REAGENTS:

1. 1-(2-Methoxyphenyl)piperazine*, 98%.
2. Acetic anhydride, reagent grade.
3. Methanol, HPLC grade.
4. Acetonitrile, HPLC grade.
5. Water, deionized, distilled.
6. Sodium acetate, anhydrous
7. Acetic acid, glacial.
8. Nitrogen, 99.995%.
9. Toluene, HPLC grade.
10. Sampling medium, 1-(2-methoxyphenyl)-piperazine in toluene, 43 mg/L. (see APPENDIX A)
11. Ureas derived from the isocyanate. (See APPENDIX B).
12. Dimethyl sulfoxide, reagent grade.
13. Mobile phase, acetonitrile and buffer solution to achieve appropriate mobile phase.
14. Buffer solution. Dissolve 15 g anhydrous sodium acetate in 1 L distilled-deionized water. Add 1 L methanol. Add glacial acetic acid to bring pH to 6.0.
15. Urea calibration stock solution, 0.01 μg/μL urea in methanol.
16. Reagent calibration stock solution, 1.0 μg/μL 1-(2-methoxyphenyl)-piperazine in methanol.
17. Helium, prepurified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Midget impinger, 25-mL
2. Personal sampling pump, 1.0 L/min, with flexible connecting tubing free of phthalate plasticizer.
   NOTE: Avoid collection of plasticizer in the toluene during sampling. Fluran™ tubing is an acceptable, PVC tubing is not.
3. Liquid chromatograph (HPLC) with electrochemical (ECHD) detector (+0.80 V vs. Ag/AgCl), recorder, integrator and column (page 5521-1)
4. Ultrasonic water bath.
5. Vials, 4-mL glass, with screw caps and 20-mL glass, screw caps with cone-shaped polyethylene liner and shrinkable sealing bands.
6. Pasteur pipets, 7-cm glass, disposable.
7. Flasks, volumetric, glass, 10-mL
8. Syringes, sizes appropriate for preparing standard solutions.
9. Pipets, 5- and 15-mL glass, delivery, with pipet bulb.
10. Hot plate, spark free, 60 °C.
11. Evaporator, Mini-Vap, 6-port or equivalent.
12. pH meter.
13. Vacuum oven.
14. Buchner funnel, fritted glass, medium porosity, 100-mL.
15. Vacuum pump.
16. Flask, filtration, 500-mL.

SPECIAL PRECAUTIONS: Preparation of urea derivatives, samples, and standards should be done in a hood to avoid exposure to isocyanate and solvent vapors. Isocyanates are known respiratory irritants.[4] Toxicity of 1-(2-methoxyphenyl)piperazine is unknown.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL sampling medium to an impinger.
3. Connect the assembled impinger to a sampling pump.
4. Sample 5 to 500 L of air at 1.0 L/min.
   NOTE 1: Toluene evaporates during sampling; when level of solution drops below 10 mL, restore volume to 15 mL with toluene.
   NOTE 2: The reagent in the sampling medium reacts with isocyanates to form ureas:
   $$CH_3OC_6H_4NC_4H_8NH + R\text{-}N{=}C{=}O \rightarrow CH_3OC_6H_4NC_4H_8NC(=O)NHR$$
5. Prepare blank samples by transferring 15 mL sampling medium to 20-mL vials.
6. Transfer the sample solution to a 20-mL vial for shipment. Rinse both impinger parts with 2 to 3 mL toluene and add rinsings to the sample. Secure vial's screw cap with sealing band. Refrigerate samples as soon as possible. If samples are to be shipped, carefully pack the vials to avoid breakage or spillage of sample.

SAMPLE PREPARATION:

7. Add 25 μL acetic anhydride to acetylate the excess 1-(2-methoxyphenyl)piperazine remaining in the sample solution, to provide for efficient chromatography.
   NOTE: The acetylation reaction is:

$$CH_3OC_6H_4NC_4H_8NH + CH_3C(=O)OC(=O)CH_3 \rightarrow CH_3OC_6H_4NC_4H_8NC(=O)CH_3 + CH_3C(=O)OH$$

8. Evaporate the acetylated sample to dryness under a gentle stream of nitrogen while warming to 60 °C on a hotplate.
9. Redissolve the residue in 5.0 mL methanol, while agitating the sample in an ultrasonic water bath for 15 min.

CALIBRATION AND QUALITY CONTROL:

10. Prepare at least six working standards containing 0.01 to 4.0 μg/mL of the appropriate urea(s) (TDIU, HDIU, and/or MDIU) and 100 μg/mL of 1-(2-methoxyphenyl)piperazine by adding aliquots of calibration stock solutions to 2 mL methanol in a 10-mL volumetric flask. Add 10 μL acetic anhydride to each standard. Mix and dilute to the mark with methanol.
    NOTE: The standard solutions need include only ureas derived from the diisocyanates expected in the air samples.
11. Analyze working standards together with samples and blanks (steps 13 through 15). Prepare a calibration graph for the urea in terms of quantity of isocyanate, M (ECHD area vs. mmol of isocyanate group per sample). Molecular weights of typical ureas are: TDIU = 558.7 g/mol; MDIU = 634.8 g/mol; HDIU = 552.7 g/mol; NDIU = 594.7 g/mol.

$$M = \frac{(C) \cdot MW_I \cdot (5)}{MW_U}, \ \mu g/sample.$$

Where: M is the quantity of isocyanate per sample (μg)
C is the concentration of urea in the standard solution (μg/mL)
5 is the liquid volume of a sample (mL)
MW_u is the molecular weight of the urea
MW_I is the molecular weight of the isocyanate

12 Prepare control samples by adding 0.1, 1.0 and 10.0 μg of urea to 15 mL sampling medium. Prepare these samples for analysis (steps 7 through 9).

MEASUREMENT:

13. Set the HPLC system according to manufacturer's recommendations and to the conditions given on page 5521-1.
14. Inject a 10-μL aliquot of the sample solution from step 10. Capacity factors for the urea derivatives are:

Isocyanate	Mobile Phase: Acetonitrile	Mobile Phase: Buffer Solution	Capacity Factor (k')[a]
2,4-TDI	30%	70%	2
MDI	35%	65%	4
2,4-TDI	40%	60%	3
HDI	40%	60%	3
NDI	60%	40%	3

[a]$k' = (t_r - t_o) / t_o$, where t_r is the retention time of the urea and t_o is the retention time of an unretained compound.

15. Measure peak area.

CALCULATIONS:

16. Read from calibration graph the quantity, M (μg per sample), of isocyanate.
17. Calculate the concentration of isocyanate, C_M (mg/m^3), in the air volume sampled, V (L):

$$C_M = \frac{M}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The stability of 2,4-TDIU in toluene was investigated using groups of six samples stored at room temperature for up to two weeks or at 4 °C for 1 week with the following results:

Quantity (μg)	Storage Period (days)	Storage Temperature	Percent Recovery, 95% Confidence Interval
1.9	0	room	99 ± 11
3.8	0	room	98 ± 4
1.9	7	room	78 ± 7
1.9	7	4 °C	88 ± 7
3.8	7	room	67 ± 6
3.8	14	room	70 ± 11

The data demonstrate sample instability at room temperature (about 22 °C) and suggest that the samples are somewhat unstable even at 4 °C.

Estimates of the limits of quantitation (LOQs) (expressed in terms of the quantity of diisocyanate per sample) were made from the electrochemical detector calibration curves used for the analysis of field samples or control samples: 2,4-TDI, 0.5 μg [1, Sequence 6043]; 2,6-TDI, 0.7 μg [1, Sequence 6043]; MDI, 0.3 μg [1, Sequence 6019]; HDI, 1 μg [5]; NDI, 0.6 μg [1, Sequence 6878-C]. The corresponding limits of detection (LODs) were: 2,4-TDI, 0.2 μg; 2,6-TDI, 0.2 μg; MDI, 0.09 μg; HDI, 0.3 μg; NDI, 0.2 μg.

REFERENCES:

[1] NIOSH - Measurement Research Support Branch Analytical Report, Sequences #6019, 6043, 6100, 6354, and 6878-C (NIOSH, unpublished, 1988).
[2] "MDHS 25: Methods for the Determination of Hazardous Substances, Organic Isocyanates in Air. Laboratory Method Using 1-(2-Methoxyphenyl)piperazine Solution and High Performance Liquid Chromatography," Occupational Medicine and Hygiene Laboratory, Health and Safety Executive, London, U.K. (1987).
[3] Bagon, D. A., C. J. Warwick, and R. H. Brown, Am. Ind. Hyg. Assoc. J., 45, 39-43(1984).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402
[5] User check, DataChem Inc., NIOSH analytical seq. #6543 (unpublished, Feb. 24, 1989).

METHOD REVISED BY:

M. J. Seymour and Rosa Key-Schwartz, Ph.D., NIOSH/DPSE

TABLE 1: SYNONYMS, EXPOSURE LIMITS, AND PROPERTIES

Compounds (Synonyms)	Exposure Limits, $\mu g/m^3$*			Properties
	(OSHA)	(NIOSH)	(ACGIH)	
2,4-TDI (toluene-2,4-diisocyanate)	140 (ceiling)	lowest feasible (Ca)	36 140 STEL (Ca)	Liquid; d 1.224 g/mL @ 20 °C; BP 251 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C; MP 19.5 –21.5 °C
2,6-TDI (toluene-2,-6-diiocyanate)	no PEL	lowest feasible (Ca)	no TLV	liquid; d 1.22 g/mL @ 20 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C
MDI (4,4'-methylenediphenyl isocyanate; diphenylmethane-4,4'-diisocyanate; methylenebis phenyl isocyanate)	200 (ceiling)	50; 200/10 min (ceiling)	51	solid (fused); d 1.23 g/mL @ 25 °C; MP 37.2 °C; VP 0.0002 kPa (0.00014 mm Hg) @ 20 °C
HDI (hexamethylene diisocyanate)	no PEL	35 140/ 10/min (ceiling)	34	liquid; d 1.04 g/mL @ 20 °C; BP 255 °C; 0.007 kPa (0.05 mm Hg) @ 25 °C
NDI (naphthylene diisocyanate)	no PEL	40; 70/10 min	no TLV	solid flakes; MP 127 °C; VP <0.01 Pa @ 20 °C

* 1 ppm = 7100 $\mu g/m^3$ TDI; 10208 $\mu g/m^3$ MDI; 7350 $\mu g/m^3$ HDI;
Ca = Carcinogen

APPENDIX A: PURIFICATION OF 1-(2-METHOXYPHENYL)PIPERAZINE AND PREPARATION OF SAMPLING MEDIUM

Place 25 g 1-(2-methoxyphenyl)piperazine (yellowish white solid) in a 250-mL beaker. Add approximately 125 mL pentane. Bring to a boil (CAUTION: FLAMMABLE) on a hotplate and allow to boil until all but a small amount of yellow oil is in solution. The 1-(2-methoyphenyl)piperazine will melt as it is warmed in the pentane. Decant the solution into a clean beaker, cover with a watchglass and cool in the freezer for 2 to 3 h. White, fluffy crystals will form. Filter with a Buchner funnel. Transfer the crystals to a 50-mL round bottom flask and dry briefly under vacuum to remove final traces of pentane. Store the hygroscopic crystals in an air-tight container in a refrigerator. The melting range of the crystals is 26 to 29 °C.

Prepare the sampling medium using the purified 1-(2-methoxyphenyl)piperazine. Dissolve this reagent in toluene at a concentration of 43 μg/mL.

APPENDIX B: PREPARATION OF UREA DERIVATIVE

Dissolve 0.005 mole (1 g) of 1-(2-methoxyphenyl)piperazine in 25 mL dimethyl sulfoxide. Dissolve 0.002 mole (350-500 mg) of isocyanate in 25 mL dimethyl sulfoxide. Over a period of 1-2 min, gradually add the isocyanate solution to the stirred derivatizing reagent solution. Warm the resulting solution to 60-90 °C and continue to stir for at least 30 min. Discontinue heating of the solution and add 300 mL deionized water. The urea will precipitate as a white solid. Stop stirring after addition of water. Collect the urea in a fritted-glass Buchner funnel by suction filtration. Dry the compound in a vacuum oven at 75 °C to remove water. Recrystallize until a constant melting point is obtained.

To recrystallize urea, add toluene (150 mL) to dried urea and warm mixture to 60 °C. Slowly and very carefully add just enough methanol (BP 65 °C) to completely dissolve the urea. Remove from heat and allow to cool. Collect the crystals by suction filtration and dry them in vacuum oven at 35 °C. The urea derivatives and their melting points are as follows:

Diisocyanate	Urea Derivative	MP (°C)
2,4-TDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-2,4-toluenediamine (2,4-TDIU)	212-213 (platelets)
2,6-TDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-2,6-Toluenediamine (2,6-TDIU)	231-233 (platelets)
MDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-4,4'-methylenedianiline (MDIU)	209-210 (needles)
HDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-hexamethylenediamine (HDIU)	199-200 (needles)
NDI	N,N'-bis [4-(2-methoxyphenyl)piperazine-1-carbonyl]-1,5-naphthalenediamine (NDIU)	274

ISOPHORONE

$C_9H_{14}O$ MW: 138.21 CAS: 78-59-1 RTECS: GW7700000

METHOD: 2508, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1984**
Issue 2: 15 August 1994

OSHA : 25 ppm
NIOSH: 4 ppm; Group III Pesticide
ACGIH: C 5 ppm
(1 ppm = 5.65 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.923 g/mL @ 25 °C; BP 213 °C; VP 26 kPa (0.2 mm Hg; 260 ppm) @ 20 °C; explosive range 0.8 to 3.8% v/v in air

SYNONYMS: 3,5,5-trimethyl-2-cyclohexen-1-one

SAMPLING

SAMPLER: SOLID SORBENT TUBE (petroleum-based charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L @ 25 ppm
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 67 to 283 mg/m^3 [1] (180-L samples)

ACCURACY: ± 15.3%

BIAS: 5.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.059 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: isophorone

EXTRACTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 250 °C
-COLUMN: 160 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 4 m x 3-mm glass, 10% SP2100/0.1% Carbowax 1500 on 100/120 Supelcoport or equivalent

CALIBRATION: isophorone in CS_2

RANGE: 0.2 to 10 mg per sample [2]

ESTIMATED LOD: 0.02 mg per sample

PRECISION ($\bar{S}_r$): 0.033 [1,2]

APPLICABILITY: The working range for this method is 0.35 to 70 ppm (2 to 400 mg/m^3) for a 12-L air sample. High humidity will greatly decrease breakthrough volume.

INTERFERENCES: None identified. Alternate columns may be used, e.g., 10% SP-1000 or DB-2 fused silica capillary column.

OTHER METHODS: This is Method S367 with a different column recommended [2].

REAGENTS:

1. Carbon disulfide, chromatographic grade.*
2. Isophorone.*
3. Nitrogen, prepurified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of 20/40 mesh petroleum-based charcoal (100 mg front/50 mg back) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2508-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: CS_2 is toxic and acute fire and explosion hazard (flash point = −30 °C). Work with it only in a hood.

Isophorone is a lachymator [3]; work with it should be done in a hood and caution should be taken while it is being used.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1.0 L/min for a total sample size of 2 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.02 to 10 mg isophorone per sample.
   a. Add known amounts of Isophorone to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg isophorone).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of isophorone directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg isophorone recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2508-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of isophorone found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of isophorone in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S367 [2] was validated over the range 69 to 304 mg/m^3 using a 12-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.059 with an average recovery of 104.9%, representing a non-significant bias. The concentration was independently verified by a direct hydrocarbon analyzer. Desorption efficiency was 0.860 in the range of 0.849 to 3.40 mg per sample. No breakthrough occurred when an atmosphere containing 283 mg/m^3 was sampled for 240 min at a rate of 0.19 L/min. At this time the breakthrough test was discontinued. Samples are stable for at least one week at room temperature.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S367-1 to S367-6, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S367, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Criteria for a Recommended Standard...Occupational Exposure to Ketones, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-173 (1978).

METHOD REVISED BY:

Ardith Grote, NIOSH/DPSE; S367 originally validated under NIOSH Contract CDC-99-74-45.

ISOPROPYL ACETATE

$CH_3COOCH(CH_3)_2$ MW: 102.14 CAS: 108-21-4 RTECS: AI4930000

METHOD: 1454, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 250 ppm
NIOSH: no REL
ACGIH: 250 ppm; STEL 310 ppm
(1 ppm = 4.18 mg/m^3 @ NTP)

PROPERTIES: colorless liquid; BP 89.4 °C; d 0.87 g/mL @ 20 °C; miscible in most organic solvents; VP 6.33 kPa (47.5 mm Hg) @ 20 °C

SYNONYMS: methyl isobutyl acetate

SAMPLING

SAMPLER: CHARCOAL TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 0.1 L @ 250 ppm
-MAX: 9 L

SHIPMENT: routine

SAMPLE STABILITY: not documented

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 446 to 1870 mg/m^3 [1] (8-L samples)

BIAS: 1.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [1]

ACCURACY: ±29.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: isopropyl acetate

DESORPTION: carbon disulfide, 1 mL

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 60 °C - isothermal

CARRIER GAS: helium, 30 mL/min

COLUMN: 10 ft x 1/8-inch stainless steel, packed with 5% FFAP on 100/120 mesh Supelcoport [1]

CALIBRATION: standard solutions of isopropyl acetate in carbon disulfide

RANGE: 0.05 to 15 mg per sample [1]

ESTIMATED LOD: 0.01 mg per sample [1]

PRECISION ($\hat{S}_r$): 0.007 @ 3.6 to 15 mg per sample [1]

APPLICABILITY: The working range is 1.5 to 450 ppm (6 to 1870 mg/m^3) for an 8-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is NIOSH Method S50 in a revised format [1]. Operational modifications [2] to this method are as follows: column - 30 m x 0.3-mm I.D. fused silica WCOT capillary coated with 1.0-µm DB-1. Column temperature - 45 °C for 16 min, and programmed at 16 °C/min to 150 °C and held for 8 min. Carrier gas - He, with split ratio of 1:10. Desorption - 1 h or more in 1 mL carbon disulfide with 1 µL/mL p-cymene as internal standard.

REAGENTS:

1. Isopropyl acetate, ACS reagent grade.
2. Eluent: carbon disulfide*, chromatographic grade.
   NOTE: Add 0.1% (v/v) undecane or p-cymene as an internal standard, if desired.
3. Undecane or p-cymene, ACS reagent grade.
4. Standard solutions: Isopropyl acetate in carbon disulfide in the range of 0.01 to 15 mg per sample.
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1454-1).
4. Vials, 2-mL glass, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipet, 1-mL, readable to 0.1 mL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); all work done with it must be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 0.1 to 9 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each container and cap tightly. For the internal standard method, the 1.0 mL CS_2 will contain a known amount of the chosen internal standard.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 15 mg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg isopropyl acetate). If internal standard is used, plot ratio of peak area of analyte/peak area of internal standard vs. mg isopropyl acetate.
9. Determine desorption efficiency (DE) at least once per year for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte or of a standard solution of analyte in CS_2 directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1454-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass mg (corrected for DE) of isopropyl acetate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 446 to 1870 mg/m^3 at 23 °C and pressure of 770 mm Hg using 8-L samples [3]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.067, with average recovery of 96%. A sample stability evaluation has not been performed, nor has the sample stability been determined. The accuracy of ±29.4% does not meet the NIOSH criterion of ±25%.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 3rd ed., V. 2, S50, U.S. Department of Health and Human Services, (1984).
[2] Analytical Report for Organics on Charcoal Tubes, DataChem Sequence #3031-S, Unpubl. NIOSH (1981)
[3] Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45. Department of Health, Education and Welfare. (NIOSH) Publication 77-185 (1977).

METHOD REVISED BY:

Larry B. Jaycox, Ph.D., NIOSH/DPSE.

ISOPROPYL ALCOHOL

See ALCOHOLS I (Method 1400) for procedure

ISOPROPYL ETHER 1618

$((CH_3)_2CH)_2O$ MW: 102.18 CAS: 108-20-3 RTECS: TZ425000

METHOD: 1618, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 500 ppm
NIOSH: 500 ppm
ACGIH: 250 ppm; STEL 310 ppm
(1 ppm = 4.18 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.723 g/mL @ 20 °C; BP 67.5 °C; VP 15.9 kPa (119 mm Hg, 15.7% v/v) @ 20 °C; explosive range 1.4 to 7.9% v/v in air

SYNONYMS: diisopropyl ether; 2-isopropoxypropane; 2,2'-oxybispropane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 500 ppm
-MAX: 3 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 992 to 4260 mg/m^3 [1] (3-L samples)

BIAS: 2.2% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056 [1]

ACCURACY: ±12.0%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: isopropyl ether

DESORPTION: 1 mL CS_2, 30 min

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 220 °C
-COLUMN: 80 °C

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2, 50 mL/min

COLUMN: stainless steel, 3.2-mm ID x 6.1 m, packed with 10% FFAP on 80/100 mesh Chromosorb W-AW

CALIBRATION: standard solutions of isopropyl ether and internal standard in CS_2

RANGE: 0.05 to 12 mg per sample

ESTIMATED LOD: 0.01 mg

PRECISION ($\bar{S}_r$): 0.009 [1]

APPLICABILITY: The working range is 3 to 1170 ppm (16 to 4900 mg/m^3) for a 3-L air sample. An appropriate capillary column may be used for better resolution and sensitivity. The sorbent's capacity for the analyte has not been determined under conditions of high relative humidity [1].

INTERFERENCES: None identified.

OTHER METHODS: This is Method S368 [2] in a revised format.

REAGENTS:

1. Eluent: carbon disulfide* (CS_2), chromatographic quality, containing 1% (v/v) octane, undecane, or other suitable internal standard.
2. Isopropyl ether*, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, purified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 7.0 cm long, 6-mm OD, 4-mm ID; flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 100 mg; back = 50 mg) separated by a urethane foam plug. A silanized glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1.0 L/min air flow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1618-1).
4. Vials, 2-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Flasks, volumetric, 10-mL.
7. Pipets, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); isopropyl ether is flammable and tends to form explosive peroxides [3]. All work with these compounds must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 3 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.01 to 12 mg isopropyl ether per sample.
   a. Add a known amount of isopropyl ether to eluent in 10-mL volumetric flask and dilute to the mark. Use serial dilutions as needed for smaller concentrations.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of isopropyl ether peak area to internal standard peak area vs. mg isopropyl ether).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject known amount (1 to 20 μL) of isopropyl ether or standard solution of isopropyl ether in eluent directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg isopropyl ether recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1618-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide peak area of isopropyl ether by peak area of internal standard for each chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of isopropyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of isopropyl ether in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

S368 was issued on April 21, 1976 [2] and validated over the range 992 to 4260 mg/m^3 for 3-L air samples from dynamically generated test atmospheres [1]. The isopropyl ether concentrations were verified by GC/FID analysis. Breakthrough (5% on the backup section) occurred at 26 min when sampling a test atmosphere containing 4260 mg/m^3 of isopropyl ether in dry air at a flow rate of 0.198 L/min. Average recovery for generated samples stored five days was 102.2%.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S368, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977). Available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S368, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

Charles V. Cooper, NIOSH/DPSE. Method S368 was originally validated under NIOSH Contract CDC-99-74-45.

ISOPROPYL GLYCIDYL ETHER 1620

$C_6H_{12}O_2$ MW: 116.16 CAS: 4016-14-2 RTECS: TZ3500000

METHOD: 1620, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 50 ppm
NIOSH: C 50 ppm (15 min)
ACGIH: 50 ppm; STEL 75 ppm
(1 ppm = 4.75 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.919 g/mL @ 20 °C; VP 1.25 kPa (9.4 mm Hg, 1.2%) @ 25 °C

SYNONYMS: glycidyl isopropyl ether; 1,2-epoxy-3-isopropoxypropane; (1-methylethoxy)methyl)oxirane; IGE

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 50 ppm
-MAX: 30 L

SHIPMENT: routine (refrigerate at lab)

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 121 to 484 mg/m^3 [1] (10-L samples)

BIAS: −5.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [1]

ACCURACY: ±14.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: isopropyl glycidyl ether

DESORPTION: 0.5 mL CS_2, 30 min

TEMPERATURE-INJECTION: 205 °C
-DETECTOR: 270 °C
-COLUMN: 115 °C

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2, 50 mL/min

COLUMN: stainless steel, 3.2-mm ID x 3 m, packed with 10% FFAP on 80/100 mesh Chromosorb W-AW DMCS

CALIBRATION: standard solutions of isopropyl glycidyl ether in CS_2

RANGE: 0.25 to 5 mg per sample

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.020 [1]

APPLICABILITY: The working range is 5 to 105 ppm (25 to 500 mg/m^3) for a 10-L air sample. An appropriate capillary column may be used for better resolution and sensitivity. The sorbent's capacity for the analyte has not been determined under conditions of high relative humidity.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S77 [2] in a revised format.

REAGENTS:

1. Carbon disulfide* (CS_2), chromatographic quality.
2. Isopropyl glycidyl ether*, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 7.0 cm long, 6-mm OD, 4-mm ID; flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 100 mg; back = 50 mg) separated by a urethane foam plug. A silanized glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1.0 L/min air flow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1620-1).
4. Vials, 2-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Flasks, volumetric, 10-mL.
7. Pipets, 0.5-mL.

SPECIAL PRECAUTIONS: Isopropyl glycidyl ether (flash point = 33 °C) and CS_2 (flash point = −30 °C) are serious fire and explosion hazards and are toxic. All work with these compounds must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 0.5 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.1 to 15 mg isopropyl glycidyl ether per sample.
   a. Add a known amount of isopropyl glycidyl ether to CS_2 in 10-mL volumetric flask and dilute to the mark. Use serial dilutions as needed for smaller concentrations.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (isopropyl glycidyl ether peak area vs. mg isopropyl glycidyl ether per 0.5 mL).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject known amount (1 to 20 μL) of isopropyl glycidyl ether or standard solution of isopropyl glycidyl ether in CS_2 directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg isopropyl glycidyl ether recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1620-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of isopropyl glycidyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of isopropyl glycidyl ether in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S77 was issued on February 14, 1975 [2] and was validated over the range 121 to 484 mg/m^3 for 10-L air samples from dynamically generated test atmospheres [1]. The average recoveries ranged from 93 to 95%. The isopropyl glycidyl ether concentrations were independently measured by means of a total hydrocarbon analyzer. Breakthrough was not observed after sampling 44 L from a test atmosphere containing 484 mg/m^3 of isopropyl glycidyl ether. Desorption efficiency decreased from 92.4% to 77.5% with decreasing loading from 4.8 to 1.2 mg isopropyl glycidyl ether per sample. Sample stability was not determined; however, refrigeration of the sample upon receipt by the laboratory is recommended.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S77, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977). Available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S77, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

R.A. Glaser, NIOSH/DPSE. Method S77 was originally validated under NIOSH Contract CDC-99-74-45.

KEPONE 5508

$C_{10}Cl_{10}O$ MW: 490.68 CAS: 143-50-0 RTECS: PC8575000

METHOD: 5508, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: 0.001 mg/m^3; carcinogen
ACGIH: no standard

PROPERTIES: solid; MP 350 °C (dec); VP <4 x 10^{-5} Pa (3 x 10^{-7} mm Hg; 8 μg/m^3) @ 25 °C

SYNONYMS: chlordecone, decachlorotetracyclodecanone

SAMPLING

SAMPLER: FILTER + IMPINGER (0.8-μm cellulose ester membrane + impinger with 0.1 M NaOH)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 50 L @ 1 μg/m^3
-MAX: 600 L

SHIPMENT: routine

SAMPLE STABILITY: at least 12 days @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.5 to 2.6 μg/m^3 (376-L samples)

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.23 [1]

ACCURACY: > ± 45%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: Kepone

RECOVERY FROM FILTER: 99:1 benzene:methanol, 10 mL; stand 2 h

RECOVERY FROM IMPINGER: benzene, @ pH <7, two 5-mL portions

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 335 °C
-COLUMN: 200 °C

CARRIER GAS: nitrogen, 70 mL/min

COLUMN: 1.8 m x 4-mm glass; 3% OV-1 on 80/100 mesh Chromosorb WHP

CALIBRATION: Kepone in 99:1 benzene:methanol

RANGE: 50 to 500 ng per sample

ESTIMATED LOD: 10 ng per sample

PRECISION ($\bar{S}_r$): 0.014 (filters); 0.060 (impingers)

APPLICABILITY: The working range is 0.001 to 25 mg/m^3 for 50-L air samples. Personal and area samples were collected by this method at a Mirex formulation plant.

INTERFERENCES: Partial conversion of Mirex into Kepone can occur by reaction with NaOH solution in the impinger and pH adjustment. A different column packing which may be used is 3% OV-210 on 80/100 mesh Chromosorb WHP.

OTHER METHODS: This method was originally designated P&CAM 225 [1,2].

REAGENTS:

1. Sodium hydroxide, 0.1 M, aqueous.
2. Benzene, pesticide quality.*
3. Methanol, pesticide quality.*
4. Benzene:methanol, 99:1 (v/v).*
5. Sulfuric acid, 0.05 M.
6. Kepone.*
7. Calibration stock solution, 50 μg/mL. Dissolve 100 mg Kepone in 99:1 benzene:methanol to make 10 mL solution. Dilute 50 μL of this solution to 10 mL with 99:1 benzene:methanol. Stable at least one week at 25 °C.
8. Impinger recovery stock solution, 1 μg/mL. Dissolve 25 mg Kepone in methanol to make 10 mL solution. Dilute 4 μL of this solution to 10 mL with methanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm, 37-mm, in a filter holder followed by a midget impinger with 15 mL 0.1 M NaOH. (Filter holder and impinger connected with short piece of plastic tubing.)
2. Sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Impinger, midget, with stem removed.
4. Gas chromatograph, electron-capture detector, integrator and column (page 5508-1).
5. Forceps, two pairs.
6. Volumetric flasks, 10-mL.
7. Separatory funnel, 125-mL.
8. Syringes, 10-μL, readable to 0.1-μL; 100-μL, readable to 1 μL.
9. pH paper.
10. Pipet, 5-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Methanol and benzene are flammable.

Benzene and Kepone [3] are carcinogens.

SAMPLING:

1. Connect the outlet of the impinger containing 15 mL 0.1 M NaOH and the inlet of the sampling pump to an empty impinger without a stem to protect the sampling pump from splash over.
2. Calibrate the sampling pump with a representative sampler in line.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 50 to 600 L. Do not exceed 2 mg total dust loading on the filter.
4. Separate the filter cassette and impinger for shipment to the laboratory.

SAMPLE PREPARATION:

5. Use forceps to fold and transfer the filter to a 10-mL volumetric flask.
6. Add 10.0 mL 99:1 benzene:methanol.
7. Stopper and shake the flask vigorously for 1 min. Allow the flask to stand at least 2 h.
8. Transfer the solution in the impinger to a separatory funnel. Wash the impinger with two 15-mL portions of 0.1 M NaOH, and add the washings to the separatory funnel. Add 0.05 M H_2SO_4 until the pH is less than 7.
9. Extract the Kepone with two 5-mL portions of benzene. Shake vigorously for 2 min and allow 5 min for the phases to separate. Combine the benzene layers in a 10-mL volumetric flask. Add 100 μL methanol and benzene to the mark.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards in the range 1 to 50 ng/mL.
    a. Dilute 50 μg/mL calibration stock solution with 99:1 benzene:methanol to 3.6 μg/mL.
    b. Add known amounts of 3.6 μg/mL solution to 99:1 benzene:methanol in 10-mL volumetric flasks.

c. Analyze together with samples and blanks (steps 13 through 15).
d. Prepare a calibration graph of peak area or peak height vs. ng of Kepone per sample.

11. Determine the average recovery (R) of Kepone from filters.
    a. Fortify six filters with about 7 μL of 50 μg/mL calibration stock solution.
    b. Allow the filters to air dry.
    c. Prepare samples according to steps 5 through 7.
    d. Analyze samples with standards according to steps 13 through 15.
    e. Calculate the average recovery, R (mass of Kepone found divided by mass of Kepone applied).
12. Determine the average recovery of Kepone from impingers.
    a. Fortify each of six impingers containing 15 mL 0.1 M NaOH solution with 100 μL 1-μg/mL impinger recovery stock solution.
    b. Prepare samples according to steps 8 and 9.
    c. Analyze samples with standards according to steps 13 through 15.
    d. Calculate the average recovery.

MEASUREMENT:

13. Set the gas chromatograph to conditions given on page 5508-1. t_r of Kepone = 4.6 min, and t_r of Mirex = 9.2 min for these conditions.
14. Inject 5-μL aliquots of sample solutions and standards using solvent-flush technique.
    NOTE: Rinse the syringe thoroughly after each injection with methanol and then with benzene, otherwise traces of Kepone will remain in the syringe.
15. Measure peak area or peak height.

CALCULATIONS:

16. Determine the quantities in ng of Kepone (corrected for R) on the filter (W_f), in the impinger (W_i), in the average filter blank (B_f), and in the average impinger blank (B_i) from calibration graphs based on standards analyzed with the samples.
17. Calculate the concentration, C ($\mu g/m^3$), of Kepone in the air volume sampled, V (L):

$$C = \frac{W_f + W_i - B_f - B_i}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was tested with fortified filters, fortified NaOH solutions and controlled atmospheres near 25 °C. The overall precision including pump error was 0.234 [1]. The relative standard deviation ($\bar{S}_r$) for filters was 0.228 (10 samples, pooled) for 376-L samples at 2.5 and 2.6 $\mu g/m^3$. Quantities of Kepone found in impingers were less than 50 ng. The quantity of Kepone found in each impinger corresponded to about 0.1 ng or less for each liter of air in a sample. Collection efficiencies of impingers were roughly 50%. Average recovery of 360 ng of Kepone from filters was 0.89; $\bar{S}_r$ was 0.014 for six samples. Kepone was stable on filters at room temperature for 12 days. Average recovery of 45 ng Kepone from 45-mL aliquots of 0.1 M NaOH solution was 1.01; $\bar{S}_r$ was 0.060 for 8 samples. Average recovery of 79 ng Kepone from 10-mL aliquots of 0.1 M NaOH solution was 1.13 after 14 days of storage at room temperature. Personal and area samples (45 to 84 L) were collected by this method at a Mirex formulation plant. Mirex was found on filters in quantities of 240 to 1240 μg and in impingers in quantities of 0.3 to 16 μg. Although no Kepone was detected on filters, Kepone in quantities of 0.1 to 2 μg was found in impingers. Most or all of the Kepone in each impinger was produced by chemical conversion of Mirex. The accuracy of this method is greater than ± 45%, greatly exceeding the NIOSH criterion of ± 25%.

REFERENCES:

[1] Tucker, S.P., "Backup Data Report on Kepone," Internal NIOSH MRB Report (unpublished), May 9, 1977.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 225, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH Recommended Standard for Occupational Exposure to Kepone, U.S. Department of Health, Education, and Welfare, (NIOSH), unnumbered publication (January, 1976).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE and Alexander W. Teass, Ph.D., NIOSH/DBBS.

KEROSENE

See NAPHTHAS (Method 1550) for procedure

TABLE 1 MW: TABLE 1 CAS: TABLE 1 RTECS: TABLE 1

METHOD: 1300, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA/NIOSH/ACGIH: Table 1 **PROPERTIES:** Table 1

COMPOUNDS: (SYNONYMS: Table 1)

acetone	cyclohexanone	diisobutyl ketone
2-hexanone	methyl isobutyl ketone	2-pentanone

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

	acetone	others
VOL-MIN:	0.5 L	1 L
-MAX:	3 L	10 L

SHIPMENT: MIBK must be refrigerated [1]

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED, BIAS, OVERALL PRECISION ($\hat{S}_{rT}$), and ACCURACY

see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 50 °C to 170 °C @ 10°/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass (3.5 m x 6-mm ID), packed with 10% SP2100 0.1% Carbowax 1500 on Chromosorb WHP

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 0.06 to 10 mg per sample [2]

ESTIMATED LOD: 0.02 mg per sample

PRECISION ($\hat{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: This is intended as a general method for the ketones listed above. If only certain compounds are of interest, the instrumental conditions can be changed to maximize instrument response for these compounds.

INTERFERENCES: None reported. Alternate columns, e.g., 10% SP-2100 or DB-1 fused silica capillary, can be used.

OTHER METHODS: This method combines and replaces Methods S1, S18, S19 and S20 [3], S178 and S358 [4], and 1300 (dated 2/15/84).

REAGENTS:

1. Carbon disulfide (CS_2) GC grade.*
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered, dry.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph equipped with FID, integrator and column (page 1300-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipet, TD, 1-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 3 L for acetone or 1 to 10 L for the other analytes.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.02 to 10 mg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte or of a standard solution of analyte in CS_2 directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1300-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The methods on which this method was based were validated under NIOSH Contract CDC-99-74-45 [5]. Desorption efficiency was checked by spiking known amounts of the compounds (either neat or in solutions with CS_2) on coconut shell charcoal. Samples were generated for acetone, cyclohexanone, 2-pentanone, and methyl isobutyl ketone by heating a quantity of the liquid to just below its boiling point in a 3-necked, 500-mL round bottom flask. The compound was carried through a fixed-temperature condenser to the concentrations. Samples were generated for diisobutyl ketone and 2-hexanone using a syringe pump which delivered the compounds to a heated glass-lined inlet which was swept with nitrogen, carrying the vapor to the mixing chamber. Low-level desorption efficiency checks showed the DEs to be 70% and 76% for 0.024 and 0.096 mg/sample respectively for cyclohexanone and 87% for 0.052 mg/sample of MIBK [2]. Results of the evaluation experiments are given below.

Compound	Method [2-5]	Range, mg/m³ Overall Precision ($\hat{S}_{rT}$)	Breakthrough[1] (L)	Measurement Range, mg/sample ($\bar{S}_r$)	DE[2]
Acetone	S1, 127	1200 to 4500 (0.082)	4.3	2.4 to 14.2 (0.024)	0.86
Cyclohexanone	S19	98 to 392 (0.062)	65	3.8 to 18.0 (0.025)	0.82
Diisobutyl ketone	S358	145 to 582 (0.070)	44	1.8 to 7.0 (0.032)	0.97
2-Hexanone	S178	188 to 790 (0.053)	>45	1.5 to 8.1 (0.018)	0.81
MIBK	S18	208 to 836 (0.064)	17	2.1 to 8.3 (0.008)	0.91
2-Pentanone	S20	395 to 1570 (0.063)	19	3.5 to 14.0 (0.011)	0.90

[1] 5% breakthrough, 0.2 L/min at high end of concentration range in dry air.
[2] Averaged over mass range shown.

REFERENCES:

[1] UBTL Report, Sequence #5528-J (NIOSH, unpublished, Oct. 2, 1986).
[2] Williams, Karen, Desorption Efficiency Determination for Cyclohexanone and Methyl Isobutyl Ketone, NIOSH/MRSB, Unpublished (1986).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S1, S18, S19 and S20, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, V. 3, S178 and S358, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[6] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD REVISED BY:

Ardith Grote, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General Information

Compound (Synonyms)	Formula (M.W.)	Properties*	Exposure Limits, ppm OSHA / NIOSH / ACGIH	mg/m^3/ ppm @ NTP
Acetone 2-Propanone; (CAS #67-64-1) RTECS AL3150000	CH_3COCH_3 (58.08)	liquid; BP 56 °C; d 0.791 g/mL; VP 35.5 kPa (266 mm Hg)	750; STEL 1000 250: Group III Pesticide 750; STEL 1000	2.37
Cyclohexanone Cyclohexyl ketone (CAS #108-94-1) RTECS GW1050000	$C_6H_{10}O$ (98.15)	liquid; BP 155 °C; d 0.947 g/mL; VP 0.3 kPa (2 mm Hg)	25 (skin) 25 (skin); Group III Pesticide 25 (skin)	4.01
Diisobutyl ketone (2.6,-dimethyl- 4-heptanone; CAS #108-83-8) RTECS MJ5775000	$((CH_3)_2CHCH_2)_2CO$ (142.24)	liquid; BP 169 °C; d 0.847 g/mL; VP 0.23 kPa (1.7 mm Hg)	25 25; Group II Pesticide 25	5.82
2-Hexanone (methyl n-butyl ketone; MBK; CAS #591-78-6) RTECS MP1400000	$CH_3(CH_2)_3COCH_3$ (100.16)	liquid; BP 127 °C; d 0.812 g/mL; VP 0.4 kPa (3 mm Hg)	100 1 5	4.09
Methyl isobutyl ketone (MIBK; hexone; isopropyl acetone; 4-methyl- 2-pentanone; CAS #108-10-1) RTECS SA9275000	$(CH_3)_2CHCH_2COCH_3$ (100.16)	liquid; BP 117 °C; d 0.800 g/mL; VP 2.0 kPa (15 mm Hg)	50; STEL 75 50; STEL 75 50; STEL 75	4.09
2-Pentanone (methyl propyl ketone: CAS #107-87-9) RTECS SA 7875000	$CH_3CH_2CH_2COCH_3$ (86.13)	liquid; BP 100 °C; d 0.812 g/mL; VP 3.6 kPa (27 mm Hg)	200; STEL 250 150 200; STEL 250	3.52

* Density @ 25 °C; VP @ 20 °C.

TABLE 1 MW: TABLE 1 CAS: Table 1 RTECS: Table 1

METHOD: 1301, Issue 2	EVALUATION: FULL COMPOUNDS (3) and (5): PARTIAL	Issue 1: 15 February 1984 Issue 2: 15 August 1994

OSHA/NIOSH/ACGIH: Table 1 **PROPERTIES:** Table 1

COMPOUNDS: (Synonyms in Table 1)
(1) camphor
(2) mesityl oxide
(3) 5-methyl-3-heptanone
(4) methyl-(n-amyl)-ketone
(5) ethyl butyl ketone

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% methanol in CS_2; stand in 30 min

INJECTION VOLUME: 5 µL

COLUMN: stainless steel (3 m x 3-mm ID), 10% FFAP on 80/100 Chromosorb W-AW

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 300 °C
-COLUMN: 100 to 200 °C @ 10 °C/min

CARRIER GAS: N_2 or He, 30 mL/min

CALIBRATION: standard solutions of analyte in elution solvent

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.05 mg per sample

APPLICABILITY: This method was developed to give better desorption than obtainable with carbon disulfide extraction of the charcoal. This method can be used in paint and resin manufacturing plants.

INTERFERENCES: None reported. Alternate columns, e.g., 4 m 10% SP-2100/0.1% Carbowax 1500 on Supelcoport 100/120 or DB-1 fused silica capillary may be used.

OTHER METHODS: This method combines and replaces Methods S10, S12, S13, S15 and S16 [1].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) methanol (chromatographic grade).
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at the sampling flow rate. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1301-1).
4. Vials, 2-mL glass, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipet, 1-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); all work done with it must be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 0.5 mg camphor; and 0.05 to 5 mg of the other analytes per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1301-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Laboratory testing with spiked samples and samples collected from atmospheres generated by syringe pump/air dilution and verified by FID continuous monitor [2]. Results were:

Compound	Method [1,2]	Range (mg per sample)	DE[2]	$\bar{S}_r$	S/A Breakthrough[1] Range (mg/m³)	S/A Breakthrough[1] (L)	Overall Precision $\hat{S}_{r,T}$	Bias (%)	Accuracy (±%)
Camphor	S10	0.02 to 0.40	0.97	0.018	6 to 25	>48	0.074	0.9	10.5
Mesityl oxide	S12	0.10 to 3.0	0.81	0.014	45 to 210	>48	0.071	7.0	22.8
5-Methyl-3-heptanone	S13	0.15 to 4.0	0.90	0.014	60 to 270	>36	0.10	13.1	31.0
Methyl-(n-amyl)-ketone	S15	0.5 to 10.0	0.82	0.012	200 to 925	>36	0.066	4.9	15.0
Ethyl butyl ketone	S16	0.25 to 7.0	0.94	0.022	100 to 460	>24	0.086	-3.1	26.3

[1] 5% breakthrough, 0.2 L/min at high end of concentration range in dry air.
[2] Averaged over mass range shown.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S10, S12, S13 and S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[2] Documentation of the NIOSH Validation Tests, S10, S12, S13 and S15, S16, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY:

Ardith Grote, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

TABLE 1. GENERAL INFORMATION

Compound (Synonyms) CAS RTECS	Formula (M.W.)	Exposure Limits, ppm OSHA	NIOSH	ACGIH TLV STEL	mg/m³/ppm @NTP	Properties
Camphor (CAS #76-22-2) RTECS EX1225000	$C_{10}H_{16}O$ (152.24)	2	2	2 3	6.22	solid; d 0.992 g/mL @ 25 °C; MP 174 °C; VP 0.024 kPa 0.18 mm Hg; 1470 mg/m³); sublines
Mesityl oxide (4-methyl-3-penten-2-one) (CAS #141-79-7) RTECS SB4200000	$CH_3COCH=C(CH_3)_2$; $C_6H_{10}O$ (98.15)	25	10	15 25	4.01	liquid; BP 129 °C; VP 1.1 kPa (8 mm Hg); d 0.822 g/mL
5-Methyl-3-heptanone (Ethyl amyl ketone) (CAS #541-85-5) RTECS MJ7350000	$CH_3CH_2COCH_2CH(CH_3)$-CH_2CH_3; $C_8H_{16}O$ (122.22)	25	25	25 --	5.00	liquid; BP 159 °C; VP 0.27 kPa (2 mm Hg); d 0.822 g/mL
Methyl-(n-amyl)-ketone (2-Heptanone) (CAS #110-43-0) RTECS MJ5075000	$CH_3CO(CH_2)_4CH_3$; $C_7H_{14}O$ (114.19)	100	100	50	4.67	liquid; BP 151 °C; VP 0.27 kPa (2 mm Hg); d 0.820 g/mL
Ethyl butyl ketone (3-heptanone) (CAS #106-35-4) RTECS MJ5250000	$CH_3CH_2CO(CH_2)_3CH_3$; $C_7H_{14}O$ (114.19)	50	50	50	4.67	liquid; BP 148 °C; VP 0.53 kPa (4 mm Hg); d 0.818 g/mL

*NOTE: All densities and vapor pressures are at 20 °C unless stated otherwise.

LEAD in blood and urine 8003

Pb MW: 207.19 CAS: 7439-92-1 RTECS: OF7525000

METHOD: 8003, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to lead and lead compounds.

SYNONYMS: none.

BIOLOGICAL SAMPLING		MEASUREMENT	
SPECIMEN:	whole blood; urine, end of shift	**TECHNIQUE:**	ATOMIC ABSORPTION, FLAME
CONTAINER:	10-mL lead-free tubes (blood); 125-mL polyethylene bottles (urine)	**ANALYTE:**	Pb(II)-APDC complex
ANICOAGULANT:	(blood) heparin	**EXTRACTION:**	APDC-MIBK
PRESERVATIVE:	(urine) 0.2 mL conc. HNO_3	**CALIBRATION:**	methyl isobutyl ketone solutions of Pb(II)-APDC complex
SHIPMENT:	polyethylene shippers	**QUALITY CONTROL:**	commercial controls; pooled urine or blood; urine corrected for creatinine
SAMPLE STABILITY:	blood stable 3 days @ 4 °C; indefinitely if sonicated and frozen in plastic tubes; urine stable indefinitely if kept acidified with HNO_3	**RANGE:**	5 to 150 μg/100 g blood; 5 to 150 μg/100 mL urine
CONTROLS:	commercial urine and blood lead control samples plus pooled urine and blood from non-exposed populations	**ESTIMATED LOD:**	0.05 μg Pb/g blood or mL urine [1]
		RECOVERY:	0.99
		PRECISION ($\bar{S}_r$):	0.05 [1]
		ACCURACY:	± 10.8%

APPLICABILITY: This procedure quantitates Pb^{2+} in blood or urine to assess body burden, injury to the hematopoietic system, and to comply with Federal Regulations. Blood lead is the preferred biological indicator of lead absorption. The optimum working range is 0.1 to 1.5 μg. Pb per g blood or per mL urine [2].

INTERFERENCES: Phosphate, EDTA, and oxalate can sequester lead and cause low lead readings.

OTHER METHODS: This method combines and replaces P&CAM 208 [1] and 262 [3]. Methods P&CAM 102 (dithizone), 195 (ASV), 200 (ASV) and 214 (graphite furnace AAS) [4] have not been revised. Anodic stripping voltametry (ASV) is an alternative procedure if specialized equipment is available [5].

REAGENTS:

1. Ammonium pyrrolidine dithiocarbamate (APDC). Stable 6 months.
2. Nonionic surfactant, octyl phenoxy polyethoxy ethanol (Triton X-100 or equivalent).
3. APDC-surfactant solution (APDC-Tx). Dissolve 4 g APDC and 5 mL nonionic surfactant in 40 mL deionized water. Dilute to 200 mL. Check each batch for extraction efficiency. Stable at least two months.
4. Lead nitrate $Pb(NO_3)_2$. Heat 4 h at 120 °C. Cool and store in dessicator.
5. Nitric acid, conc. 70% (w/w), redistilled.
6. Methyl isobutyl ketone (MIBK), water-saturated. Add 100 mL water to 900 mL MIBK. Shake and allow to stand 1 h.
7. Calibration stock solution (1000 μg/mL). Dissolve 1.598 g $Pb(NO_3)_2$ in 2% (w/v) HNO_3 and dilute to 1 L. Store in a polyethylene bottle. Stable 1 year.
8. Air at 40 psi, filtered to remove oil and water.
9. Acetylene, grade recommended by AAS manufacturers.

EQUIPMENT:

1. Heparinized, lead-free, "blue-top" blood collection tubes specially prepared for collecting blood samples for blood lead determinations.
2. Vacutainer needles (21-gauge) and holder.
3. Tourniquet and alcohol swabs.
4. Polyethylene bottles (wide mouth), 125-mL.
5. Culture tubes, 16 x 100-mm, with PTFE-lined screw caps.*
6. Centrifuge.
7. Rotary vibration mixer (Vortex) or equivalent.
8. Atomic absorption spectrophotometer (AAS) with lead hollow cathode or electrodeless discharge lamp.
9. Analytical balance.
10. Desiccator.
11. Pipettes, volumetric flasks and other appropriate glass or plasticware for weighing, storing, and dispensing reagents and samples.*

* All glassware and plasticware should be detergent washed, thoroughly rinsed with tap and deionized water, soaked 4 hrs in 1:1 HNO_3:H_2O and finally thoroughly rinsed with deionized water.

SPECIAL PRECAUTIONS: Samples of blood and urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood and urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect blood samples in heparinized blood collection tubes. Mix immediately. Ship at 4 °C and maintain at this temperature prior to analysis.
2. Collect urine at the end of a work shift in 125-mL polyethylene bottles containing 0.2 mL conc. HNO_3; mix. Submit a 25-mL aliquot for lead analysis and another 25-mL aliquot for creatinine determination.

SAMPLE PREPARATION:

3. Filter urine samples before analysis. Analyze a 25-mL aliquot for creatinine by standard procedures (e.g., [6]).
4. Place 2.0 mL filtered urine or 2.0 g whole blood in a 16 x 150-mm culture tube. Start a reagent blank at this point with 2 mL deionized water.
5. Add 0.8 mL APDC-surfactant solution. Cap and mix on a rotary vibration mixer for 10 sec.
6. Add 2.00 mL water-saturated MIBK. Cap and rotate on a rotary vibration mixer for 2 min. Centrifuge at 2000 rpm for 10 min. Analyze the Pb-APDC solution in MIBK within 2 h of extraction.

NOTE: If the patient is receiving EDTA therapy or if blood specimens are collected in tubes containing Na_2 EDTA as anticoagulant, add 50 µL 1.5 M $CaCl_2$ immediately before adding the MIBK [7].

CALIBRATION AND QUALITY CONTROL:

7. Prepare 6 working standards in deionized water in the range 10 to 150 µg/100 mL Pb by dilution of calibration stock solution with 2% (w/v) HNO_3. Prepare fresh daily.
   Example: 0.4 mL calibration stock stolution diluted to 1 L = 40 µg per 100 mL.
8. Analyze the working standards (steps 4, 5, 6, 12, and 13).
9. Prepare a calibration graph. Plot concentration (µg/100 mL) vs. absorbance of working standard, corrected for reagent blank.
10. Maintain standardization by analyzing a standard after every 5 samples.
11. Run a spiked control or pooled sample from exposed workers or commercial control every 10 samples or at least 3 per study.
    NOTE: Blood or urine lead background levels must be determined before spiked controls are prepared.

MEASUREMENT:

12. Set the atomic absorption spectrophotometer and lamp conditions as recommended by the manufacturer and as given on page 8003-1. Aspirate water-saturated MIBK and reduce acetylene flow until a stoichiometric flame with minimum background is obtained (< 0.01 absorbance). Record this reading.
13. Aspirate each sample and blank. Record maximum absorbances.
    NOTE: Samples with absorbance values greater than 0.35 must be diluted with MIBK and reanalyzed. Apply the appropriate dilution factor in calculations.

CALCULATIONS:

14. Calculate net absorbance (difference between the maximum absorbance of MIBK and the absorbance of the sample or blank).
15. Using metals, determine blood and urine lead levels in the samples (W_s) and average reagent blanks (B) from the calibration graph.
16. For urine samples, report µg Pb/g creatinine. For blood samples, report µg Pb/g whole blood.

GUIDES TO INTERPRETATION:

Blood lead concentrations for healthy adult suburbanites is 7 to 22 µg/100 g whole blood [2]. Urine has a wider range, 4 to 270 µg/g creatinine, for the same population; however, most normal values should be near 16 to 60 µg/g creatinine [4].

Blood lead values are commonly used for biological monitoring. A blood lead value above 40 µg/100 g is indicative of excess exposure and one above 60 µg/100 g requires removal from exposure [8].

EVALUATION OF METHOD:

Forty-two blood specimens were spiked at levels of 25 to 200 µg/100 mL. Recoveries were 94 to 106%, averaging 100% [7].

For urine, 25 specimens were spiked at concentrations from 10 to 100 µg/mL. Recoveries averaged 100% (range 95 to 106%) [7].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 208, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, p. 159, Biomedical Publications, Davis, CA (1980).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 262, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid., P&CAM 102, 195, 200, and 214.
[5] Environmental Sciences Associates, Inc. Methods Manual Methods TMA-1 and TMA-2, Bedford, MA.
[6] Hessel, D. W. Atomic Absorption Newslett., 7, 55 (1968).
[7] Zenterhofer, L. J. M., P. I. Jatlow, and A. Fappiano. Atomic Abosrption Determination of Lead in Blood and Urine in the Presence of EDTA, J. Lab. Clin. Med., 78, 664-674 (October, 1971).
[8] Occupational Safety and Health Administration, Chapter XVII, 1910.1025, Section C, 691.

METHOD WRITTEN BY:

Anthony W. Smallwood and Frederick C. Phipps, NIOSH/DBBS; Peter M. Eller, Ph.D., and Mark B. Millson, NIOSH/DPSE.

LEAD in Surface Wipe Samples 9100

Pb MW: 207.19 CAS: 7439-92-1 RTECS: OF7525000

METHOD: 9100, Issue 1 **EVALUATION: PARTIAL** **ISSUE 1: 15 August 1994**

PURPOSE: Determination of surface contamination by lead and its compounds.

LIMIT OF DETECTION: **2 μg Pb** per sample (0.02 μg/cm^2 for 100-cm^2 area) by **flame AAS** or **ICP**; **0.1 μg Pb** per sample (0.001 μg/cm^2 for 100-cm^2 area) by **graphite furnace AAS.**

FIELD EQUIPMENT:

1. Bags, plastic, sealable (e.g., with attached wire, tape or "zip"-type seal).
2. Sample pads, 2" x 2", sterile cotton gauze (Curity™, Johnson & Johnson™, or equivalent), or ashless quantitative filter paper.
   NOTE: Wash'n Dri™ wipes may also be used. Other wipes may not ash properly, or may have a significant lead blank value.
3. Gloves, latex, disposable.
4. Template, plastic, 10 cm x 10 cm, or other standard size.
5. Water, distilled, in plastic squeeze bottle.

SAMPLING:

1. Using a new pair of gloves, remove a gauze pad from its protective package. Moisten the gauze pad with approximately 1 to 2 mL of distilled water.
   NOTE 1: Apply no more distilled water than that necessary to moisten approximately the central 80% of the area of the gauze pad. Excess distilled water may cause sample loss due to dripping from the gauze pad.
   NOTE 2: If using the premoistened Wash'n Dri™, omit the distilled water.
2. Place the template over the area to be sampled. Wipe the surface to be sampled with firm pressure, using 3 to 4 vertical S-strokes. Fold the exposed side of the pad in and wipe the area with 3 to 4 horizontal S-strokes. Fold the pad once more and wipe the area with 3 to 4 vertical S-strokes.
3. Fold the pad, exposed side in, and place it in a new plastic bag. Seal and label the bag clearly. Discard the gloves.
4. Clean the template in preparation for the next wipe sample .
5. Include two blank pads (moistened and placed in bags) with each sample set.

SAMPLE PREP: Use the procedure of NIOSH Method 7105, including final sample dilution to 10 mL.
NOTE: Additional portions of nitric acid may be needed for complete digestion of the sample, including the pad. Include appropriate media and reagent blanks.

MEASUREMENT: Screening of all samples by flame AAS or ICP, followed by graphite furnace AAS for those samples giving "Not Detected" is an efficient scheme. Use the procedures of NIOSH Methods 7082 (Lead by flame AAS), 7300 (Elements by ICP), 7105 (Lead by graphite furnace AAS), or other appropriate methods.

METHOD WRITTEN WRITTEN BY: Peter M. Eller, Ph.D., QASA/DPSE

LEAD by Flame AAS 7082

Pb MW: 207.19 (Pb) CAS: 7439-92-1 (Pb) RTECS: OF7525000 (Pb)
223.19 (PbO) 1317-36-8 (PbO) OG1750000 (PbO)

METHOD: 7082, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 μg/100 g
ACGIH: 0.15 mg/m^3

PROPERTIES: soft metal;
d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING	
SAMPLER:	FILTER (0.8-μm cellulose ester membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	200 L @ 0.05 mg/m^3
-MAX:	1500 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set

ACCURACY	
RANGE STUDIED:	0.13 to 0.4 mg/m^3 [1]; 0.15 to 1.7 mg/m^3 (fume) [2]
BIAS:	− 3.1%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.072 [1]; 0.068 (fume) [2]
ACCURACY:	± 17.6%

MEASUREMENT	
TECHNIQUE:	ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME
ANALYTE:	lead
ASHING:	conc. HNO_3, 6 mL + 30% H_2O_2, 1 mL; 140 °C
FINAL SOLUTION:	10% HNO_3, 10 mL
FLAME:	air-acetylene, oxidizing
WAVELENGTH:	283.3 nm
BACKGROUND CORRECTION:	D_2 or H_2 lamp, or Zeeman
CALIBRATION:	Pb^{2+} in 10% HNO_3
RANGE	10 to 200 μg per sample [2,3]
ESTIMATED LOD:	2.6 μg per sample [4]
PRECISION ($\hat{S}_r$):	0.03 [1]

APPLICABILITY: The working range is 0.05 to >1 mg/m^3 for a 200-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.*
4. Calibration stock solution, 1000 μg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable $\geq$ one year.
5. Air, compressed, filtered.
6. Acetylene
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8-μm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140 °C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Conc. nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [2,4].
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: CO_3^{2-}, PO_4^{3-}, I^-, F^-, CH_3COO^-. If Ca^{2+} or SO_4^{2-} are present in 10-fold or greater excess, make all standards and samples 1% (w/w) in La^{2+} [3].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 0.25 to 20 μg/mL Pb (2.5 to 200 μg Pb per sample).
    a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
    b. Analyze the working standards together with the blanks and samples (steps 14 and 15).
    c. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [8]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum, or Zeeman background correction mandatory at that wavelength.
15. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

16. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
17. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 μg Pb per sample was 98%, and collection efficiency of 0.8-μm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 μg Pb per sample gave the following results [2,4]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	HNO_3 + H_2O_2	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	HNO_3 + H_2O_2	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	HNO_3 + H_2O_2	95 ± 6

*Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 μm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was > 97 ± 2%. Overall precision, $\hat{S}_{rT}$, was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

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METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements

   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.

c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.

d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six, or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180°C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180°C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in Table 1.

Table 1

Program Variables for Paint Chips Sample Digestion with Nitric Acid

Stage	(1)	(2)	(3)
Power	90%	90%	0%
Pressure, psi	50	100	0
Run Time, min	10:00	20:00	05:00
Time @ P, min	05:00	15:00	00:00
Temperature	180°C	180°C	0°C
Fan Speed	100%	100%	100%
Number of Vessels:	12		
Liquid Volume per Vessel:	5 mL		
Sample Weight:	0.1 g		

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.

LEAD by HGAAS

Pb MW: 207.19 (Pb); 223.19 (PbO) CAS: 7439-92-1 (Pb); 1317-3608 (PbO) RTECS: OF7525000 (Pb) OG1750000 (PbO)

METHOD: 7105, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990** **Issue 2: 15 August 1994**

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 μg/100 g
ACGIH: 0.15 mg/m^3

PROPERTIES: soft metal; d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING

SAMPLER:	FILTER (0.8-μm cellulose ester membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	1 L @ 0.05 mg/m^3
-MAX:	1500 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
FIELD BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	ATOMIC ABSORPTION SPECTROPHOTOMETER, GRAPHITE FURNACE
ANALYTE:	lead
ASHING:	conc. HNO_3, 3 mL; 30% H_2O_2; 1 mL; 140 °C
FINAL SOLUTION:	10 mL 5% HNO_3
WAVELENGTH:	283.3 nm
GRAPHITE TUBE:	pyrolytic coated
INJECTION:	20 μL + 10 μL matrix modifier, DRY: 110 °C, 70 sec; CHAR: 800 °C, 30 sec; ATOMIZE: 1800 °C, 5 sec.
BACKGROUND CORRECTION:	D_2, H_2, or Zeeman
CALIBRATION:	Pb^{2+} in 5% HNO_3
RANGE	0.05 to 100 μg per sample [1]
ESTIMATED LOD:	0.02 μg per sample [1]
PRECISION ($\bar{S}_r$):	0.049 [1]

APPLICABILITY: The working range is 0.002 to >1 mg/m^3 for a 200-L air sample. If high concentrations are expected, the samples should be analyzed by flame AAS. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the sample may be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control molecular absorption. High concentrations of calcium, sulfate, carbonate, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be offset by an additional sample treatment step.

OTHER METHODS: This revises and replaces P&CAM 214 (2). Method 7300 (ICP-AES) is an alternate analytical method. Method 7505 is specific for lead sulfide by X-ray diffraction. Method 7082 is a flame AAS method, with a higher working range.

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 5% (v/v). Add 50 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O (w/w), reagent grade.*
4. Calibration stock solution, 1000 μg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of HNO_3 and dilute to 1 L with 1% (v/v) HNO_3. Store in a polyethylene bottle.
5. Matrix Modifier. Place 0.2 g $NH_4H_2PO_4$ and 0.3 g $Mg(NO_3)_2$ in a 100-mL volumetric flask. Add 2 mL conc. HNO_3 and bring to volume with distilled or deionized water.
6. Argon, prepurified.
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-μm, 37-mm, in 2-piece cassette.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace atomizer and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for Argon.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140 °C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Conc. nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 1 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: Some matrices, especially bulk samples containing epoxy-based paint, may require a different digestion procedure for complete recovery of lead. See the Appendix of Method 7082 (Lead by Flame AAS) for a microwave digestion procedure which can be used for this purpose.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Rinse the watchglass and walls of the beaker with 3 to 5 mL 5% HNO_3. Allow the solution to evaporate to 0.5 mL.
7. Cool each beaker.
8. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare a series of six working standards covering the range 0.002 to 0.1 μg/mL Pb (0.02 to 1.0 μg Pb per sample).
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 5% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.

b. Analyze the working standards together with the blanks and samples (steps 12 through 14).
c. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).

10. Analyze a standard for every 10 samples to check for instrument drift.
11. Check recoveries with at least one spiked media blank per 10 samples.
    NOTE: Perform a matrix spike of a sample occasionally to check for matrix interferences. If an adequate recovery is not obtained (85 to 115%), an alternate method of analysis should be used, such as flame AAS or ICP.

MEASUREMENT:

12. Set spectrophotometer as specified by the manufacturer and to conditions on page 7105-1.
    NOTE: An alternate wavelength is 217.0 nm [3]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum, or Zeeman background correction mandatory at that wavelength.
13. Add matrix modifier to samples and standards in proper ratio of 2 to 1 (sample or standard to matrix modifier).
14. Analyze standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance value for the sample is above the linear range of the standards, dilute with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
16. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 214 [2], issued on 1/29/76, was based on a method for metal pollutants in water [4]. Air sampling and digestion procedures follow those in Method 7082. The analytical procedure was evaluated by DataChem Laboratories in 1990 [1]. The LOD was determined at 0.02 μg per sample, with a LOQ of 0.05 μg per sample. The precision of the measurement procedure was 0.049. The overall precision, bias, and accuracy of the method were not determined. The reagents for digesting various lead species are given below:

Species	Digestion Method
Pb metal	HNO_3 only
Pb metal	HNO_3 + H_2O_2
PbO	HNO_3 only
PbS	HNO_3 only
PbO_2	HNO_3 only
PbO_2	HNO_3 + H_2O_2
Pb in paint*	HNO_3 only
Pb in paint*	HNO_3 + H_2O_2

* Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

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METHOD REVISED BY:

James B. Perkins, Brent E. Stephens, and Michael P. Beesley, DataChem Laboratories, Salt Lake City, UT.

LEAD SULFIDE 7505

PbS MW: 239.25 CAS: 1314-87-0 RTECS: OG4550000

METHOD: 7505, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.05 mg (Pb)/m^3
NIOSH: <0.1 mg (Pb)/m^3; blood Pb ≤ 60 μg/100 g
ACGIH: 0.15 mg (Pb)/m^3

PROPERTIES: solid; d 7.5 g/mL; MP 1114 °C

SYNONYMS: galena (mineral)

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm nylon or Higgins-Dewell (HD) cyclone + 5-μm PVC membrane)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 600 L @ 0.05 mg (Pb)/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: 4% degradation in 45 days; protect samples from light

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: 12 to 37 μg/m^3 [1]

BIAS: not significant when samples and standards have equivalent particle size

OVERALL PRECISION ($\hat{S}_{rT}$): 0.103 [1]

ACCURACY: ca. ± 22%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: lead sulfide

DISSOLVE: filter in tetrahydrofuran

SUSPEND: dust in tetrahydrofuran

REDEPOSIT: 0.45-μm Ag membrane filter

XRD: Cu target X-ray tube
Optimize for intensity; 1° receiving slit
Graphite monochromator; scintillation detector
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of PbS in 2-propanol

RANGE 30 to 2000 μg per sample

ESTIMATED LOD: 5 μg per sample

PRECISION ($\bar{S}_r$): 0.081 (40 to 260 μg per sample [1]

APPLICABILITY: The working range is 0.06 to 4 mg/m^3 for a 500-L air sample. The method is specific for lead sulfide among other mine dusts.

INTERFERENCES: Lead oxide (PbO, Pb_3O_4), lead sulfate (anglesite), copper iron sulfide (chalcopyrite); also see APPENDIX.

OTHER METHODS: This method was originally designated P&CAM 350, which it replaces [2].

REAGENTS:

1. Lead sulfide, ACS grade, <10-μm particle size.*
   NOTE: Perform a qualitative analysis (step 10) to determine the purity of the lead sulfide. The material also must be ultrasonically wet-sieved with a 10-μm pore size sieve to approximate respirable dust. Evaporate the alcohol. Dry the sieved material in an oven at 110 °C for 1 h, cool and store in a desiccator.
2. 2-Propanol.
3. Tetrahydrofuran (THF).*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Bulk sampler: PVC membrane filter, 37-mm, 5-μm pore size in two-piece filter cassette. Sample closed face at 2 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-μm pore size (Selas Flotronics, Millipore Corp., or equivalent).
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Filtration apparatus and side arm vacuum flask with 25- and 37-μm filter holders.
8. Sieve, 10-μm, for wet sieving.
9. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; centrifuge tubes (wide mouth), 40-mL, and test tube rack; desiccator; reagent bottles, 1-L, with ground glass stoppers; drying oven; polyethylene wash bottle; Pyrex beakers, 50-mL, and matching watchglasses; and glue or tape for securing Ag filters to XRD holder.

SPECIAL PRECAUTIONS: THF is extremely flammable and should be used in a fume hood.

Avoid inhaling lead sulfide dust [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with a nylon cyclone or 2.2 L/min with an HD cyclone for a total sample size of 600 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

3. Take a high-volume bulk dust sample (e.g., 1 m^3 @ 3 L/min).
   NOTE: Protect the filters from exposure to intense light during storage.

SAMPLE PREPARATION:

4. Using forceps, place filters in 40-mL wide-mouth centrifuge tubes. Add 10 mL THF to each tube. Place the centrifuge tubes on the test tube rack in the ultrasonic bath for 10 min.
5. Place a silver filter in the filtration apparatus and attach the funnel. Pour the suspensions from the centrifuge tube into the funnel.
6. Wash the empty centrifuge tube with 5 mL THF and shake tube by hand or by vortex mixer for a few seconds. Transfer the THF to the filtration funnel. Repeat with two more 5-mL portions of THF.
7. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add THF to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sampler holder.

CALIBRATION AND QUALITY CONTROL:

8. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to correct for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}$, for each media blank (step 11). Average the values for the six media blanks.
9. Prepare and analyze working standard filters.
   a. Prepare two suspensions by weighing 10 and 100 mg of the dry, sieved lead sulfide to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
   b. Suspend the powder in the 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar. Cool to room temperature before use.
   c. Mount a silver filter on the filtration apparatus. Place 2 to 4 mL 2-propanol on the filter. Turn off the stirrer and shake the suspension vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse, and dry the pipet and take a new aliquot. Transfer the aliquot from the pipet to the filter keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the XRD sample mount. Prepare working standard filters in triplicate by this technique at, e.g., 5, 10, 30, 50, 100, 200, 500, 1000, and 2000 μg lead sulfide.
   f. Analyze by XRD (step 11). Use the same diffraction peaks and instrumental conditions as for samples. Designate the net and normalized XRD intensities for the working standard filters as I_x° (step 11.d) and $\hat{I}_x^\circ$ (step 11.e), respectively. Correct $\hat{I}_x^\circ$ for matrix absorption for standards containing more than 200 μg PbS (steps 11.f and 12).
   g. Prepare a calibration graph by plotting $\hat{I}_x^\circ$ vs. mass PbS (μg). A weighted least squares ($1/\sigma^2$) fit is preferable.
   h. Determine the slope, m (counts/μg), of the calibration graph. The intercept of the line should be zero ± 5 μg.

MEASUREMENT:

10. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2Θ) of the settled dust sample or high-volume respirable sample to determine the presence of lead sulfide and any matrix interference (see APPENDIX). If quantitative analysis is to be performed on the field sample (percent PbS), wet-sieve it through a 10-μm sieve in order to match the particle size of the standards. The expected diffraction peaks are:

	Peak (2Θ Degrees)	
	Primary	Secondary
Lead Sulfide	30.10°	25.98°
Silver	38.12°	44.28°

11. Mount the filter (sample, standard or blank) in the XRD instrument and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak and use this value of N for all analyses.
    b. Measure the diffraction peak area of the most intense interference-free diffraction peak of PbS. Scan times must be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain a total (average) background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x (the difference between the peak integrated count and the total background count).
    e. Calculate the normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank and standard:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N.$$

    NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently measured reference intensity.
    f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-Θ range used for PbS and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

12. Calculate the concentration of lead sulfide, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(T) - b}{m \cdot V}, \ mg/m^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration curve ($\hat{I}_x^o$ vs. W)
m = initial slope of calibration curve, counts/μg

$$f(T) = \frac{-R \ln T}{1 - T^R}$$ = absorption correction factor (Table 1)

$R = \sin(\Theta_{Ag})/\sin(\Theta_x)$
$T = \hat{I}_{Ag}/(\text{average } \hat{I}_{Ag}$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [4] and [5].

EVALUATION OF METHOD:

The measurement precision, $\hat{S}_r$, initially determined with 30 samples in the range 30 to 2000 μg PbS per filter was 0.0047 [6]. The same 30 samples plus five blank filters were analyzed by X-ray fluorescence for lead and sulfur and by ICP-AES for lead in order to verify the accuracy of the PbS filter depositions. A recovery study with 20 spiked samples in the range of 30 to 150 μg PbS per filter indicated a 102.6% average recovery and a 0.05 relative standard deviation.

Another recent study [1] involving 54 spiked samples in the range 40 to 250 μg PbS per filter indicated an 0.0081 precision and a 98% recovery. The overall method was also evaluated in the study using eight sets of samples collected in galena mills. A set consisted of six filters collected side by side. Average PbS in air concentrations for these sets ranged from 12 to 35 $\mu g/m^3$ and the pooled $\hat{S}_{rT}$ for seven of these averages was 0.103. The eighth set was an outlier [1].

Two stability studies [6] were performed: a short-term (47 days) and a long-term (6.5 months). In the short-term study, 15 PbS samples were exposed to various conditions from intense light to no light, from moist air to vacuum; all were analyzed at intervals. During analysis, they were all subjected to a total of over 2 h exposure to X-ray radiation at 1400 watts. Under continuous intense light, the PbS degradation was 14.4%. The smallest degradations were with no light (1.2 to 3.8%). In the long-term study, a PbS bulk sample exposed to ambient laboratory air and light conditions and a total of 36 h of X-ray radiation degraded 37.6%. A filter similarly exposed in the lab for 158 days and a total of 28 h of X-radiation degraded 12.2%. It is, therefore, recommended that the samples be protected from light.

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APPENDIX:

INTERFERENCES

If interferences are present, use a different lead sulfide peak. Lead oxide (PbO yellow-form), lead sulfate (anglesite) and copper iron sulfide ($CuFeS_2$ chalcopyrite) interfere with the primary lead sulfide peak, using copper K_α X-ray radiation. Lead oxide (Pb_3O_4 orange-form) and lead sulfate (anglesite) also interfere with the secondary lead sulfide peak. The oxides of lead do not occur naturally in appreciable amounts in galena mining but are formed when lead sulfide is heated at high temperatures (i.e., in smelting and roasting operations) [7]. Dolomite, zinc sulfide (ZnS sphalerite) and chalcopyrite that are normally found in galena mining do not interfere with the secondary lead sulfide peak; for this reason the secondary lead sulfide peak was chosen as the analytical peak. The tertiary lead sulfide peak interferes with the secondary silver peak.

When peak overlaps are not severe, a smaller receiving slit or chromium X-radiation may be used; however, a new calibration curve will be necessary.

The presence of some elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to increased background intensity. This can be minimized by a diffracted beam monochromator.

The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made (step 12 and Table 1).

Table 1. Matrix absorption correction factors for lead sulfide/silver peaks, degrees 2Θ.

Lead Sulfide		30.10	25.98		30.10	25.98
Silver		38.12	38.12		38.12	38.12
	T	f(T)	(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2013	1.2346
	0.99	1.0063	1.0073	0.73	1.2109	1.2460
	0.98	1.0128	1.0147	0.72	1.2208	1.2575
	0.97	1.0193	1.0223	0.71	1.2308	1.2693
	0.96	1.0259	1.0299	0.70	1.2410	1.2814
	0.95	1.0326	1.0377	0.69	1.2514	1.2936
	0.94	1.0394	1.0456	0.68	1.2620	1.3062
	0.93	1.0463	1.0536	0.67	1.2729	1.3190
	0.92	1.0533	1.0618	0.66	1.2839	1.3320
	0.91	1.0605	1.0701	0.65	1.2952	1.3453
	0.90	1.0677	1.0785	0.64	1.3067	1.3590
	0.89	1.0751	1.0870	0.63	1.3185	1.3729
	0.88	1.0825	1.0957	0.62	1.3305	1.3871
	0.87	1.0901	1.1046	0.61	1.3428	1.4017
	0.86	1.0978	1.1136	0.60	1.3554	1.4165
	0.85	1.1057	1.1227	0.59	1.3682	1.4318
	0.84	1.1136	1.1320	0.58	1.3813	1.4473
	0.83	1.1217	1.1414	0.57	1.3948	1.4633
	0.82	1.1300	1.1511	0.56	1.4085	1.4796
	0.81	1.1383	1.1609	0.55	1.4226	1.4963
	0.80	1.1469	1.1708	0.54	1.4370	1.5135
	0.79	1.1555	1.1810	0.53	1.4518	1.5311
	0.78	1.1644	1.1913	0.52	1.4669	1.5491
	0.77	1.1733	1.2018	0.51	1.4825	1.5676
	0.76	1.1825	1.2126	0.50	1.4984	1.5866
	0.75	1.1918	1.2235	0.49	1.5148	1.6061

T = sample transmittance (step 12).
f(T) = sample correction factor (step 12).

LINDANE 5502

See ALDRIN, Method 5502, for Procedure

$C_6H_6Cl_6$ MW: 290.82 CAS: 58-89-9 RTECS: GV4900000

METHOD: 5502, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA: 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin)
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: solid; MP 112.5 °C; VP 0.0013 Pa (9.4 x 10^{-6} mm Hg; 0.15 mg/m^3) @ 20 °C

SYNONYMS: gamma-hexachlorocyclohexane; benzenehexachloride; gamma-BHC.

SAMPLING

SAMPLER: FILTER AND BUBBLER (glass fiber + 15 mL isooctane)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 18 L @ 0.25 mg/m^3
-MAX: 240 L

SHIPMENT: transfer bubbler solutions and filters in scintillation vials; pack carefully

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.3 to 1.7 mg/m^3 [1];

BIAS: − 0.44%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.086 [1]

ACCURACY: ± 16.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTOR

ANALYTE: LINDANE

FILTER EXTRACTION: isooctane

INJECTION VOLUME: 15 µL

TEMPERATURE-FURNACE: 750 to 770 °C
-TRANSFER: 225 °C
-VENT: 205 to 260 °C
-COLUMN: 160 to 190 °C

GASES-H_2 (furnace): 150 to 160 mL/min
-N_2 (carrier): 140 mL/min

COLUMN: glass, 1.2 m x 3-mm OD; 5% SE-30 on 80/100 mesh acid-washed DMCS Chromosorb W or equivalent

CALIBRATION: solution of analyte in isooctane

RANGE: 5 to 135 µg per sample

ESTIMATED LOD: 3 µg per sample

PRECISION ($\bar{S}_r$): 0.013 [1]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m^3 for a 90-L air sample. Evaporation of isooctane from the bubbler necessitates refilling the bubbler frequently.

INTERFERENCES: None identified.

OTHER METHODS: This method combines and replaces S275 [2] and S290 [2]. Lindane has also been sampled with a filter-solid sorbent train [3].

LITHIUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

MAGNESIUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

MALEIC ANHYDRIDE

$C_4H_2O_3$ MW: 98.06 CAS: 108-31-6 RTECS: ON3675000

METHOD: 3512, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 0.25 ppm TWA
NIOSH: 0.25 ppm TWA
ACGIH: 0.25 ppm TWA
(1 ppm = 4.01 mg/m^3 @ NTP)

PROPERTIES: solid; MP 53 °C; d 1.43 @ 22 °C; VP <0.16 mm Hg @ 20 °C; vapor density (air = 1) 3.38

SYNONYMS: 2,5-furandione; cis-butenedioic anhydride; toxilic anhydride

SAMPLING

SAMPLER: BUBBLER (15 mL distilled water)

FLOW RATE: 0.2 to 1.5 L/min

VOL-MIN: 40 L @ 1.0 mg/m^3
-MAX: 500 L

SHIPMENT: plug inlet and outlet with Teflon plugs to prevent spillage during shipment.

SAMPLE STABILITY: less than 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.50 to 2.14 mg/m^3 [1] (340-L samples)

BIAS: − 6.7%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.063 [1]

ACCURACY: ± 19.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: maleic anhydride

INJECTION VOLUME: 50 µL

MOBILE PHASE: 0.5% dicyclohexylamine/0.5% formic acid/25% methanol/74% water, 1.7 mL/min

COLUMN: µ-Bondapak C_{18}, 10-µm particle size, 30 cm x 3.9-mm ID or equivalent

DETECTOR: UV @ 254 nm

CALIBRATION: standard solutions of maleic anhydride in acetone and distilled water

RANGE: 36 to 1080 µg per sample [1]

ESTIMATED LOD: 15 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.035 @ 181 to 723 µg per sample [1]

APPLICABILITY: The working range is 0.025 to 0.75 ppm (0.1 to 3 mg/m^3) for a 360-L air sample. This method does not distinguish between maleic anhydride and maleic acid, and has limited sample stability [1].

INTERFERENCES: Since maleic anhydride is converted to maleic acid, maleic acid can be considered an interference and will result in a positive bias.

OTHER METHODS: This revises Method P&CAM 302 [2]. Geyer and Saunders reported a modified mobile phase for the determination of maleic anhydride, but used the same sampling technique [3]. A method for the trace analysis of maleic anhydride in workplace air was published by Kallio [4].

REAGENTS:

1. Maleic Anhydride*, ACS reagent grade.
2. Dicyclohexylamine, ACS reagent grade.
3. Formic acid, ACS reagent grade.
4. Methanol, distilled in glass.
5. Acetone, distilled in glass.
6. Water, deionized and distilled.
7. Calibration stock solution, 1 mg/mL. Dissolve 10 mg maleic anhydride in 10 mL acetone.
8. Mobile Phase: Dilute 10 mL of dicyclohexylamine and 10 mL of formic acid to 100 mL with distilled water. Dilute 10 mL of this solution, plus 250 mL methanol, to 1 L with distilled water.

* See Special Precautions

EQUIPMENT:

1. Sampler: A 25-mL bubbler with 15 mL distilled water.
2. Personal sampling pump, 0.2 to 1.5 mL/min, with flexible polyethylene or Teflon tubing.
3. Teflon plugs and/or tubing.
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 3512-1).
5. Syringes, 50-1000-μL.
6. Volumetric flasks, 10-, 100-, and 1000-mL.
7. Pipets, 10- and 15-mL glass, delivery, with pipet bulb.
8. Graduated cylinders, glass, 25-mL.

SPECIAL PRECAUTIONS: Maleic anhydride is a powerful irritant. Avoid contact with skin, eyes, and respiratory tract [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL distilled water to a bubbler.
3. Connect outlet arm of bubbler to a second empty bubbler and then to the sampling pump.
4. Sample 40 to 500 L of air at an accurately known rate between 0.2 and 1.5 L/min.
5. Seal bubbler for shipment in a suitable container in order to prevent damage during transit. Seal the inlet and outlet of the bubbler stem by connecting a piece of Teflon tubing between them or by inserting Teflon plugs in the inlet and outlet.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Transfer the liquid from the bubbler, quantitatively, to a graduated cylinder.
8. Bring volume to 15 mL with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards (20 to 800 μg/10 mL) by adding appropriate aliquots of calibration stock solution to distilled water.
10. Analyze working standards together with samples and blanks (steps 11 through 13). Prepare a calibration graph of area vs. μg of maleic anhydride per 15 mL of sample.

MEASUREMENT:

11. Set liquid chromatograph to conditions given on page 3512-1.
12. Inject 50-μL sample aliquot.
13. Measure peak area.

CALCULATIONS:

14. Read mass, μg, of maleic anhydride (W) found in the sample from the calibration graph.
15. Calculate concentration of maleic anhydride in the actual air volume, V (L), at the sampling site:

$$C = \frac{W}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was validated over the range 0.50 to 2.14 mg/m^3 at 20 °C and pressure of 757 mm Hg using 360-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.063, with a bias of - 6.7%. Recovery of maleic anhydride was 104% in the range of 181 to 723 μg maleic acid per sample. Sample stability during storage was evaluated at 367 μg per sample. Samples showed an average loss of 13% after seven days of storage at ambient conditions compared to one-day old samples. Refrigeration of samples may retard loss but this has not been experimentally determined.

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MANGANESE

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

MBOCA in urine 8302

$(H_2NC_6H_3Cl)_2CH_2$ MW: 267.16 CAS: 101-14-4 RTECS: CY1050000

METHOD: 8302 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to 4,4'-methylenebis(2-chloroaniline)

SYNONYMS: MOCA; di-(4-amino-3-chlorophenyl)methane; 4,4'-methylenebis(2-chloroaniline)

SAMPLING

SPECIMEN: 2 urines (pre- and post-exposure)

VOLUME: 50 to 100 mL in polyethylene screw-cap bottles containing preservative

PRESERVATIVE: 3 mL of 30% (w/w) citric acid solution

SHIPMENT: freeze urine and ship in dry ice in an insulated container

STABILITY: stable for 2 days @ 25 °C and for 1 month @ −20 °C

CONTROLS: collect urine from non-exposed workers

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: heptafluorobutyryl MBOCA derivative

EXTRACTIONS: MBOCA and analyte

INJECTION VOLUME: 1 μL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 300 °C
-COLUMN: 1 min @ 90 °C; 35°/min; 4 min @ 250 °C

COLUMN: SE-54 capillary column, 30 m x 0.25-mm ID fused silica

CARRIER GAS: 5% methane in argon, 40 mL/min

CALIBRATION: control urine spiked with MBOCA; MDA as internal standard

QUALITY CONTROL: frozen pooled urine; correct for creatinine content

RANGE: 10 to 250 μg/L urine

ESTIMATED LOD: 1 μg/L urine

RECOVERY: 89% (100 μg/L of urine); 79% (4 to 25 μg/L urine)

PRECISION ($\bar{S}_r$): 0.08

ACCURACY: ± 27 to 37%

APPLICABILITY: MBOCA is commonly found in the urine of humans exposed to the compound in the plastic industry. Despite the extensive metabolism of MBOCA in the rat, analysis of the urine of exposed workers showed only MBOCA [1]. This GC-ECD method is useful in screening workers exposed to MBOCA.

INTERFERENCES: Imipramine has a similar retention time. A careful work history/questionnaire is suggested.

OTHER METHODS: This revises P&CAM 342 [2] and Method 8302 (dated 2/15/84). This method is 40-fold more sensitive than the method in the Special Hazard Review [3]. A similar, less sensitive method using GC-FID has been described [4].

REAGENTS:

1. 4,4'-Methylenebis(2-chloroaniline) (MBOCA) calibration stock solution, 200 mg/mL.* Accurately weigh 50 mg MBOCA. Dissolve in a small volume of methanol. Dilute to 250 mL with methanol. Stable five days at 25 °C.
2. 4,4'-Methylenedianiline (MDA), internal standard, 10 μg/mL in methanol.
3. Hexane.*
4. Diethyl ether.*
5. Triethylamine (TEA), 0.05 M stock solution in hexane.
6. Heptafluorobutyric anhydride (HFBA).
7. Florisil, 60 to 100 mesh, activated by the manufacturer at 650 °C, heated to 130 °C for 24 h, then deactivated by adding 10% (w/w) water and mixing 2 h on a rotary mixer at 50 rpm. Stable one week.
8. Benzene.*
9. NaOH.
10. KH_2PO_4 buffer, 0.1 M, adjusted to pH 6 with conc. HCl.
11. Sodium sulfate, granular, anhydrous.
12. Methanol.
13. Citric acid, monohydrate, granular.
14. Pooled urine sample or Hycel urine control (Hycel Co., Houston, TX).
15. HCl, conc.
16. P-5 carrier gas, 5% methane in argon.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Bottles, polyethylene, screw-top, 125-mL.
2. Gas chromatograph with ^{63}Ni electron capture detector, integrator and capillary column (page 8302-1).
3. Pipets, Pasteur.
4. Centrifuge tubes, 15-mL, graduated, glass-stoppered.
5. Mixer, rotary, 50 to 60 rpm, for 20-mm culture tubes.
6. Culture tubes, 20 x 150-mm, screw cap, PTFE-lined.
7. Mixer, vibration.
8. Chromatography column, 7-mm ID x 20 cm, with a 25-mL reservoir and PTFE stopcock.
9. pH paper, wide range.
10. Nitrogen manifold for evaporating organic solutions.
11. Pipets, 10-mL.
12. Centrifuge, table top, clinical.
13. Syringes, glass, 10- and 50-μL.
14. Waterbath, 50 °C.
15. Volumetric flasks, 100- and 250-mL.
16. Glass wool.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. MBOCA, MDA, and benzene are suspect carcinogens; handle either in a glove box or a well-ventilated hood.

Handle ethyl ether and hexane with care; both are highly flammable and should be used in a hood.

SAMPLING:

1. Collect 50 to 100 mL urine in a 125-mL polyethylene bottle containing 3 mL 30% citric acid.
2. Cap the bottle immediately after sample collection. Swirl gently to mix.
3. Ship the sample in dry ice in an insulated container.

SAMPLE PREPARATION:

4. Thaw urine sample.
5. Perform a creatinine determination on an aliquot of the urine (e.g., [5]).
6. Pipet a 5-mL aliquot of urine into a clean culture tube.
7. Adjust pH to >12 using 10 N NaOH (ca. 0.1 mL).
8. Add 1 mL methanol. Mix well.
9. Add 5 mL 1:1 diethyl ether:hexane. Shake steadily for 2 min to extract the MBOCA. Centrifuge to separate phases. Transfer the organic phase by Pasteur pipet to a culture tube. Repeat with two additional 5-mL portions of 1:1 diethyl ether: hexane, combining the organic phases. NOTE: Emulsions may form; break them by adding methanol or by repeated centrifugation.
10. Concentrate the extract to ca. 1 mL under a gentle stream of nitrogen in a hood.
11. Add 50 µL TEA, 50 µL HFBA, and 25 µL MDA to the concentrated extract. Mix well in a hood.
12. Secure the cap loosely. Heat in a waterbath at 50 °C for 15 min.
13. Remove from waterbath. Add 2 mL hexane and 5 mL KH_2PO_4 buffer. Mix well.
14. Centrifuge to separate phases completely. Transfer the organic layer containing the derivative, without disturbing the aqueous phase, with a Pasteur pipet into a 15-mL centrifuge tube.
15. If low concentration (<5 µg/L urine) is expected, use Florisil cleanup (see APPENDIX). Add 0.2 g Na_2SO_4 and mix.

CALIBRATION AND QUALITY CONTROL:

16. Prepare working standards over the range 0 (control) to 200 µg/L urine by adding aliquots of calibration stock solution to a control urine.
17. Extract 5 mL of each working standard (steps 6 through 15). Analyze the working standards with the samples (steps 20 and 21).
18. Prepare calibration graph (ratio of peak area of analyte to peak area of MDA vs. µg MBOCA/L urine).

MEASUREMENT:

19. Set gas chromatograph according to manufacturer's recommendations and to conditions on page 8302-1.
20. Inject 1 µL hexane extract from step 15.
21. Measure the peak areas of the samples and internal standard. Divide the peak area of the sample by the peak area of the internal standard on the same chromatogram.

CALCULATIONS:

22. Determine the MBOCA concentration in the urine sample, C_u (µg/L), from the calibration graph.
23. Calculate the concentration of MBOCA/g creatinine in the urine sample, C (µg/g creatinine), using the creatinine value (C_r) obtained in step 5.

$$C = \frac{C_u}{C_r}, \ \mu g \text{ MBOCA/g creatinine.}$$

GUIDES TO INTERPRETATION:

Linch, et al. [1] reported exposed workers having MBOCA at concentrations up to 370 μg/L of urine. No other reports have been found in the literature. CAL/OSHA has recommended that urinary MBOCA levels should not exceed 100 μg/L [6].

EVALUATION OF METHOD:

Spiked urine specimens containing MBOCA concentrations of 4, 30 and 150 μg/L urine were analyzed in groups of 10 for each concentration. Precision ($\bar{S}_r$) over the above analytical range was found to be 0.08 [2].

REFERENCES:

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[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 342, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).

[3] Special Hazard Review with Control Recommendations for 4,4'-Methylenebis-(2-Chloroaniline), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-188 (1978).

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[5] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-999, W.B. Saunders, Co., Philadelphia, PA (1976).

[6] California Occupational Safety and Health Administration (CAL/OSHA), Title 8, Sec. 5215; General Industry Safety Orders, 4,4'-Methylenebis(2-chloroaniline), Register 81, No. 22 (May 30, 1981).

METHOD WRITTEN BY:

William P. Tolos, NIOSH/DBBS.

APPENDIX: FLORISIL CLEANUP AND ANALYSIS (for urine containing <5 mg MBOCA/L)

1. Concentrate the extract (the organic layer from step 14) to approximately 0.5 mL under a gentle stream of nitrogen at 30 °C in a waterbath.
2. Place a small glass wool plug in a chromatographic column. Add 1.6 g of 10% deactivated Florisil. Top with 2 cm of anhydrous Na_2SO_4.
3. Pre-rinse the packed column with 10 mL hexane.
4. Transfer the 0.5 mL of derivatized extract to the column with a Pasteur pipet. Add the extract just as the level of hexane rinse is even with the Na_2SO_4 layer.
5. Quickly rinse the extract tube with several additional small quantities of hexane. Do not allow the level of rinse to fall below the Na_2SO_4 layer.
6. Discard the eluted pre-rinse.
7. Elute the column with 10 mL of 40% benzene/hexane (v/v). The solvent mixture should not fall below the Na_2SO_4 layer; discard the eluate.
8. Elute the column with 10 mL of 100% benzene. Save the eluate and concentrate to 1 mL.
9. Inject 1 μL of the concentrated benzene fraction into the GC that has been set to the conditions described on page 8302-1.

CH_3SH	MW: 48.11	CAS: 74-93-1	RTECS:	PB4375000
CH_3CH_2SH	62.13	75-08-1		KI9625000
$CH_3CH_2CH_2CH_2SH$	90.19	109-79-5		EK6300000

METHOD: 2542, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 22 October 1991**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Methyl mercaptan: methanethiol; mercaptomethane; methyl sulfhydrate
Ethyl mercaptan: ethanethiol; mercaptoethane; ethyl sulfhydrate
n-Butyl mercaptan: butanethiol; 1-mercaptobutane; 1-butanethiol

SAMPLING

SAMPLER: FILTER
(glass fiber, 37-mm, impregnated with mercuric acetate)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 10 L @ 0.5 ppm
-MAX: 150 L

SHIPMENT: protect samples from light [1,2]

SAMPLE STABILITY: at least 3 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 2

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Table 2

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE

ANALYTE: methyl, ethyl and n-butyl mercaptans

EXTRACTION: 20 mL HCl (25% v/v) plus 5 mL 1,2-dichloroethane, 2 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 250 °C
-COLUMN: 30 °C 2 min, 15 °C/min, 200 °C

COLUMN: narrow-bore, fused-silica capillary, 30 cm x 0.25-mm ID, 1 µm

CARRIER GAS: He, 1.0 mL/min; makeup gas: N_2, 20 mL/min

CALIBRATION: standard solutions of mixed mercaptans in 1,2-dichloroethane

RANGE: Table 2

ESTIMATED LOD: Table 2

PRECISION ($\bar{S}_r$): Table 2

APPLICABILITY: The working ranges are 0.2 to 10 ppm for a 20-L air sample for all three mercaptans [1-4].

INTERFERENCES: Dimethyl disulfide, diethyl disulfide and dibutyl disulfide may interfere [2-4].

OTHER METHODS: This is a modification of OSHA Method 26 for methyl mercaptan with the addition of ethyl- and n-butyl mercaptan [2].

REAGENTS:

1. Methyl mercaptan*
   gas, lecture bottle, 99.5+%.
2. Ethyl mercaptan,* 99+%.
3. n-Butyl mercaptan,* 99+%.
4. Mercuric acetate, ACS reagent grade.
5. Hydrochloric acid, ACS reagent grade.
6. 1,2-Dichloroethane, ACS reagent grade.
7. Methyl mercaptan calibration stock solution, 0.394 mg/mL. Pipet 5.0 mL methylene chloride into a vial and attach PTFE-lined cap. Add 1.0 mL pure methyl mercaptan gas (measured at 25 °C, 1 atm) to the liquid using gas-tight syringe.
8. Ethyl mercaptan calibration stock solution, 2.52 mg/mL. Dissovle 30 μL ethyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
9. n-Butyl mercaptan calibration stock solution, 3.34 mg/mL. Dissolve 40 μL n-butyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
10. Helium, purified.
11. Hydrogen, prepurified.
12. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filters impregnated with mercuric acetate. The filters are prepared by immersing 37-mm Gelman Metrigard (or equivalent) glass fiber filters with acrylic binder in 5% (w/v) aqueous solution of mercuric acetate, dried in the air, and then assembled in two-piece filter cassettes without backup pads. The filters exhibit yellowish color, but it does not affect their collection efficiency.
2. Personal sampling pump, 0.10 to 0.20 mL/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph with a flame photometric detector, capillary column, integrator.
4. Vials, glass, 2-mL and 5-mL, PTFE-lined crimp caps.
5. Syringes, 10-, 50, and 250-μL.
6. Volumetric flasks, 10-mL.
7. Pipets, 5- and 20-mL glass, delivery, with pipet bulb.
8. Separatory funnel, 30-mL.

SPECIAL PRECAUTIONS: Store methyl-, ethyl-, and n-butyl-mercaptans from flammable and oxidizing materials [5,6]. The analytes are highly flammable and irritating to the eyes. Work in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the plugs from the filter cassette immediately before sampling. Connect the cassette to the sampling pump with flexible tubing. Air being sampled should not pass through any hose or tubing before entering filter cassette.
3. Sample at an accurately known flow rate between 0.1 and to 0.2 L/min for a total sample size of 10 to 150 L.
4. Replace the plugs in the filter cassette immediately after sampling. Store protected from light.

SAMPLE PREPARATION:

5. Add 20 mL of 25% (v/v) hydrochloric acid and 5 mL of 1,2-dichloroethane to a 30-mL separatory funnel. Fold sample filter and insert into the neck of a separatory funnel, without allowing the filter to become wet. While seating the stopper, push filter into funnel.
6. Shake funnel for 2 min without venting.
7. Let stand at least 5 min, until the phases completely separate. Then drain the 1,2-dichloroethane into a vial and seal with a PTFE-lined cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples:
   a. Add known amounts of calibration stock solution to 1,2-dichloroethane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. prepare calibration graphs: either quadratic curves, i.e., peak area vs. concentration of mercaptans, or linear curves, i.e., ln (peak area) vs. ln (concentration)^2 can be used for calibration.
9. Determine recovery (R) for each lot of glass fiber filters impregnated with mercuric acetate in the concentration range of interest. Prepare four filters at each of three concentrations plus three media blanks.
   a. Apparatus for preparing and sampling gas spikes is shown in Figure 1. The apparatus is composed of glass and Teflon.
   b. Sample at a rate of 0.2 L/min for 100 min.
      NOTE: Protect the samples from light.
   c. Extract the samples (steps 5 through 7) and analyze (steps 10 and 11).
   d. Prepare separate recovery graphs for each mercaptan (R vs. μg analyte).

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2542-1. Set air and hydrogen flow rates on the flame photometric detector to manufacturer's specification. Inject 1-μL sample aliquot via the split injection mode. Retention times: methyl mercaptan, 2.4 min; ethyl mercaptan, 3.2 min; n-butyl mercaptan 6.9 min.
11. Measure peak area.

CALCULATIONS:

12. Determine the mass, μg, of methyl-, ethyl-, and n-butyl-mercaptans found in the samples (W) and in the average media blanks (B).
13. Calculate concentration, C, of the mercaptans in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method modifies OSHA Method 26, Methyl Mercaptan [2], and further develops and evaluates the procedure for ethyl- and n-butyl mercaptans, as well as methyl mercaptan [1]. The method was evaluated for recovery and extraction efficiency with gas spikes, 18 samples (6 at each level, 0.5, 1, and 2 x PEL)(Figure 1). Recoveries were 82.7% for methyl mercaptan, 89.3% for ethyl mercaptan, and 93.0% for n-butyl mercaptan. Test atmospheres of methyl- and ethyl mercaptans were generated with permeation tubes as the analyte source. Six samples at one level (1 x PEL) were collected and analyzed. Recoveries for generated samples, corrected for extraction efficiency, were 98.6 ± 8.9% for methyl mercaptan and 102 ± 7.8% for ethyl mercaptan. Samples of n-butyl mercaptan were not generated. Samples prepared by spiking impregnated filters with a solution of mixed mercaptans were found to be stable for at least three weeks at ambient temperatures when protected from light. The evaluation data are summarized in Table 2.

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[1] Xue, Zhi-Lun, Backup Data Report for Methyl, Ethyl, and n-Butyl Mercaptans (NIOSH/DPSE, unpublished, October, 1991).
[2] OSHA Analytical Laboratory, Method 26, Methyl Mercaptan, February 1981.
[3] Knarr, R. and Rapport, S.M., Determination of Methanethiol at Parts-per-Million Air Concentration by Gas Chromatography, Anal. Chem., 52, 733-736 (1980).
[4] Knarr, R. and Rapport, S.M., Impregnated Filters for the Collection of Ethanethiol and Butanethiol in Air, Am. Ind. Hyg. Assoc. J., 42, 839-941 (1981).
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[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Pratima Shah, NIOSH/DPSE, and Zhi-Lun Xue.

TABLE 1. GENERAL INFORMATION

Compound	Exposure Limits (ppm) OSHA	NIOSH	ACGIH	1 ppm = mg/m^3 @ NTP	Density @ 20 °C (g/mL)	BP (°C)	kPa (mm Hg)
Methyl mercaptan	C 10	C 0.5/15 min	1.97	2.0	0.866	6.2	> 1 atm
Ethyl mercaptan	C 10	C 0.5/15 min	2.54	2.6	0.839	35	58.9 (442)
n-Butyl mercaptan	C 10	C 0.5/15 min	3.69	3.7	0.834	98.4	4.7 (35)

TABLE 2. EVALUATION DATA

Compound	Range Studied* (mg/m^3)	Measurement Range (µg/sample)	Measurement Precision $\hat{S}_r$	LOD (µg/sample)	Overall Precision $\hat{S}_{rT}$
Methyl mercaptan	1.0 to 4.0	10 to 50	0.055	4	0.091
Ethyl mercaptan	1.3 to 5.6	10 to 50	0.059	5	0.097
n-Butyl mercaptan	1.8 to 7.4	20 to 70	0.063	7	0.086

* 180-L samples

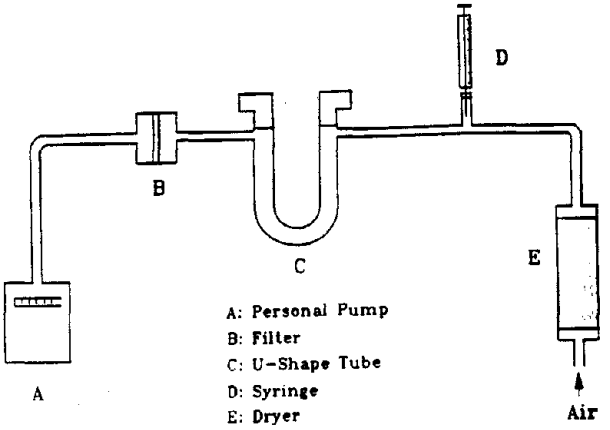

FIGURE 1. SAMPLE SPIKING AND COLLECTION SYSTEM

MERCURY

Hg MW: 200.59 CAS: 7439-97-6 RTECS: OV4550000

METHOD: 6009, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 0.1 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin)
ACGIH: 0.05 mg/m^3 (skin)

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; HP −39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C; Vapor Density (air=1) 7.0

SYNONYMS: quicksilver

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Hopcalite in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.5 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [2] (10-L samples)

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{2+} in 1% HNO_3

RANGE: 0.1 to 1.2 μg per sample

ESTIMATED LOD: 0.03 μg per sample

PRECISION ($\bar{S}_r$): 0.042 @ 0.9 to 3 μg per sample [4]

APPLICABILITY: The working range us 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [3].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [4,5,6]. This method is based on the method of Rathje and Marcero [7] and is similar to the OSHA method ID 145H [2].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg^{2+}, 1000 μg/mL. Commercially available or dissolve 0.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 μg/mL. Place 0.1 mL 1000 μg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v). Dilute 14 mL conc. HNO_3 to 1 L with deionized water.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hopcalite held in place by glass wool plugs (SKC, Inc., Cat. #226-17-1A, or equivalent).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the sorbent may be used if particulate mercury is to be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder, or integrator.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-μL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and contact with the skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known rate of 0.15 to 0.25 L/min for a total sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hopcalite sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 h or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards, a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in

the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series (six levels each) of working standards covering the range 0.01 to 0.5 μg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height vs. solution concentration, μg/sample).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 μg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
    a. Remove the bubbler from the BOD bottle.
    b. Rinse the bubbler with deionized water.
    c. Allow the recorder tracing to establish a stable baseline.
    d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
    e. Quickly add 5 mL 10% stannous chloride solution.
    f. Quickly place the bubbler into the BOD bottle.
    g. Allow the spectrophotometer to attain maximum absorbance.
    h. Vent the mercury vapor from the system.
    i. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
    j. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot (W, μg) from the calibration graph.
18. Calculate the concentration C (mg/m^3), of mercury in the air volume sampled, V (L):

$$C = \frac{W \cdot \frac{V_s}{V_a} - B}{V}.$$

Where: Vs = original sample volume (step 8; normally 50 mL)
Va = aliquot volume (step 9; normally 20 mL)
B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [7]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [8]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m^3 and an adsorbent tube loading of 1 to 7 μg was used. The Hydrar material sometimes used is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [9]. OSHA also validated a method for mercury using Hydrar [2]. An average 99% recovery, with $\bar{S}r = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 μg) of mercury added (as $Hg(NO_3)_2$) [10]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at -15 °C; longer storage times were not investigated [10].

REFERENCES:

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[3] NIOSH/MRSB. Reports for analytical Sequence Nos. 5854, 5900, 6219, and 6311, NIOSH (Unpublished, 1987-1988).
[4] NIOSH Manual of Analytical Methods, 3rd. ed., Method 6000. (1984).
[5] NIOSH Manual of Analytical Methods. 2nd. ed., V. 4, S199, U.S. Dept. of Health. Education, and Welfare Publ. (NIOSH) 79-141 (1979).
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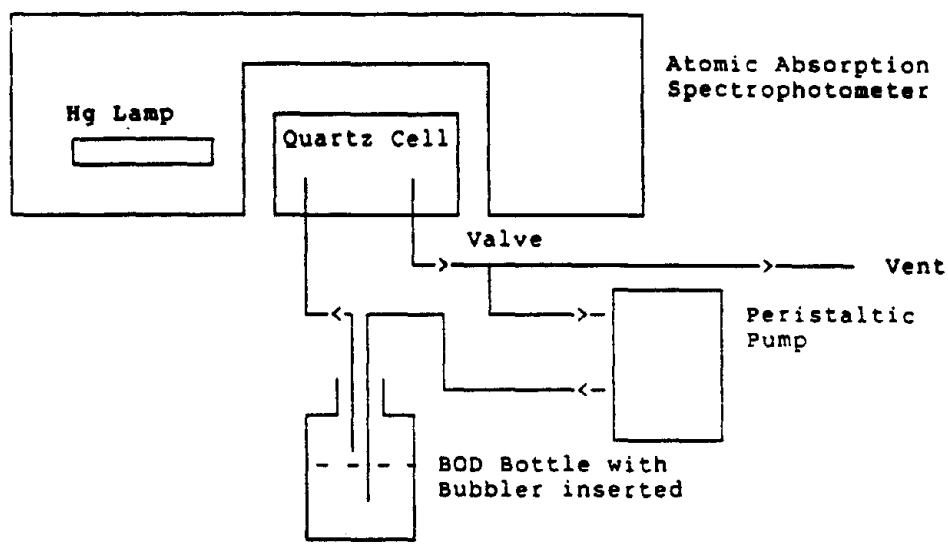
[10] Eller, P.M., NIOSH, unpublished data (1987-88).

METHOD WRITTEN BY:

Keith R. Nicholson and Michael R. Steele, DataChem Laboratories, Inc., Salt Lake City, Utah, under NIOSH contract No. 200-87-2533.

APPENDIX: COLD VAPOR MERCURY ANALYSIS SYSTEM

1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hopcalite tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow that will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination from adsorbed mercury.



MESITYL OXIDE

See KETONES II (Method 1301) for procedure

TABLE 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 8310, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to the following metals or their compounds: aluminum, barium, cadmium, chromium, copper, iron, lead, manganese, molybdenum, nickel, platinum, silver, strontium, tin, titanium, and zinc.

SYNONYMS: vary according to the compound

SAMPLING		MEASUREMENT	
SPECIMEN:	urine	**TECHNIQUE:**	INDUCTIVELY-COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)
VOLUME:	50 to 200 mL in polyethylene bottle	**ANALYTE:**	elements above
PRESERVATIVE:	5.0 mL conc. HNO_3 added after collection	**EXTRACTION MEDIA:**	polydithiocarbamate resin
SHIPMENT:	frozen in dry ice	**FINAL SOLUTION:**	4% HNO_3, 1% $HClO_4$; 5 mL
STABILITY:	not established	**WAVELENGTH:**	depends upon element; Table 2
CONTROLS:	collect at least 3 urine specimens from unexposed workers	**BACKGROUND CORRECTION:**	spectral wavelength shift
		CALIBRATION:	elements in 4% HNO_3, 1% $HClO_4$
		QUALITY CONTROL:	spiked urines; corrected for creatinine
		RANGE:	0.25 to 200 μg per sample [1]
		ESTIMATED LOD:	0.1 μg per sample
		PRECISION ($\bar{S}_r$):	Table 2
		ACCURACY:	Table 2

APPLICABILITY: This method measures urine concentrations of metals. It is particularly useful for workers exposed to several metals simultaneously. This is a simultaneous, multielemental analysis, but is not compound specific.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection and interelement correction factors. Background corrections are also made [1,2].

OTHER METHODS: This method uses a measurement technique similar to that of Method 7300 (Elements by ICP) for air samples.

REAGENTS:

1. Polydithiocarbamate resin, prepared as described in the APPENDIX.
2. Nitric acid, conc.*
3. Perchloric acid, conc.*
4. Dissolution acid, 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.*
5. Metals standards, 1000 μg/mL. Commercially available or prepared per instrument manufacturer's recommendations.
6. Argon.
7. Deionized water.
8. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in 50 mL boiled, deionized water; dilute to 100 mL. Store in a polyethylene bottle.

* See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125- or 250-mL, plastic-lined screw-cap.**
2. Inductively-coupled plasma-atomic emission spectrometer equipped for determination of elements of interest.
3. Regulator, two-stage, for argon.
4. Filtering apparatus for 50 mL liquid with 47-mm cellulose ester, 0.8-μm pore size filters.
5. Beakers, Griffin, 50-mL, with watchglass covers.**
6. pH meter and electrodes.
7. Volumetric flasks, 5- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, suitable for use at 100 °C.
10. Mechanical shaker.
11. Low temperature oxygen plasma asher (acid ashing may be substituted; see Step 9).

** Clean all labware with detergent, soak 12 h in 10% (v/v) HNO_3, and soak 12 h in deionized water.

SPECIAL PRECAUTIONS: Concentrated acids are extremely corrosive. Work with concentrated acids only in fume hoods and wear appropriate safety equipment (safety glasses or face shield, gloves, and labcoat). Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect a 50-mL urine sample in a polyethylene bottle.
2. Add 5 mL conc. HNO_3 as a preservative.
3. Pack samples in an insulated shipping container under refrigeration (e.g., styrofoam with dry ice) for transportation to laboratory.

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the sample (e.g., [3]).
5. Adjust the sample pH to 2.0 ± 0.1 with 5 M NaOH and then add 60 ± 10 mg polydithiocarbamate resin.
   NOTE: Start reagent blanks, in triplicate, at this step. Include resin and filters (step 7).
6. Agitate samples (on the shaker) for at least 12 h.
7. Filter samples through a 0.8-μm cellulose ester membrane filter, saving the filtrate and resin. Place the collected resin and filter in a clean 50-mL beaker.
8. Adjust filtrate pH to 8.0 ± 0.1 with 5 M NaOH, add more resin, then repeat steps 5 and 6, combining the filters and resins from the two extractions.
9. Ash filters and resins in a low temperature oxygen plasma asher for 6 h or until ashing is complete (200 watts at 1 to 2 torr, or manufacturer's recommendations).

NOTE: Steps 5 to 10 of Method 7300 (Elements by ICP), an $HNO_3/HClO_4$ digestion, may be substituted for the low temperature oxygen plasma ashing. Use a final solution volume of 5.0 mL (step 11).

10. Add 0.5 mL dissolution acid and warm on a hotplate (15 min at 50 °C).
11. Transfer solutions quantitatively to 5-mL volumetric flasks and dilute to volume with distilled deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to manufacturer's recommendations.
    NOTE: Typically, an acid blank and 10 μg/mL multi-element solutions are used.
13. Analyze a standard for every 10 samples.
14. Check measurement recoveries with at least three spiked unexposed urine samples per 10 samples.
    NOTE: For urine spikes, split a 100-mL control urine sample and analyze 50 mL without spiking. Subtract the metal quantity found in the unspiked portion from the metal quantity found in the spiked portion in order to determine measurement recovery.

MEASUREMENT:

15. Set the spectrometer to conditions specified by the manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the sample solutions with 1 volume dissolution acid plus 9 volumes deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentration for the sample, C_s (μg/mL), and the average blank, C_b (μg/mL), from the analyses data.
18. Using the solution volumes of sample, V_s (mL), and blank, V_b (mL), calculate the concentration, C (μg/mL), of each element in the volume of urine collected, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

19. Report the results as μg metal/g creatinine.

GUIDELINES TO INTERPRETATION:

Acceptable and unacceptable levels for metals have not been determined by this method. Lauwerys [4] discusses metals and can be consulted for guidance and interpretation.

EVALUATION OF METHOD:

Recovery of these 16 metals from spiked urine samples are shown in Table 2 (recoveries ranged from 77 to 100%). The precisions determined for the various elements are also given in Table 2 [1].

REFERENCES:

[1] Hull, R. D. Analysis of Trace Metals for Occupationally Exposed Workers, Morbidity and Mortality Weekly Report, 33, (1984).
[2] Hull, R. D. ICP-AESMulti-element Analysis of Industrial Hygiene Samples, NTIS Publication No. PB85-221414, 1985.
[3] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-997, W. B. Saunders Co., Philadelphia, PA (1976).
[4] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).
[5] Hackett, D. S. and S. Siggia. Selective Concentration and Determination of Trace Metals Using Polydithiocarbamate Chelating Ion-Exchange Resins, Environmental Analysis, p. 253, (G. W. Ewing, ed.), Academic Press, NY (1977).
[6] Bray, J. T. and F. J. Reilly. Extraction of Fourteen Elements from a Sea Water Matrix by a Polydithiocarbamate Resin, Jarrell-Ash Plasma Newsletter, 4, 4 (1981).

METHOD WRITTEN BY:

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TABLE 1. GENERAL INFORMATION

Element (Formula)	Atomic Weight	CAS #	RTECS
Aluminum (Al)	26.98	7429-90-5	BD0330000
Barium (Ba)	137.34	7440-39-3	CQ8370000
Cadmium (Cd)	112.40	7440-43-9	EU9800000
Chromium (Cr)	52.00	7440-47-3	GB4200000
Copper (Cr)	63.54	7440-50-8	GL5325000
Iron (Fe)	55.85	7439-89-6	NO4565500
Lead (Pb)	207.19	7439-92-1	OF7525000
Manganese (Mn)	54.94	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	7439-98-7	QA4680000
Nickel (Ni)	58.71	7440-02-0	QR5950000
Platinum (Pt)	195.09	7440-06-4	TP2160000
Silver (Ag)	107.87	7440-22-4	VW3675000
Strontium (Sr)	87.62	7440-24-6	VW3500000
Tin (Sn)	118.69	7440-31-5	XP7320000
Titanium (Ti)	47.90	7440-32-6	XR1700000
Zinc (Zn)	65.37	7440-66-6	ZG8600000

TABLE 2. RECOVERY OF METALS FROM URINE [1,2]

Element (Formula)	Wavelength (nm)	Quantity Added, µg/50 mL sample	Precision, $\bar{S}_r$ (n = 4)	Precision, % Recovery	Accuracy ± %
Aluminum (Al)	308.2	20	0.088	100	17.2
Barium (Ba)	455.4	0.4	0.11	80	41.6[a]
Cadmium (Cd)	226.5	1.0	0.12	100	23.5
Chromium (Cr)	205.6	1.0	0.078	100	15.3
Copper (Cu)	324.8	10	0.042	100	8.2
Iron (Fe)	259.9	40	0.059	100	11.6
Lead (Pb)	220.4	10	0.040	100	7.8
Manganese (Mn)	257.6	10	0.50	85	113[a]
Molybdenum (Mo)	281.6	2.0	0.16	100	31.4[a]
Nickel (Ni)	231.6	2.0	0.42	80	102[a]
Platinum (Pt)	203.7	0.4	0.29	77	79.8[a]
Silver (Ag)	328.3	2.0	0.12	100	23.5
Strontium (Sr)	421.5	4.0	0.25	100	49.0[a]
Tin (Sn)	190.0	2.0	0.21	100	41.2[a]
Titanium (Ti)	334.9	2.0	0.16	86	45.4[a]
Zinc (Zn)	213.9	200	0.089	100	17.4

[a] Does not meet the NIOSH criterion of ± 25% accuracy.

APPENDIX: POLYDITHIOCARBAMATE RESIN PREPARATION

The procedure used for preparation of the polydithiocarbamate resin is that of Hackett and Siggia [5] as modified by Bary and Reilly [6].

1. Dissolve 72 g polyethyleneimine, molecular weight 1800, in 1 L tetrahydrofuran and 28 g polymethylenepolyphenyl isocyanate in 1 L tetrahydrofuran.
   NOTE: Polyethyleneimine stored for one year would not dissolve in the solvent; however, fresh polyethyleneimine readily dissolved.
2. Pour these two solutions simultaneously into a large flask, allowing the two streams to mix before entering the flask.
3. Let the mixture stand at least 12 h with occasional mild agitation, then remove the solvent by filtration.
4. Wash the product twice with methanol and once with deionized water.
5. Add the product to 300 mL carbon disulfide, 100 mL ammonium hydroxide and 500 mL isopropyl alcohol; let stand 72 h.
6. Filter to remove the resin from the solvent mixture. Wash the resin three times with methanol and allow it to dry.
7. Grind and sieve the resin, saving the 60/80 mesh size for use.

METHANOL 2000

CH_3OH MW: 32.04 CAS: 67-56-1 RTECS: PC1400000

METHOD: 2000, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA: 200 ppm
NIOSH: 200 ppm (skin); STEL 250 ppm (skin)
ACGIH: 200 ppm (skin); STEL 250 ppm (skin)
(1 ppm = 1.310 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 64.5 °C; d 0.792 g/mL @ 20 °C; VP 15.3 kPa (115 mm Hg; 15.1% v/v) @ 20 °C; explosive range 6 to 36% v/v in air

SYNONYMS: carbinol; methyl alcohol; wood alcohol

SAMPLING

SAMPLER:	SOLID SORBENT TUBE (silica gel, 100 mg/50 mg)
FLOW RATE:	0.02 to 0.2 L/min
VOL-MIN:	1 L @ 200 ppm
-MAX:	5 L
SHIPMENT:	routine
SAMPLE STABILITY:	6 weeks
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	desirable, 1 to 10 mL

ACCURACY

RANGE STUDIED:	140 to 540 mg/m^3 [1] (5-L samples)
BIAS:	− 4.4%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.063 [1]
ACCURACY:	± 14.5%

MEASUREMENT

TECHNIQUE:	GAS CHROMATOGRAPHY, FID
ANALYTE:	methanol
DESORPTION:	1 mL water; stand 4 h
INJECTION VOLUME:	5 µL
TEMPERATURE-INJECTION:	200 °C
-DETECTOR:	250 - 300 °C
-COLUMN:	80 °C
CARRIER GAS:	N_2 or He, 30 mL/min
COLUMN:	glass, 2 m x 2-mm ID, 60/80 mesh Tenax GC or equivalent
CALIBRATION:	solutions of methanol in water
RANGE:	0.1 to 6 mg per sample
ESTIMATED LOD:	0.01 mg per sample [2]
PRECISION ($\hat{S}_r$):	0.032 [1]

APPLICABILITY: The working range is 25 to 900 mg/m^3 (19 to 690 ppm) for a 5-L air sample. The method is applicable to STEL determinations. At high concentrations of methanol or at high relative humidity, a large silica gel tube is required (700 mg front section).

INTERFERENCES: None identified. Positive identification by mass spectrometry may be necessary in some cases. Alternative gas chromatographic columns, e.g., SP 1000, SP-2100, FFAP, or DB Wax capillary column are also confirmation aids.

OTHER METHODS: This method combines and replaces Methods S59 [3] and P&CAM 247 [4].

REAGENTS:

1. Water, distilled.
2. Methanol.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler, glass tube, 7 cm long, 4-mm ID, containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 100 mg, back = 50 mg). A silylated glass wool plug precedes the front section and a 4-mm urethane foam plug follows the back section.
   NOTE: At high relative humidity or high methanol concentrations, use a larger tube: 15 cm long, 8-mm ID, with three sections of silica gel (700 mg, 150 mg, 150 mg).
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2000-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL distilled water to each vial. Attach crimp cap to each vial.
7. Allow to stand 4 h with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 6 mg methanol per sample.
   a. Add known amounts of methanol to distilled water in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg methanol).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of methanol directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg methanol recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with distilled water, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methanol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methanol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S59 [3] was issued on January 17, 1975, and validated over the range 140 to 540 mg/m^3 at 25 °C and 758 mm Hg, using 5-L samples [1]. Overall precision, $\hat{S}_{rT}$, was 0.063 with average recovery for 18 samples 94.2%, representing a non-significant bias. The atmospheres were generated by calibrated syringe pump. Desorption efficiency was 0.92 at 1.3 mg methanol and 0.84 at 0.65 mg methanol per sample. Breakthrough (5% on back section) occurred at 52 min when sampling an atmosphere containing 541 mg/m^3 in dry air at 0.2 L/min.

Additional data were gathered using a larger (700 mg front section) silica gel tube under high humidity conditions; these were published in P&CAM 247 [4]. A comparison of the data is consistent with a recommended maximum sample volume of 5 L.

Method	Front Section, mg silica gel	Test Conditions mg/m^3	Test Conditions % RH	Breakthrough Capacity, mg methanol	Breakthrough V, L
S59 [1,3]	100	540	0	5.6	10.4
P&CAM 247 [4]	700	534	85	4.6	8.75

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #4121-K (unpublished, November 3, 1983).
[3] NIOSH Manual of Analytical Methods, V. 2, S59, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, V. 1, P&CAM 247, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD REVISED BY:

Charles Neumeister, NIOSH/DPSE; S59 originally validated under NIOSH Contract CDC-99-74-45.

2-METHOXYETHANOL

See ALCOHOLS IV (Method 1403) for procedure

METHYL ACETATE

CH_3COOCH_3 MW: 74.08 CAS: 79-20-9 RTECS: AI9100000

METHOD: 1458, Issue 2 **EVALUATION: FULL** **Issue 1: 16 December 1974**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: 200 ppm; STEL 250 ppm
ACGIH: 200 ppm; STEL 250 ppm
(1 ppm = 3.03 mg/m^3)

PROPERTIES: liquid; d = 0.9244 g/mL @ 25 °C; BP = 54.05 °C; VP 23 kPa (173 mm Hg) @ 20 °C; vapor density (air = 1) 2.8

SYNONYMS: acetic acid methyl ester; methyl acetic ester; methyl ethanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/minute

VOL-MIN: 0.2 L @ 200 ppm
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: at least 6 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 343 to 1130 mg/m^3 [1] (7-L samples)

BIAS: 7.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.0547 [1]

ACCURACY: ± 16.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl acetate

EXTRACTION: 1 mL CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (2 min) to 150 °C (10 °C/min)

COLUMN: DB-wax; 30 m, 0.32-mm ID, 1-µm film thickness

CARRIER GAS: He, 1 mL/min;

MAKEUP GAS: N_2, 30 mL/min

CALIBRATION: solutions of methyl acetate in CS_2

RANGE: 7 µg to 1000 µg [2]

ESTIMATED LOD: 2 µg [2]

PRECISION ($\bar{S}_r$): 0.036 @ 20 to 876 µg per sample [2]

APPLICABILITY: The working range is 0.3 to 1330 ppm (1 to 440 mg/m^3) for a 7-L air sample [1]. The method may be adapted for other esters with appropriate changes in chromatographic conditions.

INTERFERENCES: Any compounds with similar retention times.

OTHER METHODS: This revises Method S42 [1]. Improved recovery of analyte may be achieved with the addition of 5% butyl carbitol to the CS_2 desorption procedure [3,4].

REAGENTS:

1. Methyl acetate (reagent grade).
2. Carbon disulfide (chrom. grade).
3. Prepurified helium.
4. Hydrogen, prepurified.
5. Decane, reagent grade, or other suitable internal standard.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph equipped with FID, integrator and column (page 1458-1).
5. Vials, 2-mL, glass, PTFE-lined crimp caps.
6. Syringe, 10-μL, readable to 0.1 μL, and other convenient sizes.
7. Pipet, 1-mL, readable to 0.1 mL.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (F.P. = −30°C). Use only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurate flow rate between 0.01 and 0.2 L/min for a total sample size of 0.2 to 10 L.
4. Cap the samplers with plastic caps and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL to CS_2 to each vial and attach a crimp cap to each vial.
7. Allow to stand 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 2 to 2000 μg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg methyl acetate).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of analyte or of a standard solution of analyte in CS_2 directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. μg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations to conditions given on page 1458-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute, reanalyze, and apply appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE), of methyl acetate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 343 to 1330 mg/m^3 at 24 °C and 761 mm Hg using 7-liter samples [1]. Breakthrough capacity was 14 mg when sampling dry air containing 1330 mg/m^3. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.0547. Desorption efficiency (DE) of methyl acetate from charcoal tubes was 85.7% in the range of 87 to 342 μg per sample [2]. Sample storage stability was evaluated at 203 μg per sample [2]. Samples stored at ambient temperature in the dark had a 91.8% recovery after three days when compared to day 1 samples. Samples stored at 5 °C gave recoveries of 96.4% on day 6 and 90.4% on day 9. Therefore, methyl acetate is stable on charcoal for at least 6 days and up to 9 days, when refrigerated at 5 °C.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S42, U.S. Dept. of Health, Education, and Welfare, Publ. (NIOSH) 77-157B (1977).
[2] Pendergrass, S.M., Methyl Acetate Method Development (Unpublished report), NIOSH/MRSB, 1990.
[3] Analysis of NIOSH Samples for Methyl Acetate, NIOSH/MRSB/MDS, Sequence #7034, Cincinnati, Ohio (unpublished, 1990).
[4] Beck, S, T. Stock, and L. Whitehead, Improved Efficiency of Desorption of Oxygenated Solvents from Activated Charcoal Using a New Polar Additive to Carbon Disulfide, Appl. Occup. Environ. Hyg. 5(3), 171-177, 1990.

METHOD REVISED BY:

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METHYL ACRYLATE

$CH_2=CHCOOCH_3$ MW: 86.09 CAS: 96-33-3 RTECS: AT2800000

METHOD: 1459, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 10 ppm (skin)
NIOSH: 10 ppm (skin)
ACGIH: 10 ppm (skin)
(1 ppm = 3.58 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 80.5 °C; d 0.9574 @ 20 °C; VP 65 mm Hg @ 20 °C; Vapor Density (air = 1) 2.95

SYNONYMS: Methyl propenoate, 2-propenoic acid methyl ester.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 10 ppm
-MAX: 5 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 13.9 to 58.4 mg/m^3 [1] (6-L samples)

BIAS: −10.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.066

ACCURACY: ±23.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPH, FID

ANALYTE: methyl acrylate

DESORPTION: 1.0 mL carbon disulfide; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

CARRIER GAS: He, 30 mL/min

COLUMN: stainless steel, 10 ft x ⅛-in, 50/0 FFAP on 100/120 mesh Supelcoport

DETECTOR: FID

CALIBRATION: standard solution of methyl acrylate in carbon disulfide with undecane or other suitable internal standards in the range 10 to 350 µg per sample

RANGE: 35 to 350 µg per sample [2]

ESTIMATED LOD: 10 µg per sample [3]

PRECISION ($\hat{S}_r$): 0.049

APPLICABILITY: The working range is 2 to 100 ppm (7 to 360 mg/m^3) for a 5-L air sample.

INTERFERENCES: Alternate chromatographic columns to circumvent interferences are SE-54 and SP-1000 fused silica capillary columns [4].

OTHER METHODS: This revises Method S38 [2]. An independent analytical method provided by N. Gjoes et al. uses spectrometry for identification of methyl acrylate [5].

REAGENTS:

1. Eluent: carbon disulfide, chromatographic quality, with 0.1% v/v undecane, or other suitable internal standard.
2. Methyl Acrylate, ACS reagent grade.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1459-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS:

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately know flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 10 to 350 μg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyte together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. μg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1459-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S38 for methyl acrylate was issued on 12/6/74, and evaluated over a range of 13.9 to 58.4 mg/m^3 at an atmospheric temperature of 23°C and a pressure of 764 mm Hg, using 6-L samples [1]. Breakthrough was determined by sampling a generated atmosphere at a concentration of 59 mg/m^3 for 240 min at a flow rate of 0.190 L/min. Desorption efficiency (DE) was determined by spiking charcoal tubes at three levels, 0.087, 0.175, and 0.350 mg of methyl acrylate. Desorption efficiencies were 0.810, 0.785, and 0.841, respectively. The measurement precision ($\bar{S}_r$) was 0.049, and the overall precision, including pump error, was 0.066. The mean bias for samples generated at three concentration levels (0.5, 1 and 2 x PEL) was -10.4%, resulting in an overall accuracy of ± 23.3%. Sample storage stability was not determined.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S38, U.S. Department of Health, Education, and Welfare, Publ (NIOSH) (1978).
[3] NIOSH Manual of Analytical Methods, Second Edition Method Update Information, (1990).
[4] A. Horna, Taborsky J., Churacek J., and Dufka O. "IV. Gas-liquid Chromatographic Studies of C_1 – C_8 n-Alkyl and C_3 – C_6 isoalkyl acrylates and their hydrogen halide and halogen addition derivatives," J. Chromatogr., 348(1), (1985).
[5] N. Gjoes, et al. "Identification of Methyacrylates by Mass Spectrometry," Anal. Chem. Acta, 149, 87-99 (1983).

METHOD WRITTEN BY:

Jim Xue, NIOSH, DPSE.

METHYLAL

$CH_3OCH_2OCH_3$ MW: 76.10 CAS: 109-87-5 RTECS: PA8750000

METHOD: 1611, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
(1 ppm = 3.11 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8593 g/mL @ 20 °C; BP 42 °C; MP −105 °C; VP 44 kPa (330 mm Hg; 43% v/v) @ 20 °C; explosive range 1.6 to 17.6% v/v in air

SYNONYMS: dimethoxymethane; formal; formaldehyde dimethyl acetal

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 1000 ppm
-MAX: 3 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1684 to 6670 mg/m^3 [1] (2-L samples)

BIAS: + 4.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.060 [1]

ACCURACY: ± 15.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylal

DESORPTION: 1 mL hexane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 190 °C
-DETECTOR: 250 °C
-COLUMN: 195 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6-mm OD, packed with 50/80 mesh Porapak Q or equivalent

CALIBRATION: standard solutions of methylal in hexane

RANGE: 3 to 12 mg per sample

ESTIMATED LOD: 0.1 mg per sample

PRECISION ($\bar{S}_r$): 0.017 [1]

APPLICABILITY: The working range is 480 to 1930 ppm (1500 to 6000 mg/m^3) for a 2-L air sample. Samples containing smaller quantities of methylal may have low desorption efficiency. Breakthrough capacity at high humidity is not known.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S71 [2].

REAGENTS:

1. Hexane, chromatographic quality.*
2. Methylal, reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1611-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 20-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: n-Hexane is extremely flammable (flash point = −22 °C). Methylal is also very flammable (flash point = −18 °C) and will attack some forms of plastics and rubber. Work with these only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 3 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL hexane to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 12 mg methylal per sample.
   a. Add known amounts of pure methylal to hexane in 10-mL volumetric flasks and dilute to the mark. Prepare solutions in the range 0.1 to 12 mg methylal/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg methylal).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (1 to 20 μL) of pure methylal or a standard solution of methylal in hexane directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg methylal recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1611-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with hexane, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylal found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_b) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methylal in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S71 [2] was issued on February 14, 1975, and validated over the range 1684 to 6670 mg/m^3 at 22 °C using 2-L air samples [1]. Samples of methylal in dry air were generated using a three-neck round-bottom generator flask containing the liquid methylal. An accurately measured flow of nitrogen gas was used to sweep the vapors out of the flask. Overall precision, s_r, was 0.060 with average recovery of 104%. Desorption efficiency was 78, 81, and 88%, respectively, at 3.1, 6.2, and 12.3 mg methylal taken per sample. Breakthrough (5% on back section) occurred at 20 min when sampling an atmosphere containing 6250 mg/m$_3$ methylal at 0.183 L/min at 0% RH. Breakthrough at high humidity was not tested, nor was sample stability.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S71, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S71 originally validated under NIOSH Contract CDC-99-74-45.

METHYL-(n-AMYL)-KETONE

See KETONES II (Method 1301) for procedure

METHYL CELLOSOLVE ACETATE

$CH_3COOCH_2CH_2OCH_3$ MW: 118.15 CAS: 110-49-6 RTECS: KL5950000

METHOD: 1451, Issue 2 **EVALUATION: FULL** **Issue 1: 6 December 1974**
Issue 2: 15 August 1994

OSHA : 25 ppm (skin)
NIOSH: 0.1 ppm (skin)
ACGIH: 5 ppm (skin)
(1 ppm = 4.83 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 145 °C; MP −65 °C; Flash point 49 °C; d 1.005 @ 20 °C; VP 2 mm Hg (1700 mg/m^3) @ 20 °C

SYNONYMS: 2-methoxyethyl acetate; glycol monomethyl ether acetate; ethylene glycol monomethyl ether acetate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.2 L @ 25 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: at least 15 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 51 to 214 mg/m^3 [2] (20-L samples)

BIAS: − 0.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.078 [2]

ACCURACY: ± 13.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl cellosolve acetate

EXTRACTION: carbon disulfide, 1 mL

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 225 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C

CARRIER GAS: helium, 30 mL/min

COLUMN: 10 ft x 1/8-in stainless steel packed with 5% FFAP stationary phase on 100/200 mesh Supelcoport

CALIBRATION: standard solutions of methyl cellosolve acetate in carbon disulfide

RANGE: 30 to 4500 µg per sample [2]

ESTIMATED LOD: 10 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.0441 [2]

APPLICABILITY: The working range is 0.3 to 47 ppm (1.5 to 225 mg/m^3) for a 20-L air sample. Better sensitivity may be achieved if a capillary column is used in place of a packed column. A 30-m x 0.32-mm fused silica capillary column coated internally with 1.0 µm of DB-5, with appropriate instrument conditions, is recommended.

INTERFERENCES: High humidity conditions may cause inefficient collection of organic vapors.

OTHER METHODS: This is an adaptation of NIOSH Method S39 [2] and OSHA Method 53, issued 1/85. [1] Operational modifications [3] to the OSHA method are as follows: column −30 m x 0.32-mm I.D. fused silica capillary coated with 1.0 µm DB-5. Column temperature: 40 °C for 4 min and programmed at 4 °C/min. to 85 °C. Desorption: 30 min in 1.0 mL methylene chloride/methanol, 95/5(v/v) containing 1 µL/mL toluene as internal standard.

REAGENTS:

1. Methyl cellosolve acetate, ACS reagent grade.
2. Eluent: carbon disulfide*, chromatographic grade, with 0.1% v/v undecane (optional internal standard).
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-m ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph equipped with FID, integrator and column (page 1451-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringe, 10 μL, readable to 0.1 μL.
6. Pipet, 1-mL, readable to 0.1 mL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.2 to 20 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 10 to 4500 μg per sample.
   a. Add known amounts of methyl cellosolve acetate to 1 mL eluent in sample vials.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or ratio of peak area of analyte to peak area of internal standard vs. μg methyl cellosolve acetate).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. μg methyl cellosolve acetate.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1451-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. If internal standard is used, divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methyl cellosolve acetate in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 51 to 214 mg/m^3 at 23 °C and pressure of 762 mm Hg using 20-L samples [2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.078, with average recovery of 99.8% [2]. Sample stability of methyl cellosolve acetate on charcoal was determined by OSHA to be at least 15 days at 0 °C [1].

REFERENCES:

[1] OSHA Manual of Analytical Methods, Method 53, U.S. Occupational Safety and Health Administration, Salt Lake City, Utah (1985).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S39, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Analytical Report for Organics on Charcoal Tubes, Data Chem Sequence # 6227, Unpubl. NIOSH (1988).

METHOD REVISED BY:

Rosa J. Key-Schwartz, Ph.D., NIOSH/DPSE.

CH_3Cl MW: 50.49 CAS: 74-87-3 RTECS: PA6300000

METHOD: 1001, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : 100 ppm; C 200 ppm; P 300 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; STEL 100 ppm (skin)
(1 ppm = 2.06 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.8 (air = 1); BP −24.2 °C; MP −97.7 °C; explosive range 7.6 to 19% v/v air

SYNONYMS: chloromethane.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 0.4 L @ 100 ppm
-MAX: 3 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 95% recovery after 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 110 to 460 mg/m^3 (1.5-L air samples); 300 to 1200 mg/m^3 (0.5-L air samples) [1]

BIAS: 1.04%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.052 [1]

ACCURACY: ± 12.41%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl chloride

DESORPTION: 3 mL CH_2Cl_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 260 °C
-COLUMN: 100 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6-mm OD, packed with 80/100 mesh Chromosorb 102

CALIBRATION: standard solutions of methyl chloride in CH_2Cl_2

RANGE: 0.1 to 1 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.017 @ 0.16 to 0.62 mg per sample [1]

APPLICABILITY: The working range is 31 to 320 ppm (66 to 670 mg/m^3) for a 1.5-L air sample. The method is applicable to STEL determinations.

INTERFERENCES: None reported. An alternate GC column is fused silica capillary, 30 m x 0.315-mm, coated with 0.25-µm Durawax DX-4 at 45 °C [2].

OTHER METHODS: This combines and revises Methods S99 [3] and P&CAM 201 [4].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality, methyl chloride-free.*
2. Methyl chloride, 99.5%.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8-mm OD, 6-mm ID, followed by 7 cm long, 6-mm OD, 4-mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., "Blue Ice") and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1001-1).
5. Bottles, glass, 15-mL, with PTFE-lined septum crimp caps.
6. Syringes, gas-tight, 10-μL, and 0.1- to 1-mL.
7. Pipet, TD, 3-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows at ca. 30 mL/min, with T-connection and septum.

SPECIAL PRECAUTIONS: Methyl chloride has poor warning properties, is a narcotic and a suspect carcinogen and teratogen [5,6]. Methylene chloride is a suspect carcinogen [6,7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing, with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 0.4 to 3 L (e.g., at 0.1 L/min for 15 min for STEL measurement and 0.01 L/min for 50 to 300 min for TWA measurement).
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Pipet 3.0 mL CH_2Cl_2 into each of several bottles.
6. Place, in order, the back and front sorbent sections of the front sampler tube into a bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 h.

7. Place, in order, the back and front sorbent sections of the back sampler tube into a second bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 h.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Pipet 3.0 mL CH_2Cl_2 into each of a series of bottles. Cap the bottles.
   b. Using a gas-tight syringe, add known amounts of methyl chloride (0.005 to 0.5 mL; 0.01 to 1 mg at NTP) by bubbling the gas slowly through the CH_2Cl_2. Gently shake the bottles.
   c. Analyze with samples and blanks (steps 10 and 11).
   d. Prepare calibration graph (peak area vs. mg methyl chloride).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Using a gas-tight syringe, slowly inject a known amount of methyl chloride (0.005 to 0.5 mL) through the septum of the DE apparatus into a stream of nitrogen which carries the analyte into a large (400 mg/200 mg) sorbent tube. Allow the nitrogen to flow an additional 1 min.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 10 and 11).
   d. Prepare a graph of DE vs. mg methyl chloride recovered.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1001-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CH_2Cl_2, reanalyze and apply the appropriate dilution factor in calculations.
11. Measure peak area.
    NOTE: Methyl chloride elutes before CH_2Cl_2 under these conditions.

CALCULATIONS:

12. Determine the mass, mg (corrected for DE) of methyl chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
13. Calculate concentration, C, of methyl chloride in the air volume sample, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S99 was issued on March 18, 1977 [3], and validated with generated atmospheres monitored by total hydrocarbon analyzer [1,8]. Average recovery was 105% with $\bar{S}_r$ = 0.05 for eighteen 1.5-L samples in the range 110 to 460 mg/m^3 and 101% with $\bar{S}_r$ = 0.05 for eighteen 0.5-L samples in the range 300 to 1200 mg/m^3. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 135 min at 0.0235 L/min from an atmosphere containing 410 mg/m^3 methyl chloride in air at 80% RH, and at 24.4

min when sampling at 0.105 L/min from an atmosphere containing 1425 mg/m^3 at 84% RH. Desorption efficiency for 18 samples in the range 0.16 to 0.62 mg methyl chloride averaged 0.99 with s_r = 0.02. Desorption with carbon disulfide, chloroform, or ethanol as eluent gave lower recoveries. Samples stored in the laboratory for seven days gave a mean recovery of 95% relative to samples analyzed immediately after collection.

REFERENCES:

[1] Backup Data Report S99, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield VA 22161.
[2] UBTL report for Sequence #4131-L,M (NIOSH, unpublished, November 28, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S99, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ibid., Vol. 1, P&CAM 201, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] NIOSH Current Intelligence Bulletin 43, Monohalomethanes, U.S. Department of Health and Human Services, Publ. (NIOSH) 84-117 (September 27, 1984).
[6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[7] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
[8] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Y. T. Gagnon and G. David Foley, NIOSH/DPSE.

METHYLCHLOROFORM

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

METHYLCYCLOHEXANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

METHYLCYCLOHEXANOL

$CH_3C_6H_{10}OH$ MW: 114.19 CAS: 25639-42-3 RTECS: GW0175000

METHOD: 1404, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 100 ppm
NIOSH: 50 ppm
ACGIH: 50 ppm
(1 ppm = 4.67 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 155 – 180 °C; d 0.92 g/mL @ 20 °C; VP 0.2 kPa (1.5 mm Hg) @ 20 °C

SYNONYMS: hexahydromethylphenol; hexahydrocresol

SAMPLING

SAMPLER: CHARCOAL TUBE (coconut shell charcoal, 100/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 215 to 920 mg/m^3 [1] (12-L samples)

BIAS: ± 2.9% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.063 [1]

ACCURACY: ± 14.0%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylcyclohexanol

DESORPTION: 1.0 mL methylene chloride

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 140 °C

COLUMN: 10% FFAP on 80/100 mesh Chromosorb W, 12 ft x 1/8 in stainless steel

CALIBRATION: standard solutions of methylcyclohexanol in methylene chloride

RANGE: 0.55 to 17 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.019 @ 2.7 to 11.3 mg per sample [1]

APPLICABILITY: The working range is 10 to 300 ppm (46 to 1400 mg/m^3) for a 12-L air sample. Methylcyclohexanol is usually present as a 50:50 mixture of meta- and para- isomers.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S374 [2].

REAGENTS:

1. m-Methylcyclohexanol*, ACS reagent grade.
2. p-Methylcyclohexanol*, ACS reagent grade.
3. Methylene chloride*, distilled in glass.
4. Nitrogen, purified.
5. Hydrogen, prepurified
6. Air, filtered, compressed.
7. Calibration stock solution, 14.8 mg/mL. Add 80 μL m-methylcyclohexanol and 80 μL p-methylcyclohexanol to 10 mL methylene chloride.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 25 mm/Hg. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 mL/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph with a FID detector, recorder, integrator and column (page 1404-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL and other sizes as needed,

SPECIAL PRECAUTIONS: Methylcyclohexanol can irritate the eyes and upper respiratory tract and can cause liver and kidney damage. Methylene chloride is an irritant, can be absorbed through the skin, and is a suspect carcinogen [3]. Prepare samples in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 15 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sections of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL methylene chloride to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of methylcyclohexanol to methylene chloride in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain concentrations in the range 0.02 to 10 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (area vs. mg of methylcyclohexanol).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (2 to 20 μL) of a 50:50 mixture of methylcyclohexanol isomers directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12)
e. Prepare a graph of DE vs. mg methylcyclohexanol recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1404-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with methylene chloride, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE), of methylcyclohexanol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methylcyclohexanol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 215 to 920 mg/m^3 and had an overall sampling and measurement precision, $\hat{S}_{rT}$, of 0.063. Concentrations obtained for seventeen generated samples averaged 2.9% higher than the independently determined concentration. Average recoveries of 2.71 mg of meta- and para- isomers of methylcyclohexanol was determined at 942 mg/m^3 while sampling 0.19 L/min. Breakthrough occurred in 116 min corresponding to a capacity of 20.8 mg per sample. Sample stability during storage was evaluated at 5.45 mg per sample. Samples showed 99.8% recovery after eight days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Methylcyclohexanol, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S374, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 90-117 (1990), available as GPO Stock #1990-751-238 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

M.J. Seymour, NIOSH/DPSE, originally evaluated under NIOSH Contract 210-76--123 (1977).

METHYLCYCLOHEXANONE

$CH_3C_6H_9(=O)$ (3 isomers) MW: 112.17 CAS: 1331-22-2 RTECS: GW1575000

METHOD: 2521, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 100 ppm (skin) (2-methyl isomer)
NIOSH: 50 ppm (skin); STEL 75 ppm (2-methyl isomer)
(1 ppm = 4.59 mg/m³ @ NTP)
ACGIH: 50 ppm (skin); STEL 75 ppm (2-methyl isomer)
(1 ppm = 4.59 mg/m³ @ NTP)

PROPERTIES:

Isomer	BP, °C	d, g/mL @ 20 °C
2-$CH_3C_6H_9O$	165	0.925
3-$CH_3C_6H_9O$	169	0.914
4-$CH_3C_6H_9O$	170	0.914

SYNONYMS: Isomers: 2-methylcyclohexanone; CAS #583-60-8.
3-methylcyclohexanone; CAS #591-24-2.
4-methylcyclohexanone; CAS #589-92-4.
Mixture of isomers: CAS #1331-22-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Porapak Q, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 460 mg/m³
-MAX: 6 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 213 to 852 mg/m³ [1] (3-L samples)

BIAS: 0.69%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 11.35%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 3- and 4-methylcyclohexanone

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 260 °C
-COLUMN: 190 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 3-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of 3 – and 4 – methylcyclohexanone isomers in acetone

RANGE: 0.5 to 4 mg per sample

ESTIMATED LOD: 0.09 mg [1]

PRECISION ($\bar{S}_r$): 0.041 @ 0.7 to 2.9 mg per sample [1]

APPLICABILITY: The working range is 100 to 800 mg/m³ (20 to 170 ppm) for a 5-L air sample. This method was developed for the 3- and 4-methylcyclohexanones. 2-Methylcyclohexanone is not of major commercial importance and has not been tested with this method. The use of a capillary column would give better sensitivity; however, all the isomers may not elute as a single peak.

INTERFERENCES: None reported.

OTHER METHODS: This revises Method S375 [2].

REAGENTS:

1. Acetone, reagent grade.*
2. Analytes: 3-methylcyclohexanone* and 4-methylcyclohexanone*, reagent grade.
3. n-Hexane, chromatographic quality.*
4. Calibration stock solution, 45.7 mg/mL. Dilute 457 mg (0.5 mL at 20 °C) of a 50/50 mixture of 3- and 4-methylcyclohexanone to 10 mL with acetone.
5. Desorption efficiency (DE) stock solution, 274 mg/mL. Dilute 2.74 g (3.0 mL at 20 °C) of a 50/50 mixture of 3- and 4-methylcyclohexanone to 10 mL with hexane.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID; containing two sections of 50/80 mesh Porapak Q (front = 150 mg; back = 75 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and follows the back section. Flame-sealed ends with plastic caps. Pressure drop across the tube at 0.05 L/min airflow must be less than 1.4 kPa. Tubes are commercially available (e.g. SKC Inc. Cat No. ST 226-115).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2521-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL, readable to 0.1 μL, and 25-, 100-, 300-, and 500-μL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetone, methylcyclohexanone, and n-hexane are highly flammable. All work should be performed in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the end caps from the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 to 0.05 L/min for a total sample size of 1 to 6 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Attach cap to each vial and shake vigorously.
7. Allow to stand 15 min. Analyze within one day after desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 4 mg methylcyclohexanone per sample.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg methylcyclohexanone).

9. Determine desorption efficiency (DE) at least once for each lot of Porapak Q used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg methylcyclohexanone recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2521-1. Inject a 5-μL sample aliquot manually using solvent flush technique. Do not use an autosampler because of possible plugging of the syringe needle with Porapak Q.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. A retention time of ca. 9 min is expected under these conditions. Acetone elutes before the single peak observed for the methylcyclohexanone isomers.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylcyclohexanone found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methylcyclohexanone in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S375 was issued on February 18, 1977 [2]. The precision and accuracy were determined by analyzing generated atmospheres of 50/50 mixtures of 3- and 4-methylcyclohexanone containing 213, 426, and 852 mg/m^3 at 22 °C and 759 mm Hg using 3-L samples [1,3]. The concentration of methylcyclohexanone was determined using the rate of delivery of a syringe drive system and the flow rates of the dilution air. The stability of the concentrations was monitored with a total hydrocarbon analyzer; no bias was found. Storage stability was determined to be at least seven days at room temperature. Breakthrough of the front section of the Porapak Q tube was not observed after sampling 8.1 L of a test atmosphere containing 852 mg/m^3 at $\geq$ 80% RH for 185 min at 0.044 L/min. Desorption efficiencies for samples spiked with methylcyclohexanone in the range 0.73 to 2.93 mg per sample were 0.91 to 0.94.

REFERENCES:

[1] Backup Data Report for Methylcyclohexanone, S375, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S375, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-157 (1978).

[3] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Julie R. Okenfuss, NIOSH/DPSE: S375 originally validated under NIOSH Contract 210-76-0123.

METHYLENE CHLORIDE

CH_2Cl_2 MW: 84.94 CAS: 75-09-2 RTECS: PA8050000

METHOD: 1005, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 August 1994

OSHA : 500 ppm; C 1000 ppm; P 2000 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.323 g/mL @ 20 °C; BP 40 °C; MP −95 °C; VP 47 kPa (349 mm Hg; 46% v/v) @ 20 °C; not flammable

SYNONYMS: dichloromethane; methylene dichloride.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (2 coconut shell charcoal tubes, 100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2.5 L

SHIPMENT: separate front and backup tubes

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1700 to 7097 mg/m^3 (1-L samples) [1]

BIAS: − 4.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: ± 14.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylene chloride

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 to 225 °C
-DETECTOR: 250 °C
-COLUMN: 60 to 90 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3-mm ID stainless steel, 10% SP-1000 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of CH_2Cl_2 in CS_2 with internal standard

RANGE: 0.03 to 10 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [3,4]

PRECISION ($\bar{S}_r$): 0.026 @ 1.3 to 5.3 mg per sample [1]

APPLICABILITY: The working range is 9 to 3000 ppm (30 to 10,400 mg/m^3) for a 1-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. The method was validated using a 6 m x 3-mm ID stainless steel column packed with 10% FFAP on 100/120 mesh Supelcoport. Alternate chromatographic columns are 10% TCEP on 80/100 Chromosorb PAW, SP-2100, SP-2100 with 0.1% Carbowax 1500, or DB-1 fused silica capillary column.

OTHER METHODS: This revises Methods S329 [2], 1005 (dated 2/15/84), P&CAM 127 [3], and the criteria document method [5]. OSHA Method 59 uses larger (350 mg) sorbent sections and has been evaluated for 10-L air samples at 1 ppm methylene chloride [6].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% v/v decane, benzene, or other suitable internal standard.
2. Methylene chloride.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: separate front and backup glass tubes with plastic caps, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg). A silylated glass wool plug is placed at each end of each tube. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: Two commercially available tubes, each containing 150 mg charcoal in two beds, may be used in tandem.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1005-1).
4. Vials, 2-mL, PTFE-lined septum crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 2.5 L.
4. Separate the front and backup tubes and cap each tube to prevent migration of methylene chloride between tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections (i.e., front and backup tubes) of the sampler in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 10 mg methylene chloride per sample.
   a. Add known amounts of methylene chloride to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg methylene chloride).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of methylene chloride directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg methylene chloride recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1005-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylene chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methylene chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S329 [2] was issued on June 6, 1975, and validated over the range 1700 to 7100 mg/m^3 at 25 °C and 763 mm Hg using a 1-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.073 with average recovery 95.3%, representing a non-significant bias. The concentration of methylene chloride was independently verified by calibrated syringe pump. Desorption efficiency was 0.97 in the range 1.3 mg to 5.3 mg methylene chloride per sample. Breakthrough (5% on back section) occurred at 18.5 min when sampling an atmosphere containing 6726 mg/m^3 methylene chloride at 0.187 L/min at 0% RH. The stability of methylene chloride on charcoal was not determined. The method was used in NIOSH Sequences #7745 (4/8/93), #7620N (2/16/93), #7716M (1/22/93), and #7716F (1/21/93) [7].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, NIOSH, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
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[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] User check, UBTL, NIOSH Sequence #3990-R (unpublished, November 3, 1983).

[5] Criteria for a Recommended Standard...Occupational Exposure to Methylene Chloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-138 (1976).
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[7] NIOSH Sequences (unpublished) (1993).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon; NIOSH/DPSE; S329 originally validated under NIOSH Contract CDC-99-74-45.

$CH_2(C_6H_4NH_2)_2$ MW: 198.27 CAS: 101-77-9 RTECS: BY5425000

METHOD: 5029, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: lowest feasible; carcinogen
ACGIH: 0.1 ppm (skin); suspected human carcinogen
(1 ppm = 8.11 mg/m^3 @ NTP)

PROPERTIES: solid; MP 92 °C; BP 399 °C;
VP 0.2 x 10^{-7} kPa (1.5 x 10^{-7} mm Hg)
@ 25 °C

SYNONYMS: p,p'-diaminodiphenylmethane; MDA.

SAMPLING	
SAMPLER:	FILTER (acid-treated glass fiber, 37-mm)
FLOW RATE:	1 to 2 L/min
VOL-MIN:	10 L @ 0.1 ppm
-MAX:	1000 L
SHIPMENT:	transfer filter to glass vial; extract with 4 mL 0.1 N methanolic KOH before shipping
SAMPLE STABILITY:	stable at least 60 days @ 20 °C [1]
FIELD BLANKS:	2 to 10 field blanks per set
MEDIA BLANKS:	at least 3 per set

ACCURACY	
RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT	
TECHNIQUE:	HPLC, UV AND ELECTROCHEMICAL DETECTION
ANALYTE:	4,4'-methylenedianiline (MDA)
EXTRACTION:	0.1 N KOH In methanol
INJECTION VOLUME:	25 µL
MOBILE PHASE:	0.1 N sodium acetate in 30% acetonitrile/70% H_2O @ 1 mL/min
COLUMN:	C_{18} column, 4-µm particle size
DETECTOR:	UV, 245 nm; electrochemical (ECHD), glassy carbon electrode at +0.75 to +0.85 V vs. Ag/AgCl electrode
CALIBRATION:	MDA in 0.1 N methanolic KOH
RANGE: UV:	0.3 to 5 µg per sample [1]
ECHD:	0.025 to 0.5 µg per sample [1]
ESTIMATED LOD:	0.12 to 1.2 µg per sample [4]
PRECISION ($\bar{S}_r$):	0.027
ESTIMATED LOD: UV:	0.12 µg per sample
ECHD:	0.007 µg per sample [1]

APPLICABILITY: The working range is 0.025 ppb to 1.2 ppm (0.0002 to 10 mg/m^3) for a 100-L air sample, and the method is applicable to STEL measurements. The method is specific for MDA and the use of UV and electrochemical detectors in series gives greater reliability to the analysis, and allows a wide measurement range. The method has been applied to wipe samples.

INTERFERENCES: 4,4'-Diphenylmethane diisocyanate (MDI) will interfere owing to its conversion to MDA on the acid-treated glass fiber filter. Other aromatic amines do not interfere.

OTHER METHODS: Methods with acetylation, and the determination of the acetic anhydride derivative of MDA either by HPLC/UV [2] or by GC/EC (OSHA Method 57) [3] have been reported.

REAGENTS:

1. 4,4'-Methylenedianiline (MDA),* reagent grade.
2. Acetonitrile, distilled in glass.
3. Water, deionized.
4. Sodium acetate, reagent grade.
5. HPLC Mobile Phase: 0.1 N sodium acetate in 30% acetonitrile/70% water.
6. Methanol, distilled in glass.
7. Potassium hydroxide, reagent grade.
8. Calibration stock solution,* 1.0 μg/μL. Dissolve 0.01 g MDA in 10 mL 0.1 N methanolic KOH.
9. Extraction solution: 0.1 N potassium hydroxide in methanol.
10. Sulfuric acid solution: 0.26 N in water. Add, with caution, 1.5 mL concentrated sulfuric acid to deionized water and dilute to 200 mL.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: filter, acid-treated glass fiber (Gelman AE or equivalent), with a paper O-ring, in a 37-mm polystyrene 3-piece cassette. NOTE: Prepare filter by adding 0.5 mL 0.26 N sulfuric acid to glass fiber filter on a glass tray. Heat for 1 hour at 100 °C. Load the filter, backed by a paper O-ring, into a cassette and seal with shrink band to enable open-face sampling.
2. Personal sampling pump, 1 to 2 L/min, with flexible tubing.
3. High performance liquid chromatograph (HPLC), with UV detector, 245-nm, and an electrochemical detector, glassy carbon electrode operated at +0.75 to +0.85V with reference to silver/silver chloride reference electrode, oxidative mode.
4. Wipe Tabs (Whatman Smear Tabs or equivalent).
5. Sample filter apparatus: 0.45-μm, PTFE.
6. Syringe, 10-mL, disposable.
7. Vials, glass, scintillation, 20-mL, with PTFE-lined caps.
8. Syringes, microliter, readable to 0.1-μL.
9. Pipets, 2-, 4-, and 10-mL.
10. Tweezers.
11. Ultrasonic water bath.
12. Gauze Pad (Johnson Gauze sponges 2x2, 12 ply or equivalent).

SPECIAL PRECAUTIONS: 4,4'-Methylenedianiline is a potential human carcinogen [4,5]. Avoid contact with acid and base solutions. Handle the acid-treated filters with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front piece and rear plug immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample open-faced at an accurately controlled flow rate between 1 and 2 L/min for a sample volume of 10 to 1000 L.
4. Within 4 hours of completion of sampling, transfer the filter with tweezers to a glass vial. Discard the paper O-ring. Add 4.0 mL 0.1 N methanolic KOH.
   NOTE: Wipe sampling and skin pad instructions:
   a. Identify surfaces to be wiped, usually a 100-cm^2 area.
   b. Add wetting agent (isopropanol) if needed and wipe in square pattern.
   c. Place in 20-mL scintillation vial.
   d. If wetting agent was used, allow the solvent to evaporate.
   e. Add 0.1 N methanolic KOH to vial (10 mL for gauze pads, 2 mL for smear tabs).
5. Pack securely for shipment. Include appropriate number of blanks in the shipment.

SAMPLE PREPARATION:

6. Agitate the samples for 1 hour in an ultrasonic water bath.
7. Filter the sample solution through a 0.45-μm PTFE filter and a disposable syringe into a clean vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Make serial dilutions as needed to obtain MDA concentrations in the range 0.025 to 1 μg/mL.
   b. Analyze together with samples and blanks (steps 11 through 13).
   c. Prepare a calibration graph (peak area vs. concentration of MDA, μg per sample) for each detector (UV and ECHD).
9. Determine the recovery at least once for each lot of filters used for sampling in the range of interest. Prepare six filters at each of three concentration levels plus three media blanks.
   a. Add known amounts of MDA in methanol to the filters, using a microliter syringe.
   b. Cover filters. Allow to stand overnight for solvent evaporation.
   c. Extract with 4.0 mL extracting solutions, prepare samples (steps 6 and 7) and analyze (steps 11 through 13) together with standards and blanks.
   d. Determine recovery (R). Construct a graph of R vs. μg MDA recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set liquid chromatograph to manufacturer's recommendations and parameters given on page 5029-1.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak areas for UV and ECHD responses.

CALCULATIONS:

14. Determine the mass, μg (corrected for recovery) of MDA found on the sample filter (W) and in the average blank filter (B).
16. Calculate concentration (C) of MDA in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

A calibration curve for the UV absorption detector was constructed from 8 standards over the range 0.03 μg/mL to 1.22 μg/mL [1]. The curve was linear over this region and the LOD was determined to be 0.03 μg/mL. A calibration curve for the ECHD over the range 0.001 μg/mL to 0.12 μg/mL was linear and the LOD was determined to be 0.002 μg/mL. Test samples were prepared by spiking acid-impregnated filters with known amounts of MDA from a solution in methanol. Samples were prepared in triplicate at levels between 0.009 μg per filter and 3.7 μg per filter. (See Table 1 for results):

a. To evaluate extraction efficiency, the filters were analyzed immediately.
b. To assess storage stability, spiked filters were stored in glass scintillation vials for 1 month prior to analysis.

c. To investigate the stability of MDA on the filter during sampling, spiked filters were attached to a sampling pump and 1000 L of laboratory air was drawn through them at 2.5 L/min before analysis.

Table 1: Average Percent Recovery (n=3) of 4,4'-Methylenedianiline From Filter Media

Spiked Amount (μg)	Extraction Efficiency (S.D.) (%)	Storage Stability[a] (%)	Sampling Stability (%)
3.71	94.5 (0.8)	94.4 (1.0)	94.4 (1.0)
1.80	91.3 (0.2)	91.1 (0.4)	90.8 (1.7)
0.93	85.9 (0.8)	86.4 (0.9)	85.5 (0.4)
0.37	84.8 (0.9)	86.0 (0.7)	84.9 (1.0)
0.09	82.0 (2.7)	82.0 (3.8)	77.0 (3.5)
0.037	80.0 (4.1)	83.0 (4.1)	77.0 (3.1)

[a] - Stored in glass scintillation vial for 1 month.

Nine spiked filters were prepared independently and submitted for analysis as a single blind test. Recoveries were 80 to 95% when spiked with 0.012 to 1.2 μg per filter.

During method ruggedization, recoveries were observed to drop significantly during shipment in cassettes. The reason has not been determined but stability has been achieved by field extraction of the filter with methanolic KOH. Solutions and extracted filters were prepared, shipped, stored for 60 days, and analyzed. The data are shown in Table 2.

Table 2: Stability of Extracted Filter Solutions

Spiked Amount (μg)	N	% Recovery (S.D.)
9.9	4	92.1 (0.017)
5.1	4	90.4 (0.042)
1.0	4	100.0 (0.050)
0.0	2	NA

WIPE SAMPLING-This analytical method was used to analyze environmental samples collected on gauze pads and smear tabs. MDA was spiked onto acid-treated gauze pads, plain gauze pads, and smear tabs at 92, 9.2, and 0.92 μg per sample. Sets of each concentration were extracted immediately after allowing the spiking solution to evaporate, one day, one week, and one month after spiking. The extraction solution consisted of 10 mL 0.1 N methanolic KOH for the gauze pads and 2 mL for the smear tabs. The best recovery was obtained when the media were extracted immediately after the methanol evaporated. The same-day samples were reanalyzed at various times to determine if MDA would react with the medium when in solution. Recoveries are given in Table 3.

Table 3: Recoveries of MDA from Gauze Pads and Smear Tabs

Samples & Loading	Average Recovered after			
	0 day	1 day	7 days	30 days
Acid-treated Gauze Pads				
9.3 μg	96	89	87	86
0.93 μg	98	90	86	85
0.09 μg	97	85	85	87
Untreated Gauze Pad				
9.3 μg	97	73	70	53
0.93 μg	98	70	63	46
0.09 μg	93	62	60	55
Smear Tab				
9.3 μg	93	64	53	51
0.93 μg	87	62	48	46
0.09 μg	85	56	44	42
Solutions				
9.3 μg	98	97	98	96
0.93 μg	95	96	95	97
0.09 μg	98	97	94	98

MDA was extracted with greater than 90% extraction efficiency from all the media tested. The extraction efficiency did not decrease when the analyte was isolated from the media by extraction or media elimination. However, upon evaporation of the solvent from the spikes, the MDA begins to react with the media and loss of MDA begins immediately. This is shown by the decrease in recovery and the appearance of a yellow discoloration of the white medium. Although the recovery stabilizes, the addition of sulfuric acid to the pads does not prevent the loss of about 7% of the analyte during the first day. Addition of the 0.1 N methanolic KOH serves as an efficient stabilizer when added to the sample with no recovery loss. The improved recovery following field extraction, the imprecise mode of treated media preparation, and safety considerations of using acid-treated media for wipe samples were factors in using field extraction for surface and dermal samples.

REFERENCES:

[1] Neumeister, C. E. Method Development for 4,4'-Methylenedianiline, Sequence #4752, NIOSH/MRSB, Cincinnati, OH., (NIOSH, unpublished, November 20, 1986).

[2] Anderson, C. C. and E. C. Gunderson, Methods Validation Study of High Performance Liquid Chromatographic Technique for Determining the MPDA and MDA Content of Air samples, SRI International, Menlo Park, CA (1986).

[3] Elskamp, C. J. Method 57 (4,4'-Methylenedianiline), Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (1986).

[4] Federal Register 29, Part 2, CFR Parts 1910 and 1926 (May 12, 1989).

[5] NIOSH Current Intelligence Bulletin #47, 4,4'-Methylenedianiline (MDA), U. S. Dept. of Health and Human Services (NIOSH) Publication No. 86-115 (1986).

METHOD WRITTEN BY:

Charles Neumeister, NIOSH/DPSE.

METHYL ETHYL KETONE 2500

$CH_3CCH_2CH_3$ MW: 72.11 CAS: 78-93-3 RTECS: EL6475000

METHOD: 2500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: 200 ppm: STEL 300 ppm
ACGIH: 200 ppm: STEL 300 ppm
(1 ppm = 2.95 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.805 g/mL @ 20 °C; BP 79.6 °C; MP −86 °C; VP 13 kPa (100 mm Hg; 13% v/v) @ 25 °C; explosive range 2 to 10% v/v in air

SYNONYMS: 2-butanone; MEK

SAMPLING

SAMPLER: SOLID SORBENT TUBE (carbon molecular sieve, 160 mg/80 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 200 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: 6 weeks @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 295 to 1180 mg/m^3

BIAS: 6.21%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069 [1]

ACCURACY: ± 17.83%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl ethyl ketone (MEK)

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 55 to 75 °C

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass or stainless steel, 4 m x 2-mm ID; 20% SP-2100/0.1% Carbowax 1500 on Supelcoport 100/120

CALIBRATION: MEK solutions in CS_2

RANGE: 0.15 to 5 mg per sample

ESTIMATED LOD: 0.004 mg per sample [1,2]

PRECISION ($\bar{S}_r$): 0.04 [1]

APPLICABILITY: The working range is 17 to 560 ppm (50 to 1650 mg/m^3) for a 3-L air sample. The method is applicable to 15-min samples. This method was developed to give improved sample stability compared to conventional charcoal tubes [2,3]. Side-by-side comparisons of this method and Method S3 were made in a sporting goods manufacturing plant in which MIBK, THF, and toluene were also present. This method has also been used successfully for acetone [4].

INTERFERENCES: Under the given conditions, acetone and isopropanol have retention times similar to MEK. Mass spectrometry and other GC columns, e.g., SP-1000, or 30 m x 0.32-mm WCOT capillary coated with 1 µm DB-1, are aids to resolving interferences.

OTHER METHODS: This method is similar, except for the sampler, to Methods P&CAM 127 [5] and S3 [6,7], which it replaces.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) benzene* or other suitable internal standard.
2. Methyl ethyl ketone
3. Nitrogen or helium, purified.
4. Hydrogen prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID. Two sections of 60/80 mesh carbon molecular sieve separated by 2-mm foam plug (front = 160 mg, back = 80 mg) (SKC Cat. No. 226-81, Supelco ORBO-90, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2500-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C). Work with it only in a hood. Benzene is a human carcinogen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 12 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.004 to 5 mg MEK per sample.
   a. Add known amounts of MEK to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg MEK).
9. Determine desorption efficiency (DE) at least once for each batch of Ambersorb XE-347 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of MEK directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg MEK recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2500-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of MEK found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of MEK in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was evaluated with spiked samplers and with atmospheres generated by syringe pump/air dilution, verified by infrared absorption. Breakthrough (80% RH, 200 ppm, 0.3 L/min) = 16.4 L; DE (4 to 18 mg per sample) = 1.03; storage stability (0.7 to 4 mg per sample) = 90% after six weeks at 25 °C; precision and accuracy as given on page 2500-1 (15 samples) [1]. A user check gave an estimated LOD of 0.004 mg MEK per sample [2].

REFERENCES:

[1] Slick, E. J., NIOSH, unpublished data (1983).
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[5] NIOSH Manual of Analytical Methods, V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[6] Ibid., V. 2, S3, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[7] Documentation of the NIOSH Validation Tests, S3, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY:

Judd C. Posner, Ph.D., NIOSH/DPSE.

METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood 8002

(1) $CH_3CH_2COCH_3$	MW:	72.11	CAS:	78-93-3	RTECS: EL6475000
(2) CH_3CH_2OH		46.07		64-17-5	KQ6300000
(3) C_7H_8		92.14		108-88-3	XS5250000

METHOD: 8002, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to 2-butanone, ethanol, and toluene.

SYNONYMS: (1) MEK: 2-butanone; methyl ethyl ketone
(2) ethanol: ethyl alcohol
(3) toluene: methyl benzene

BIOLOGICAL SAMPLING

SPECIMEN: venous blood, after 2 or more h exposure

CONTAINER: 5-mL heparin-coated vacuum tube

SHIPMENT: air express @ 4 °C

STABILITY: stable @ 4 °C for 3 weeks

CONTROLS: pre-shift whole blood samples as well as whole blood samples from non-exposed controls

ACCURACY: (1) ±28.6%
(2) ±13.0%
(3) ±26.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: MEK, ethanol, toluene (simultaneous)

TEMPERATURE-INJECTION: 150 °C
- DETECTOR: 200 °C
-COLUMN: 85 °C (4 min), 85 to 200°C @ 16 °C/min, 220°C (4 min)

CARRIER GAS: helium, 25 mL/min

COLUMN: glass, 3 m × 2-mm ID, 5% Carbowax 20 M on 100/120 mesh Chromosorb WHP

CALIBRATION: blood standards containing analytes

RANGE: (1) 0.1 to 8 μg/mL
(2) 0.01 to 0.6 mg/mL
(3) 1 to 600 μg/mL

RECOVERIES: (1) 0.90 @ 2 μg/mL blood;
(2) 0.98 @ 0.05 mg/mL blood;
(3) 0.93 @ 2 μg/mL blood

PRECISION ($\bar{S}_r$): (1) 0.095 (1 μg/mL blood);
(2) 0.056 (0.1 mg/mL blood);
(3) 0.098 (1 μg/mL blood)

APPLICABILITY: MEK and toluene are commonly found in trace amounts in humans working in the paint spray industry. Occasionally, traces of ethanol are also present. This method can be used in screening workers exposed to these central nervous system depressants.

INTERFERENCES: Ethanol concentrations in excess of the stated range may interfere with the MEK peaks at low concentration (< 0.2 μg MEK/mL blood). Ethanol in excess of the stated range also increases blood toluene concentration [1]. When substances other than the analytes are suspected to be present in the blood, record their identities to determine possible interferences [2].

OTHER METHODS: None are known that can determine these constituents simultaneously. Other methods require extraction or distillation for concentration of trace amounts of these chemicals in blood.

REAGENTS:

1. Methyl ethyl ketone, calibration stock solution (3.864 mg/mL). Dilute 1.2 mL MEK (2-butanone) to 250 mL with distilled water. Stable several months at 4 °C.
2. Toluene calibration stock solution (3.81 mg/mL). Dilute to 1.1 mL toluene to 250 mL with acetone. Stable several months.
3. Ethanol calibration stock solution (157.8 mg/mL). Dilute 10 mL absolute ethanol to 50 mL with distilled water. Stable several months at 4 °C.
4. Citric acid.
5. Sodium citrate.
6. Dextrose.
7. Acetone.
8. Isobutanol, 8 μg/mL (aqueous), internal standard.
9. Acidium citricum dextrose solution (ACD). Accurately weigh 4.8 g citric acid, 13.2 g sodium citrate, and 14.7 g dextrose. Dissolve and dilute to 1 L with distilled water.
10. Blood (human), from blood centers or from individuals not exposed to the analytes.* Can be stored at 4 °C for three weeks.

* See Special Precautions.

EQUIPMENT:

1. Tubes, heparin-coated, vacuum, 5-mL.
2. Gas chromatograph with flame-ionization detector, electronic integrator, and column (page 8002-1).
3. Rotator for mixing blood specimens.
4. Vials, screw-cap septum with caps, 7-mL.
5. Septum discs, PTFE-lined.
6. Heater, Dri-block with temperature control (30 to 100 °C) to accommodate the 7-mL size vials.
7. Micropipettes, 100- to 1000-μL.
8. Syringes, gas-tight, 1-mL, with valve.
9. Syringes, tuberculin, disposable, 1-mL, with 21-gauge needle.
10. Volumetric flasks, 50- and 250-mL.

SPECIAL PRECAUTIONS: Samples of blood collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

SAMPLING:

1. Collect 5 mL venous whole blood in a vacuum tube containing heparin. Invert the tube gently several times to mix.
2. Ship samples in polyfoam packs containing bagged ice or refrigerant.

SAMPLE PREPARATION:

3. Pipet 0.5 mL ACD solution and 0.25 mL isobutanol solution into a 7-mL glass screw-cap vial and mix.
4. Using a tuberculin syringe with a 21-gauge needle, draw 0.25 mL of blood from the vacuum tube and add to the vial.
5. Secure the PTFE-lined septum disc and cap tightly to the vial.
6. Mix the solution very slowly on a rotator for 5 min.

CALIBRATION AND QUALITY CONTROL:

7. Prepare working standard solutions. Pipet 2 mL from each of the calibration stock solutions into separate 200-mL volumetric flasks. Dilute to the mark with deionized water. The resultant concentrations are 38.1 and 38.6 μg/mL for toluene and MEK, respectively; and 1.58 mg/mL for ethanol. Prepare fresh standards every 92 h.
8. Make blood standards at 5 different concentrations ranging from 0 to 8 μg MEK and toluene/mL blood and from 0 to 500 μg ethanol/mL blood. Add aliquots of the working standards to 2 mL blood with a microliter syringe. Prepare fresh blood standards every 92 h and store at 4 °C.
9. Analyze the blood standards (steps 3 through 6 and 12 through 14).
10. Plot the concentrations (μg/mL) vs. the ratio of the peak areas of each analyte to the peak areas of the internal standard (isobutanol) on the same chromatogram to establish the calibration graph.
11. Include a blood control with each run.

MEASUREMENT:

12. Heat the sealed vial in a block heater at 60 °C for 15 min.
13. Remove a 1-mL aliquot of the head space vapor inside the sealed vial with a heated 60 °C gas-tight syringe and inject into the gas chromatograph.
    NOTE: Temperature control of blood and syringe is very important for accurate results. Heat the gas-tight syringe to 60 °C in an oven.
14. Measure the peak areas. Divide the peak area for each analyte by the peak area for the internal standard on the same chromatogram.

CALCULATIONS:

15. Determine the concentrations of MEK, toluene, and ethanol in blood from the calibration graph.

GUIDES TO INTERPRETATION:

1. Blood-alcohol analyses are usually reported in mg/dL or % w/v blood alcohol concentration (BAC). Thus, a BAC may be reported as 300 μg/mL or 30 mg/dL, or 0.03 g/dL, or 0.03% w/v. Legal blood alcohol concentrations are reported in reference [3].
2. Single toluene inhalation exposures of 50 and 100 ppm in air for 3 h produced average blood (human) toluene concentrations of 1.6 and 3.9 ppm, respectively [4]. Another study reported blood toluene levels ranging from 4.1 to 7.3 ppm for exposure to 200 ppm toluene in air [5].
3. The Biological Exposure Index for toluene is 1 mg/L in end-of-shift venous blood [6].

EVALUATION METHOD:

1. Ten spiked replicate blood samples at the blood concentration of 1 μg/mL for MEK and toluene and 10 μg/mL for ethanol were analyzed. The precision data obtained for each analyte were 9.5, 9.8, and 5.6%, respectively.
2. Average recoveries of 10 replicate blood samples for MEK, toluene and ethanol were 90, 93 and 98%, at 3 μg/mL of MEK, 2 μg/mL toluene, respectively, and 0.05 mg/mL of ethanol, respectively, in pooled blood.

REFERENCES:

[1] Waldron, H. A., N. Cherry, and J. D. Johnson. The Effects of Ethanol on Blood Toluene Concentrations, Int. Arch. Occup. Environ. Health, 51, 365-369 (1983).
[2] Hachenberg, H. and A. P. Schmidt. Gas Chromatographic Headspace Analysis, 2nd ed., Heyden and Son Ltd., Philadelphia, PA (1979).
[3] Dubowski, K. M. Alcohol Analysis: Clinical Laboratory Aspects, Part II, Laboratory Management, 27-36 (April, 1982).
[4] Stewart, R. D., C. L. Hake, H. V. Forster, A. J. Lebrun, J. E. Peterson, and A. Wu. Toluene: Development of a Biological Standard for Industrial Worker by Breath Analysis, NIOSH Contract Report No. 99-72-84 (1975).
[5] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).
[6] 1993-1994 Threshold Limit Values and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1993).

METHOD WRITTEN BY:

William P. Tolos, NIOSH/DBBS.

$C_8H_{16}O_4$ MW: 176.21 CAS: 1338-23-4 RTECS: EL9450000; 21837

METHOD: 3508, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : no PEL
NIOSH: C 0.2 ppm/15 min
ACGIH: C 0.2 ppm
(1 ppm = 7.2 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.170 g/mL @ 20 °C; flash point (open cup) 82 °C

SYNONYMS: MEKP; MEK peroxide; 2-butanone peroxide

SAMPLING		MEASUREMENT	
SAMPLER:	IMPINGER (15 mL dimethyl phthalate)	**TECHNIQUE:**	VISIBLE ABSORPTION SPECTROPHOTOMETRY
FLOW RATE:	0.5 to 2 L/min	**ANALYTE:**	diphenylcarbazide oxidation product
VOL-MIN:	52 L @ 0.2 ppm	**SAMPLE PREPARATION:**	note liquid volume; remove 5 mL aliquot; add 5 mL diphenylcarbazide color reagent; heat at 85 ± 5 °C for 15 min; cool in room temperature water bath exactly 5 min
-MAX:	520 L		
SHIPMENT:	transfer to silanized, foil-wrapped vials; ship in dry ice		
SAMPLE STABILITY:	90% recovery after 21 days @ −4 °C [2]	**ANALYSIS:**	color development; absorbance @ 565 nm
BLANKS:	2 to 10 field blanks per set	**CALIBRATION:**	standard solutions of methyl ethyl ketone peroxide in dimethyl phthalate
		RANGE:	75 to 750 µg per sample [1]
ACCURACY		**ESTIMATED LOD:**	75 µg per sample [1]
RANGE STUDIED:	not studied for generated samples	**PRECISION ($\hat{S}_r$):**	0.052 [2]
BIAS:	not determined		
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined		
ACCCURACY:	not determined		

APPLICABILITY: The working range is 0.11 to 1.1 ppm (0.75 to 7.5 mg/m^3) for a 100-L air sample [1]. This method has not been tested with aerosol generation or field samples. Special care must be taken in the conditioning of the glassware and in the storage of the samples.

INTERFERENCES: The diphenylcarbazide color reaction is relatively non-specific. Most ketones, except acetone, will exhibit positive interference at high levels. Other peroxides or any strong oxidant could also interfere with this procedure. Substances which catalyze the decomposition of peroxide may cause a significant decrease in the measurement; in particular, the presence of metal ions adsorbed on the glassware.

OTHER METHODS: This revises P&CAM 331 [1].

REAGENTS:

1. Acetic acid, glacial, reagent grade.
2. Dimethyl phthalate (DMP), reagent grade.
3. Water, distilled, deionized.
4. Toluene.
5. Methanol.
6. Isopropyl alcohol, reagent grade.
7. Sulfuric acid, conc.
8. Diphenylcarbazide (DPC) solution, 0.25% (w/v). Dissolve 0.25 g ± 0.01 g reagent grade DPC in DMP in an Al foil-covered 100-mL volumetric flask. Agitate in ultrasonic bath to aid dissolution. Dilute to 100 mL.
   NOTE: This solution is light-sensitive. Prepare immediately before using.
9. Color reagent. Mix 30 mL 0.25% DPC solution with 20 mL glacial acetic acid.
10. Methyl ethyl ketone peroxide (MEKP), 60%, technical grade, in dimethyl phthalate. Standardize as in APPENDIX.
11. Calibration stock solution.* Pipet ca. 10 μL of 60% MEKP into a 50-mL pre-weighed volumetric flask. Accurately weigh the flask plus MEKP; dilute to the mark with dimethyl phthalate. Wrap flask in Al foil. Prepare in duplicate.
12. Sodium thiosulfate solution, 0.1 N, standardized. Commercially available, or prepare as in APPENDIX.
13. Sodium iodide solution, 20% (w/v). Dissolve 20 g sodium iodide in 100 mL methanol.
14. Sodium bisulfite.
15. Nochromix.
16. Dichlorodimethylsilane, 5% (w/v), in toluene (Sylon CT, or equivalent).

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget impinger, 25-mL, silanized.*
2. Personal sampling pump, 0.5 to 2 L/min, with splashover protection (empty impinger placed between sampler and personal sampling pump) and flexible connecting tubing.
3. Vials, 20-mL, silanized, PTFE-lined screw caps.*
4. Aluminum foil.
5. Stopwatch.
6. Cold chest, insulated, dry-ice cooled.
7. Waterbath, 85 ± 5 °C.
8. Waterbath, 25 ± 5 °C.
9. Spectrophotometer, visible, 565 nm.
10. Cuvettes, matched glass, 1-cm pathlength.
11. Laboratory glassware, silanized:*
    a. pipets, TD, 10-μL; 1-, 5-, 10-, and 15-mL.
    b. volumetric flasks, 25-, 50-, and 100-mL; and 1-L, with glass stoppers.
    c. beakers, 150-mL and 1-L.
    d. burets, 50-mL.
    e. graduated cylinder, 50-mL;
    f. Erlenmeyer flasks or iodine flasks, 250-mL.
    g. test tubes, 18-mm x 150-mm, silanized, with glass stoppers and test tube rack.*
12. Ultrasonic bath.
13. Pipets, disposable, 2-mL.
14. Balance, readable to 0.1 mg.
15. Drying oven, 120 °C.
16. Stirrer, magnetic.

* It is very important to use glassware that has been thoroughly cleaned and silanized to remove heavy metal ions that catalyze peroxide decomposition.

For new glassware:

a. Wash in detergent, rinse with tap water, then deionized water.
b. Soak overnight in Nochromix solution (conc. sulfuric acid and a packet of Nochromix).
c. Rinse well with deionized water, dry in oven, then cool to room temperature.
d. Silanize by filling with 5% dichlorodimethyl-silane in toluene for 1 min. Rinse with toluene, then methanol, and dry.

After each use:

a. Rinse with methanol, wash in detergent, thoroughly rinse with tap water, then rinse four to five times with deionized water.
b. Rinse again with methanol. Dry overnight at 120 °C. Cool to room temperature.

SPECIAL PRECAUTIONS: MEKP is shock and heat sensitive. Store below 25 °C. MEKP solutions are extremely irritating and corrosive to the skin and eyes and may cause permanent eye injury. Use safety goggles. Dispose of waste MEKP solutions as follows:

a. Prepare 250 mL saturated aqueous sodium bisulfite in a 1-L beaker.
b. Store in a hood. Add all waste solutions containing MEKP to this beaker.
c. Allow to stand one week before disposing of the two-phase mixture.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Pipet 15 mL dimethyl phthalate into the impinger. Mark the level. Wrap with aluminum foil.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 52 to 520 L.
4. Check liquid level in impinger and add dimethyl phthalate if necessary to bring level to 15.0 mL. Quantitatively transfer the contents of each impinger to a silanized, Al foil-wrapped vial and seal tightly. Quickly place in a cold chest.
5. Whenever possible, hand-deliver the samples packed in dry ice. Otherwise, ship samples in container with dry ice. Mark "FRAGILE" on the container.
6. Upon receipt in the laboratory, store vials in the freezer. Complete analysis as soon as possible.

SAMPLE PREPARATION:

7. Adjust sample volume to 15.0 mL if necessary. Transfer in duplicate exactly 5.0 mL (1/3) of each sample or field blank to silanized test tubes.
8. Pipet 5.0 mL color reagent into the test tubes. Stopper and invert several times to mix.
9. Loosen the stoppers and heat the test tubes in a waterbath at 85 ± 5 °C for 15 min.
10. Cool in a waterbath at 25 ± 5 °C for exactly 5 min.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards in duplicate.
    a. Pipet, e.g., 1.0, 2.0, 5.0, and 10.0 mL calibration stock solution to 25-mL silanized volumetric flasks, fitted with glass stoppers. Dilute to the mark with DMP. These working standards contain ca. 5, 10, 25, and 50 mg MEKP/mL (25, 50, 125, and 250 μg MEKP per 5-mL aliquot).
    b. Process the working standards together with samples, field blanks, media blanks, and reagent blanks (steps 7 through 10 and 12 and 13) during the same time period using the same batch of reagents.
    c. Prepare calibration graph (absorbance vs. μg MEKP). Extrapolate to zero concentration (y-intercept). Any sample whose absorbance is less than twice the "blank" should be reported as less than that level (about 25 μg MEKP per 5-mL aliquot). Perform a volumetric dilution to extend the range upward.

MEASUREMENT:

12. Set spectrophotometer according to manufacturer's instructions. Set zero with dimethyl phthalate vs. air.
13. Read sample absorbance at 565 nm vs. air when a stable value is obtained.
    NOTE: See SPECIAL PRECAUTIONS for procedure for disposal of waste MEKP solutions.

CALCULATIONS:

14. Determine the mass, μg, of MEKP in the 5-mL aliquot of sample, W, and the average media blank, B, from the calibration graph.
15. Calculate the concentration, C, of MEKP in the air volume sampled, V (L):

$$C = \frac{3 \cdot (W - B)}{V}, \text{ mg/m}^3.$$

NOTE: Correct for the average media blank, B, only if it exceeds twice the reagent blank (y-intercept).

EVALUATION OF METHOD:

This method is based on P&CAM 331 which was issued on August 29, 1980 [1] and was studied using technical grade MEKP containing 58.7% MEKP [2].

A two-level factorial experiment was run to study the effect of three different parameters on the color produced in the reaction between MEKP and DPC. A reaction bath temperature of 85 °C and reaction time of 15 min were determined to be optimum. Samples containing 204 μg MEKP per 5 mL stored in the freezer for 21 days showed 10% loss of MEKP. MEKP standard solutions were tested for interference with acetone, methyl ethyl ketone, cyclohexanone, and 3-methyl-2-butanone. All these ketones, except acetone, exhibited positive interference. Stability of MEKP solutions was tested using various substances which could be likely co-contaminants. At freezer temperatures, samples containing styrene were stable for a week.

After 4 hrs at 1 L/min airflow through impingers containing MEKP standards in DMP, less than 10% of the MEKP carried over from the front to the backup bubbler.

The RSD of slopes of the calibration line determined from three levels approximately to 100, 170, and 210 μg/10 mL sample obtained over a six-month period was 9.8%. When the standards and samples were run on the same day, the RSD was 5.2%.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 331, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).
[2] Okenfuss, J. R. and J. C. Posner. Investigation of an Air Sampling and Analytical Method for Methyl Ethyl Ketone Peroxide, available as Order No. PB 81-167868 from NTIS, Springfield, VA 22161 (1980).

METHOD REVISED BY:

Judd C. Posner, Ph.D., NIOSH/DPSE and Julie R. Okenfuss.

APPENDIX:

1. STANDARDIZATION OF 60% MEKP STOCK SOLUTION
   a. Weigh to nearest mg, 1 g 60% MEKP in a 100-mL volumetric flask. Dilute to the mark with isopropyl alcohol and cover flask with foil.
   b. Place ca. 25 mL isopropyl alcohol in a 250-mL iodine flask. Add 5 mL glacial acetic acid then add 10 mL 20% sodium iodide solution to the flask.
   c. Pipet exactly 10.0 mL MEKP-isopropyl alcohol solution (from step 1.a above) into the flask, cover and let stand in the dark for 15 min.
   d. Add 10 mL distilled water to the flask immediately before titrating.
   e. Titrate with 0.1 N sodium thiosulfate from a yellow to colorless end point. Record the volume in mL used. Titrate a blank containing all reagents except MEKP in exactly the same way.
   f. Calculate the weight % MEKP:

$$C_s = \frac{(V_s - V_b)\ 4.405}{W}$$

where: C_s = percent MEKP as the cyclic dimer
V_s = volume of 0.1 N $Na_2S_2O_3$ used to titrate the sample (mL)
V_b = volume of 0.1 N $Na_2S_2O_3$ used to titrate the blank (mL)
W = weight of commercial MEKP used (g)
4.405 = constant containing the milliequivalent weight of MEKP (as the cyclic dimer) and various dilution factors.

2. STANDARDIZATION OF SODIUM THIOSULFATE, 0.1 N (or use commercially available standard)
   a. Prepare the following solutions:
      (1) Potassium dichromate, 0.1000 N. Dissolve 4.904 g anhydrous $K_2Cr_2O_7$, primary standard grade, in distilled water; dilute to 1 L.
      (2) Starch indicator. Prepare a thin paste of 1 g soluble starch in a few mL distilled water. Bring 200 mL distilled water to a boil, remove from heat and stir in the starch paste. Prepare fresh before use.
      (3) Sodium thiosulfate solution. Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled, cooled distilled water; dilute to 1 L. Add 5 mL $CHCl_3$ as preservative. Age 2 weeks before standardizing.
   b. Place 80 mL distilled, deionized water in 150-mL beaker, stirred with magnetic stirrer. Add 1 mL conc. H_2SO_4, 10.0 mL 0.1000 N $K_2Cr_2O_7$ and ca. 1 g KI. Allow to stand in dark for 6 min. Titrate with sodium thiosulfate solution. Upon approaching end point (brown changing to yellowish green), add 1 mL starch indicator solution and continue titrating to the end point (blue to light green). Calculate the normality, N, of the sodium thiosulfate solution:

$$N = \frac{1}{\text{mL } Na_2S_2O_3 \text{ used}}$$

5-METHYL-3-HEPTANONE

See KETONES II (Method 1301) for procedure

METHYL IODIDE

CH_3I MW: 141.94 CAS: 74-88-4 RTECS: PA 9450000

METHOD: 1014, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: 2 ppm (skin; suspect carcinogen)
ACGIH: C 0.2 (skin; suspect carcinogen)
(1 ppm = 5.80 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.28 g/mL @ 25 °C; BP 42.5 °C; MP −66 °C; VP 50 kPa (375 mm Hg; 49% v/v) @ 20 °C; not combustible

SYNONYMS: iodomethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 5 ppm
-MAX: 50 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	17 to 52 mg/m^3 [1] (53-L samples)
BIAS:	− 10.0%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.070 [1]
ACCURACY:	± 20.03%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl iodide

DESORPTION: 1 mL toluene, stand 8 h

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 190 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 3 m x 3.2-mm OD stainless steel, packed with Chromosorb 101

CALIBRATION: solutions of methyl iodide in toluene

RANGE: 0.5 to 5 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.045 @ 0.7 to 2.8 mg per sample [2]

APPLICABILITY: The working range of this method is 10 to 100 mg/m^3 (1.7 to 17 ppm) for a 50-L air sample. High humidity during sampling will decrease breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S98 [3].

REAGENTS:

1. Toluene, reagent grade (distilled in glass).
2. Methyl iodide, reagent grade.*
3. Calibration stock solution, 250 mg/mL. Prepare in toluene.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 6-mm OD, 4-mm ID, flame-sealed ends and plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1014-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL, readable to 0.1 μL, 25-, 50- and 100-μL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1-mL with pipet bulb.

SPECIAL PRECAUTIONS: Methyl iodide is an acute neurotoxin and may produce severe narcosis. It is a suspected carcinogen [4,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 15 to 50 L.
4. Cap the samples. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL toluene to each vial. Attach cap to each vial.
7. Allow to stand overnight with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 5 mg methyl iodide per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 through 12).
   c. Prepare a calibration graph by plotting peak area vs. mg methyl iodide.
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (1 to 20 μL) of calibration stock solution or a dilution thereof directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg methyl iodide recovered.

10. Analyze three quality control blind spikes or three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph operating parameters according to manufacturer's recommendations and those given on page 1014-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate the concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S98 was issued on April 11, 1975 [3] and evaluated using atmospheres containing methyl iodide generated in dry air [1]. The samples were analyzed by gas chromatography along with spiked samplers to correct for desorption efficiency (DE) which was determined to be 0.85, 0.91 and 0.92 at 0.7, 1.4 and 2.8 mg methyl iodide, respectively, from 100 mg of SKC Lot 105 activated coconut shell charcoal. Long-term stability of methyl iodide on the charcoal has not been investigated.

When an atmosphere containing 52 mg/m^3 methyl iodide in dry air was sampled at a rate of 1 L/min for 4 hrs, the concentration of methyl iodide in the effluent was 2% of that in the influent, indicating near breakthrough. Therefore, the adsorptive capacity of this lot of charcoal is approximately 12.5 mg methyl iodide, and the breakthrough volume is approximately 240 L under the conditions investigated.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S98, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] UBTL, Inc., NIOSH Sequence #3428-M (unpublished, April 21, 1982).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S98, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Current Intelligence Bulletin 43, Monohalomethanes, U.S. Department of Health and Human Services, Publ. (NIOSH) 84-117 (1984).

[5] NIOSH-OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; S98 originally validated under NIOSH Contract CDC-99-74-45.

METHYL ISOAMYL ACETATE

See ESTERS I (Method 1450) for procedure

METHYL ISOBUTYL CARBINOL

See ALCOHOLS III (METHOD 1402) for procedure

METHYL ISOBUTYL KETONE

See KETONES I (Method 1300) for procedure

METHYL METHACRYLATE

$H_2C=C(CH_3)COOCH_3$ MW: 100.12 CAS: 80-62-6 RTECS: OZ5075000

METHOD: 2537, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: 100 ppm
ACGIH: 100 ppm
(1 ppm = 4.10 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.944 g/mL @ 20 °C; BP 100 °C; VP 4.7 kPa (35 mm Hg) @ 20 °C; explosive range 1.7 to 8.2% v/v in air

SYNONYMS: methacrylic acid methyl ester.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 8 L

SHIPMENT: in dry ice

SAMPLE STABILITY: ≥ 7 days @ 25 °C [1]; ≥ 32 days @ 4 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 193 to 725 mg/m^3 (3-L samples) [3]

BIAS: 2.55%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.063 [3]

ACCURACY: ± 12.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl methacrylate

DESORPTION: 2 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 100 °C

CARRIER GAS: He, 1 mL/min, makeup 20 mL/min

COLUMN: 30 m x 0.25-mm ID DB-1; 1-µm film fused silica capillary [2]

CALIBRATION: standard solutions of methyl methacrylate in CS_2

RANGE: 0.03 to 1 mg per sample [2,3]

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.007 @ .56 to 2.35 mg per sample [1]

APPLICABILITY: The working range is 2.4 to 270 ppm (10 to 1100 mg/m^3) for a 3-L air sample. Because of the similarity in the chemical structures and properties of methyl methacrylate and ethyl methacrylate and the available stability and desorption efficiency data this method may also be useful for determining ethyl methacrylate in air [4].

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises NIOSH Method S43 [5], which utilized a 20-ft x 1/8-inch stainless steel column, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport with nitrogen as carrier gas at 30 mL/min.

REAGENTS:

1. Methyl methacrylate, chromatographic quality.
2. Carbon disulfide, reagent grade.*
3. Undecane, 99%
4. Eluent: carbon disulfide, containing 0.1% (v/v) undecane or other suitable internal standard.
5. Calibration stock solution, 94.4 mg/mL. Dilute 10.0 mL methyl methacrylate to 10 mL with eluent.
6. Helium, prepurified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections (front = 400 mg; back = 200 mg) of XAD-2 resin (20/50 mesh), contained and separated by plugs of silylated glass wool. Tubes are commercially available (SKC, ST 226-30-06 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 2537-1).
4. Syringes, microliter, 10-μL, readable to 0.1 μL.
5. Pipets, various sizes to prepare standards.
6. Flasks, volumetric, 10-mL.
7. Vials, 2- and 5-mL, glass with PTFE-lined screw caps.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (has flash point = −30 °C); work with it only in a hood. Methyl methacrylate may cause irritation of the nose, throat, skin and eyes [6].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at a known flow rate between 0.01 to 0.05 L/min for a sample size of 1 to 8 L.
4. Cap the samplers. Pack securely for shipment in a cold container at 4 °C or lower.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections in separate 5-mL vials. Discard plugs.
6. Add 2.0 mL eluent to each vial. Cap each vial.
7. Allow to stand 30 min. with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to mark. Use serial dilutions as needed to obtain methyl methacrylate concentrations in the range 0.005 to 0.5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of XAD-2 used. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of media blank samplers.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution directly into front sorbent section with a microliter syringe.
   c. Cap the tubes and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).

e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to condition given on page 2537-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.
12. Measure peak area. Divide the peak area of the analyte by the peak area of the internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b \geq W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of methyl methacrylate in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S43 was issued on July 6, 1979, and validated with generated atmospheres over the concentration range 193 to 725 mg/m^3 [3,7]. Average recovery was 98.1% (18 samples) in the range 0.56 to 2.35 mg/sample. Overall precision ($\hat{S}_{rT}$) was estimated to be 0.063. Breakthrough volume was 6.46 L for 786 mg/m^3 methyl methacrylate in air with 90% relative humidity. In order to achieve greater sensitivity, analytical modifications in the method were made [2]. Desorption efficiency was checked by spiking 0.56 to 2.4 mg per sample onto XAD-2 tube; DE found was in the range 0.96 to 1.0. Storage studies over 32 days at 4 °C showed an average recovery of 97.3% [2].

A storage and stability study for ethyl methacrylate was performed on XAD-2 using 0.14 to 1.4 mg of analyte per sample at 20 °C and also at 4 °C for 23 days. The results of the study indicated an average recovery in the range 95 to 10% [4].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 (1977).

[2] Tanguay, James F., Method Modification Efforts for Methyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished, 1988).

[3] Backup Data Report for Methyl Methacrylate, S43, prepared under NIOSH Contract 210-76-0123 (1979).

[4] Tanguay, James F., Method Development Efforts for Ethyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished, 1989).

[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S43, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).

[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[7] NIOSH Research Report Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; S43 originally validated under NIOSH Contract No. 210-76-0123.

α-METHYLSTYRENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

$CH_3OC(CH_3)_3$ MW: 88.15 CAS: 1634-04-4 RTECS: KN5250000

METHOD: 1615, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA : No permissible exposure limit
NIOSH: No recommended exposure limit
ACGIH: No threshold limit value
(1 ppm = 3.6 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.74 g/mL @ 20 °C;
BP 55.2 °C; VP 32.6 kPa (245 mm Hg)
@ 25 °C

SYNONYMS: MTBE; 2-methoxy-2-methyl-propane.

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(two charcoal tubes in series; front 400 mg; back 200 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 2 L @ 10 ppm
-MAX: 96 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C, 3 weeks @ −7 °C (92% recovery) [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl tert-butyl ether (MTBE)

DESORPTION: 2 mL CS_2, 30 min

INJECTION VOLUME: 1 µL, split ratio 60:1

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: 0 °C for 7 min; 5 °C/min to 25 °C, and then 25 °C/min to 250 °C (hold 5 min)

CARRIER GAS: He, 1 to 2 mL/min

COLUMN: fused silica capillary, 50 m x 0.3-mm ID, 0.5-µm film of bonded dimethylsilicone gum (polydimethylsiloxane)

CALIBRATION: standard solutions of MTBE in CS_2

RANGE: 0.06 to >10 mg per sample [1]

ESTIMATED LOD: 0.02 mg per sample [1]

PRECISION ($\bar{S}_r$): 0.033 @ 9 µg to ~10 mg per sample [1]

APPLICABILITY: The working range is 0.2 to >35 ppm (0.75 to >125 mg/m^3) for an 80-L air sample. This method is designed for the determination of MTBE in gasoline and may be used for the determination of other components of gasoline.

INTERFERENCES: 2,3-Dimethylbutane may interfere if initial chromatographic temperatures are higher than 0 °C.

OTHER METHODS: This is a new method [1].

REAGENTS:

1. Methyl tert-butyl ether,* reagent grade.
2. Carbon disulfide,* reagent grade.
3. Calibration stock solution, 7.41 mg/mL. Dilute 40 μL methyl tert-butyl ether to 4.00 mL with carbon disulfide.
4. Helium, prepurified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.
7. Liquid nitrogen or carbon dioxide for subambient cooling of GC oven.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Two glass tubes in tandem, each 8 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing activated coconut shell charcoal held by plugs of silated glass wool (front tube = 400 mg, back tube = 200 mg). Pressure drop across tubes at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.1 to 0.2 L/min with flexible connecting tubing.
3. Gas chromatograph with sub-ambient cooling, flame ionization detector (page 1615-1).
4. Vials, 5-mL, 2-mL with PTFE-lined crimp caps.
5. Pipettes, TD, 4-, 2- and 1-mL.
6. Syringes, 1-mL, 250-, 100-, 25-, and 10-μL.

SPECIAL PRECAUTIONS: Methyl tert-butyl ether and carbon disulfide are extremely flammable (flash points -28 °C and -30 °C, respectively. Carbon disulfide is also toxic. Work with these compounds in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.1 to 0.2 L/min for a sample size of 2 to 96 L.
4. Separate the tubes, cap, and pack securely for shipment. Chilling of the samples is necessary if they are not expected to be analyzed within five days.

SAMPLE PREPARATION:

5. Add 2.0 mL carbon disulfide to 5-mL vials. Loosely cap vials.
6. Place front and back sorbent sections in separate vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least seven working standards.
   a. Prepare standards in capped vials by mixing various volumes (i.e., 5 to 230 μL) of calibration stock solution with carbon disulfide to a total volume of 4.00 mL to obtain concentrations in the range of 0.010 to 5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
9. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each level plus three media blanks.
   a. Use the 400-mg charcoal tube for DE determination. Hold charcoal in the tube by silanzied glass wool.
   b. Prepare three DE stock solutions by mixing 4, 40, and 160 μL of methyl tert-butyl ether and making up a total volume to 4.00 mL with carbon disulfide to produce corresponding concentrations of 0.741, 7.41 and 29.62 μg/μL.

c. Inject 24 μL of the 0.741 μg/μL stock solution, 7 and 19 μL of the 7.41 μg/μL solution, 7, 11, and 14 μL of the 29.62 μg/μL stock solution onto the tubes near the glass wool plug and draw clean air through the tubes at 0.1 L/min for 1 to 2 minutes.
d. Seal tube with plastic caps. Allow to stand overnight.
f. Prepare a graph of DE vs. mg of MTBE recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure the calibration curve and DE are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1615-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.
    NOTE 1: If the sample peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in the calculations.
    NOTE 2: The given conditions are recommendations for the determination of MTBE in gasoline. An initial temperature lower than 0 °C will produce better peak resolution but longer analysis time.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of MTBE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of MTBE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

A calibration curve in the concentration range 0.74 to 111 mg/mL MTBE in carbon disulfide indicated a linear correlation with a coefficient of 0.9998 and s_r of 3.3% [1]. Other calibration curves at lower concentrations, covering the recovery/stability range, i.e. 9.3 to 426 μg/mL MTBE in CS_2, indicated linear correlation coefficients >0.998. The LOD and LOQ values varied between 19 to 22 μg/mL and 36 to 73 μg/mL, respectively.

A six-level, 31-day storage stability study, conducted at −7 °C, in the range 17.8 to 415 μg MTBE in gasoline spiked on 400 mg charcoal tubes, indicated recoveries of 99.0 ± 4.3% for the first day, 93.2 ± 2.0% for the 17th day, 91.9 ± 7.1% after 23-day storage and 89.0 ± 5.2% after 31-day storage. A five-day room-temperature stability study at 415 μg MTBE in gasoline spiked in 400 mg charcoal tubes indicated a 100.0 ± 4.6% recovery.

Four charcoal tubes spiked with 415 μg MTBE in gasoline had air drawn for six hours at 100 mL/min and then were stored at −7 °C for five days indicating 103.6 ± 9.0% recovery. No sample loss occurred due to breakthrough at the 415-μg per sample MTBE level.

Charcoal tubes which were spiked with 10 mg MTBE in gasoline and which had 6 to 78 L of air drawn through them did not indicate any breakthrough of MTBE. Light hydrocarbons i.e. n-butane, and isopentane, which are not retained by the charcoal, did break through.

REFERENCES:

[1] Palassis, J., R.W. Hartle, and J.L. Holtz. Development of a Method for Determination of Methyl tert-Butyl Ether (MTBE) in Gasoline Vapors and Liquid Gasoline Samples, Appl. Occup. Environ. Hyg. 8(11):964-969 (1993).

METHOD WRITTEN BY:

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MINERAL SPIRITS

See NAPHTHAS (Method 1550) for procedure

MOLYBDENUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

MONOMETHYLANILINE 3511

$C_6H_5NH(CH_3)$ MW: 107.16 CAS: 100-61-8 RTECS: BY4550000

METHOD: 3511, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 2 ppm (skin)
NIOSH: 0.5 ppm (skin)
ACGIH: 0.5 ppm (skin)
(1 ppm = 4.38 mg/m^3 @ NTP)

PROPERTIES: liquid, discolors on standing; MP - 57 °C; BP 194 - 196 °C; d = 0.989 g/mL @ 20 °C; VP 40 Pa (0.3 mm Hg) @ 20 °C

SYNONYMS: N-methylaniline; N-methylbenzenamine

SAMPLING

SAMPLER: MIDGET BUBBLER (0.05 M sulfuric acid, 10 mL)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 11 L @ 2 ppm
-MAX: 100 L

SHIPMENT: take care to prevent spillage

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 4.38 to 17.52 mg/m^3 [1] (100-L samples)

BIAS: none [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089 [1]

ACCURACY: ± 26.38%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: monomethylaniline

EXTRACTION: neutralize with 1 mL 4M NaOH

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2, 50 mL/min

TEMPERATURE-INJECTOR: 245 °C
-DETECTOR: 275 °C
-COLUMN: 170 °C

COLUMN: 60/80 mesh Chromosorb 103, 2ft x 1/8"-O.D., with an Ascarite precolumn

CALIBRATION: standard solutions of monomethylaniline in sulfuric acid

RANGE: 0.1 to 3 mg per sample [1]

ESTIMATED LOD: 8 µg per sample

PRECISION ($\bar{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 0.2 to 7 ppm (1 to 30 mg/m^3) for a 100-L air sample. Using a nitrogen-specific detector instead of a FID will greatly increase sensitivity. This alternate detector has been used for amines with a 30-m x 0.25-mm x 0.25-µm film DB-5 (5% methyl, phenyl-50% dimethyl-polysiloxane) fused-silica capillary column with a liner packed with KOH-coated glass wool.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S153 [2].

REAGENTS:

1. Monomethylaniline*, ACS reagent grade.
2. Sulfuric acid, 0.05 M, ACS reagent grade.
3. Sodium hydroxide,* 4 M.
4. Calibration stock solution.

* See Special Precautions

EQUIPMENT:

1. Sampler: Midget bubbler containing 10 mL 0.05 M sulfuric acid.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible polyethylene or PTFE tubing.
3. pH paper or meter
4. Vials, glass, 20-mL with PTFE-lined caps.
5. Gas chromatograph with a flame ionization detector, recorder, integrator and column (page 3511-1).
6. Graduated cylinders, 10-mL
7. Syringes, 10- and 500-μL.
8. Volumetric flasks, 10-mL.
9. Pipets, 1- and 10-mL glass, delivery, with pipet bulb.

SPECIAL PRECAUTIONS: Monomethylaniline is toxic by inhalation, ingestion, and skin absorption [3,4]. Sodium hydroxide is corrosive to tissue. Wear gloves and work in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach outlet of impinger to the sampling pump. Place an empty bubbler or impinger in line behind the sampler to catch any splashover during sampling.
3. Sample 11 to 100 L of air at an accurately known flow rate in the range 0.2 to 1.0 L/min.
4. The temperature and pressure of the atmosphere being sampled should be recorded.
5. Transfer samples to 20 mL vial for shipping. Place in a suitable shipping container to prevent damage or spilling during transit.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Bring the volume of each sample to 10 mL with 0.05 M sulfuric acid.
8. Add 1 mL 4 M sodium hydroxide and mix thoroughly. The pH of the resulting solution should be greater than 10.
9. Analyze sample immediately to avoid loss of amine as the free base.

CALIBRATION AND QUALITY CONTROL:

10. Prepare at least six working standards (0 to 300 μg/ mL of monomethylaniline).
    a. Add appropriate aliquots of calibration stock solution to 0.05 M sulfuric acid. Follow neutralization procedure as in step 8.
    b. Analyze working standards together with samples and blanks (steps 13 through 15).
    c. Prepare a calibration graph of area vs. amount of monomethylaniline, μg per mL.
11. Determine recovery for each batch of sulfuric acid made up in the concentration range of interest. Prepare four 10 mL portions of sulfuric acid at each of five monomethylaniline levels plus three media blanks.
    a. Put a 10 mL portion of sulfuric acid in a 20-mL vial.
    b. Spike aliquot of calibration solution into 10 mL of 0.05 M sulfuric acid with a microliter syringe.
    c. Cap and let stand overnight.

d. Neutralize following step 8 and analyze along with working standards and blanks (steps 13 through 15).
e. Prepare graph of recovery vs. μg monamethylaniline.

12. Analyze three quality control spikes and three analyst spikes to ensure that calibration graph and recovery graph are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given page 3511-1.
14. Inject 5-μL sample aliquot.
    NOTE: If peak area is above the linear range of the working standards, dilute, reanalyze, and apply appropriate dilution factor in calculations.
15. Measure peak area.

CALCULATIONS:

16. Determine mass, μg (corrected for recovery), of monomethylaniline (W) found in the sample and the average media blank.
17. Calculate concentration of monomethylaniline in the air volume sampled V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 4.38 to 17.52 mg/m^3 using 100-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.089, with essentially 100% recovery, representing a non-significant bias. Sample stability during storage was evaluated at 791 μg n-methylaniline per sample. Samples showed 98.3% recovery after seven days of storage.

REFERENCES:

[1] Backup Data Report for n-methylaniline, Documentation of NIOSH Validation Tests. U.S. Department of Health, Education, and Welfare, (NIOSH) Publication 77-185 (April, 1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S153, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Hawley's Condensed Chemical Dictionary, 11th ed. Sax, N.I. and Lewis, R.J., Eds. Van Nostrand Reinhold Co., New York, NY (1987).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, US DHHS (NIOSH) Publ. 81-123 (1981).

METHOD REVISED BY:

Paula Fey O'Connor, NIOSH/DPSE.

CH_3NHNH_2 MW: 46.07 CAS: 60-34-4 RTECS: MV5600000

METHOD: 3510, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 0.2 ppm (skin)
NIOSH: C 0.04 ppm/120 min; carcinogen
ACGIH: C 0.2 ppm (skin; Suspect Carcinogen)
(1 ppm = 1.88 mg/m^3 @ NTP)

PROPERTIES: liquid; MP −52.4 °C; BP 87.5 °C; d 0.874 g/mL @ 25 °C; VP 6.6 kPa (49.6 mm Hg) @ 25 °C; vapor density (air = 1) 1.59; flammability limits in air 2.5 to 97% v/v

SYNONYMS: hydrazomethane; 1-methylhydrazine; methylhydrazine

SAMPLING

SAMPLER: BUBBLER
(0.1 M hydrochloric acid)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 3 L @ 0.2 ppm
-MAX: 20 L

SHIPMENT: remove bubbler stem and rinse with 0.1 M hydrochloric acid; seal bubblers with non-reactive stopper

SAMPLE STABILITY: at least five days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.17 to 0.78 mg/m^3 [1] (20-L samples)

BIAS: − 3.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.106 [1]

ACCURACY: ± 21.6%

MEASUREMENT

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: monomethylhydrazine phosphomolybdic acid complex

DILUTION: 7.5 mL of phosphomolybdic acid solution and 0.1 M hydrochloric acid to 25 mL

WAVELENGTH: 730 nm; 5-cm cell

CALIBRATION: standard solutions of monomethylhydrazine sulfate in 0.1 M hydrochloric acid

RANGE: 1 to 100 μg per sample [1]

ESTIMATED LOD: 0.7 μg per sample [2]

PRECISION ($\hat{S}_r$): 0.029 @ 3.9 to 16.0 μg per sample [1]

APPLICABILITY: The working range is 0.027 to 2.7 ppm (0.05 to 5 mg/m^3) for a 20-L air sample. This method is applicable to STEL and ceiling measurements.

INTERFERENCES: Other hydrazines, as well as stannous ion, ferrous ion, zinc, sulfur dioxide and hydrogen sulfide, may give a positive interference. Negative interference in the method may occur by oxidation of the monomethylhydrazine by halogens, oxygen(especially in the presence of copper (I) ions) and hydrogen dioxide.

OTHER METHODS: This revises Method S149 [2]. Method P&CAM 248 [3] describes an acid-coated silica gel sorbent tube/gas chromatographic method for the determination of hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine and phenylhydrazine, but sample stability problems have been noted with it [4].

REAGENTS:

1. Methylhydrazine sulfate*, ACS reagent grade.
2. Hydrochloric acid, ACS reagent grade.
3. Collection medium, 0.1 M hydrochloric acid. To 300 mL of distilled water in a 1000-mL volumetric flask, add 8.6 mL of concentrated hydrochloric acid with caution. Mix and bring to volume with distilled water.
4. Phosphomolybdic acid solution. Dissolve 15 g of phosphomolybdic acid in 500 mL distilled water, allow to stand one day, and filter before use through a fluted paper filter.
5. Water, deionized and distilled.
6. Calibration stock solution, 1 mg/mL. Weigh 100 mg of methylhydrazine sulfate in a 100-mL volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

* See Special Precautions

EQUIPMENT:

1. Sampler: 25-mL bubbler with 15 mL 0.1 M hydrochloric acid.
2. Personal sampling pump, 1.5 L/min, with flexible polyethylene or PTFE tubing.
3. Glass or non-reactive stopper for bubbler.
4. Glass tube, 5 cm long by 6-mm I.D., loosely packed with glass wool.
5. Spectrophotometer, set at 730 nm.
6. Spectrophotometer cells, 5-cm.
7. Test tube, large.
8. Volumetric flasks, 25-mL, 100-mL, 500-mL, 1000-mL.
9. Pipets, 10-, 15-, 25-, and 50-μL; 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 87 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

SPECIAL PRECAUTIONS: Monomethylhydrazine may be fatal if inhaled, swallowed or absorbed through skin contact [5,6]. Contact may cause burns to skin and eyes. Vapor may cause irritation to eyes, nose, throat, and skin. Handle with caution and use appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL 0.1 M hydrochloric acid to a bubbler.
3. Connect outlet arm of bubbler to the glass-wool-packed tube (to prevent splashover into the pump) and then to the sampling pump with the flexible tubing.
4. Sample at an accurately known rate between 0.5 and 1.5 L/min for a total air sample of 3 to 20 L.
5. Remove bubbler stem and rinse with 0.1 M hydrochloric acid into bubbler body. Seal bubbler with an inert stopper for shipment in a suitable container in order to prevent damage during transit.

SAMPLE PREPARATION:

6. Transfer the liquid from the bubbler, quantitatively, to a 25-mL volumetric flask.
7. Add 7.5 mL of phosphomolybdic acid solution and bring volume to 25 mL with 0.1 M hydrochloric acid.
8. Transfer an aliquot of this solution to a large test tube and heat to 87 °C for 50 min. Place test tube under running tap water to cool before measurement.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards over the range of 10 to 100 μg/25 mL.
   a. Add aliquots (10, 25, 50 and 100 μL) of calibration stock solution to 15 mL of 0.1 M hydrochloric acid in 25-mL volumetric flasks. Prepare a reagent blank using only 15 mL of

0.1 M hydrochloric acid.

b. Add 7.5 mL of phosphomolybdic acid solution to all standards and blank and bring the volume up to 25 mL with 0.1 M hydrochloric acid.
c. Transfer aliquots of these solutions to large test tubes and heat to 87 °C for 50 min.
d. Place test tubes under running tap water to cool before measurement.
e. Analyze working standards together with samples and reagent blanks (steps 10 through 12) on a spectrophotometer at 730 nm, using a 5-cm cell. Correct standards for reagent blank absorbance.
f. Prepare a calibration graph of absorbance vs. amount (μg) of monomethylhydrazine per sample.

MEASUREMENT:

10. Set spectrophotometer according to manufacturer's recommendations and to conditions on p. 3510-1 to monitor 730 nm.
11. Fill 5-cm sample cell with sample or standard.
12. Measure absorbance.

CALCULATIONS:

13. Determine mass, μg, of monomethylhydrazine found in the sample (W) and blank (B) from the calibration graph.
15. Calculate concentration of monomethylhydrazine in the actual air volume, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 0.17 to 0.78 mg/m^3 using 20-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.106. Collection efficiency of the bubblers was determined to be 96.5% at 1.7 mg/m^3 for a 20-L sample. Sample stability during storage was evaluated at 8 μg monomethylhydrazine per sample. Samples showed 104.4% recovery after five days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Monomethylhydrazine, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S149, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] L.R. Cook, R.E. Glenn and G.E. Podolak, Am. Ind. Hyg. Assoc. J., 40, 69-74 (1979).
[5] NIOSH Criteria for a Recommended Standard....Occupational Exposure to Hydrazines, DHEW (NIOSH) Publ. No. 78-122 (1978).
[6] NIOSH/OSHA Occupational Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

E.R. Kennedy, Ph.D., NIOSH/DPSE.

NAPHTHALENE

See POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC) (Method 5506)
or
POLYNUCLEAR AROMATIC HYDROCARBONS (GC) (Method 5515)
or
HYDROCARBONS, AROMATIC (Method 1501)
for procedures

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1550, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Petroleum ether (benzin), rubber solvent, petroleum naphtha, VM&P naphtha, mineral spirits, Stoddard solvent, kerosene (kerosine), coal tar naphtha.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1.3 L @ 400 mg/m^3; 0.2 L @ 2500 mg/m^3
-MAX: 20 L @ 400 mg/m^3; 3.2 L @ 2500 mg/m^3

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; 5 to 10 mL

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.05 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: naphtha hydrocarbons

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL (packed column); 0.1 to 1 µL (capillary column)

TEMPERATURE-INJECTION: 200 to 250 °C
-DETECTOR: 250 to 300 °C
-COLUMN: 50 to 250 °C @ 8 °/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 6-mm, 10% SP-2100 on Supelcoport 80/100 or 30-m fused silica capillary, 0.325-mm ID, 1.0-µm DB-1 or equivalent

CALIBRATION: solutions of bulk naphtha in CS_2

RANGE: 0.5 to 10 mg per sample [2,3,4]

ESTIMATED LOD: 0.1 mg per sample

PRECISION ($\bar{S}_r$): 0.01 [1]

APPLICABILITY: The working range is 100 to 2000 mg/m^3 for a 5-L air sample. This is a general procedure for analysis of various types of hydrocarbon mixtures called "naphthas" which are used as thinners in paints and varnishes and as general purpose solvents.

INTERFERENCES: Most naphthas are quite complex. The components elute over a wide temperature range by gas chromatography, making interferences from other substances possible. Columns and conditions must be chosen to obtain the desired degree of separation for a given mixture.

OTHER METHODS: This method combines and replaces Methods S86 [2], S380 [3] and S382 [4]. A similar method appears in the criteria document [5].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) octane, 0.5% (v/v) hexadecane or other suitable internal standard.
   NOTE 1: Use an internal standard which is not a major constituent of the sample.
   NOTE 2: Use toluene in place of carbon disulfide for low-boiling analytes [5].
2. Naphtha bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1550-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL (1-μL syringe for capillary columns) and other convenient sizes for preparing standards, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, delivery, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size which contains between 0.5 and 8 mg naphtha.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment. Ship a bulk sample (5 to 10 mL) in a separate container from the sorbent tubes.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 10 mg naphtha per sample.
   a. Add known amounts of naphtha bulk sample to eluent in 10-mL volumetric flasks and dilute to the mark.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg naphtha).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of naphtha bulk sample directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg naphtha recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1550-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The columns and conditions given provide moderate to good separation of components. If less resolution is needed, use shorter, less efficient columns as were used in validation of Methods S86 [2], S380 [3] and S382 [4].
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of naphtha found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of naphtha in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S86 (Naphtha, Coal Tar), S380 (Petroleum distillate) and S382 (Stoddard Solvent) were issued on March 14, 1975 [2,3,4]. They were validated at 24 °C and approximately 755 mm Hg using 10-, 4- and 3-L air samples, respectively, of 2-50-W Hi-Flash Solvent (Neville Chemical Co.; BP 154 to 195 °C; d 0.893 g/mL), VM&P Naphtha (Amsco Product 1101; BP 120 to 147 °C; d 0.743 g/mL) and Stoddard Solvent (Fisher Scientific Co.; BP 159 to 176 °C; d 0.774 g/mL) [1]. Overall precision and recovery were as shown below, representing a non-significant bias in each method. Breakthrough tests in dry air showed a capacity of 20 to 25 mg of each solvent tested. Capacity at high relative humidity was not determined.

Method	Overall Precision ($\hat{S}_{rT}$)	Bias	Range Studied Accuracy	mg/m^3	mg per sample	Avg. DE	Ref.
S86[b]	0.051	5.99%	±15.0%	193 to 809	2 to 8	0.88	[1,2]
S380[a]	0.052	−4.37%	±12.5%	937 to 3930	4 to 16	0.96	[1,3]
S382[b]	0.052	−3.10%	±11.4%	1417 to 5940	4.5 to 18	0.95	[1,4]

NOTES: (a) Data based on experiments using an internal standard method with a 10 ft., 1/8" stainless steel column packed with 10% OV-101 on 100/120 mesh Supelcoport.
(b) Data based on experiments using an internal standard method with a 6 ft., 1/8" stainless steel column packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S86, S380, S382, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, Method S86, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Ibid, V. 3, S380, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, S382.
[5] Criteria for a Recommended Standard...Occupational Exposure to Refined Petroleum Solvents, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-192 (July, 1977).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S86, S380 and S382 originally validated under NIOSH Contract CDC-99-74-55.

Table 1. General information.

NAME CAS # RETECS	Boiling Range (°C)	Vapor Pressure, kPa (mm Hg) @ 20 °C	Liquid Density (g/mL @ 15 °C)	Predominant Hydrocarbon Species	Exposure Limits, mg/m³ OSHA NIOSH ACGIH
Petroleum ether (a) 8032-32-4 OI6180000	30 to 60	13 (100) (13 °C)	0.63 to 0.66	C_5-C_6 aliphatic	-- 350; C 1800 --
Rubber solvent (a) SE7449000 8030-30-6	45 to 125	(c)	0.67 to 0.85	C_5-C_8 aliphatic	2000 (500 ppm) 350; C 1800 1590 (400 ppm)
Petroleum naphtha (b) (Petroleum distillates mixture) 8002-05-9 SE7449000	30 to 238	5 (40)	0.6 to 0.8	C_6-C_8	2000 (500 ppm) 350; C 1800 --
VM&P naphtha (a) 8032-32-4 OI6180000	95 to 160	0.3 to 3 (2 to 20)	0.72 to 0.76	C_7-C_{11} <20% aromatic	-- 350, C 1800 1370 (300 ppm)
Mineral spirits (a) 8052-41-3 WJ89250000	150 to 200	0.2758(2)	0.77 to 0.81	C_9-C_{12} <20% aromatic	2900 (500 ppm) 350; C 1800 525 (100 ppm)
Stoddard solvent (a) 8052-41-3 WJ8925000	150 to 210	0.2758 (2)	0.75 to 0.80	C_9-C_{12} <20% aromatic	2900 (500 ppm) 350; C 1800 525 (100 ppm)
Kerosene (a) 8008-20-6 OA5500000	175 to 325	(c)	0.8	C_9-C_{16} <20% aromatic	-- 100 --
Coal tar naphtha (b) 8030-30-6 DE3030000 (NIOSH)	110 to 190	<0.7 (<5)	0.86 to 0.89	C_8-C_{10} aromatic	400 (100 ppm) 400 (100 ppm) --

(a) As defined by NIOSH Criteria Document [5].
(b) As defined for OSHA PEL.
(c) Not available.

$C_{10}H_7NH_2$ MW: 143.19 CAS: (1) 134-32-7 (2) 91-59-8 RTECS: (1) QM1400000 (2) QM2100000

METHOD: 5518, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987** **Issue 2: 15 August 1994**

OSHA : (1) carcinogen (29 CFR 1910.1004)
(2) carcinogen (29 CFR 1910.1009)
NIOSH: same as OSHA
ACGIH: (1) no TLV
(2) human carcinogen

PROPERTIES: (1) solid; MP 50 °C; VP 0.53 Pa (0.004 mm Hg); 31 mg/m^3) @ 20 °C;
(2) solid; MP 113 °C; VP 0.48 Pa (0.0036 mm Hg; 27 mg/m^3) @ 20 °C

SYNONYMS: (1): 1-naphthylamine; alpha-naphthylamine; 1-aminonaphthalene.
(2): 2-naphthylamine; beta-naphthylamine; 2-aminonaphthalene.

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (glass fiber + silica gel, 100 mg/50 mg)

FLOW RATE: 0.2 to 0.8 L/min

VOL-MIN: 30 L @ 0.5 μg/m^3
-MAX: 100 L

SHIPMENT: dry ice

SAMPLE STABILITY: 82 to 100% after 22 days at −15 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 4 to 70 μg/m^3 [1] (50-L samples)

BIAS: not determined [1]

OVERALL PRECISION ($\hat{S}_{rT}$): ≤ 0.10 [1]

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: α- and β-naphthylamines

DESORPTION: 0.05% (v/v) acetic acid in 2-propanol, 0.5 mL

INJECTION VOLUME: 1 μL

TEMPERATURE-INJECTOR: 190 °C
-DETECTOR: 165 °C
-COLUMN: 163 °C

CARRIER GAS: He, 24 mL/min

COLUMN: glass, 1.8 m x 2-mm ID, packed with 3% OV-225 on Chromosorb WHP

CALIBRATION: standard solution of analytes in 0.05% (v/v) acetic acid in 2-propanol

RANGE: 0.15 to 3.5 μg per sample

ESTIMATED LOD: 0.01 μg per sample [2]

PRECISION ($\bar{S}_r$): (1) 0.08 @ 0.3 μg per sample [2]
(2) 0.09 [2]

APPLICABILITY: The working range is 0.003 to 0.07 mg/m^3 (0.0005 to 0.01 ppm) for a 50-L air sample.

INTERFERENCES: The retention time of 1-nitronaphthalene is between those of the analytes and interferes with their determination. Column alternative: 10% Carbowax, 20 M, 4% KOH.

OTHER METHODS: This revises P&CAM 264 [2].

REAGENTS:

1. α-Naphthylamine and β-naphthylamine.*
2. 2-Propanol.
3. Acetic acid, glacial.
4. Eluent, 0.05% (v/v) acetic acid in 2-propanol.
5. Calibration stock solution, 500 μg/mL.* Weigh 5 mg of each analyte into a 10-mL volumetric flask. Dilute to volume with eluent. Prepare in duplicate. Stable one month if refrigerated.
6. Hydrogen, purified.
7. Helium, purified.
8. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler (Fig. 1): high-efficiency glass fiber filter (Gelman Spectrograde or equivalent), 13-mm diameter, followed by 100 mg and 50 mg beds of 20/45 mesh silica gel. Tubes are commercially available.
   NOTE: Some other glass fiber filters contained an impurity with the same GC retention time as α-naphthylamine [1].
2. Personal sampling pump, 0.2 to 0.8 L/min, with flexible connecting tubing.
3. Insulated container, with dry ice.
4. Gas chromatograph, FID and column (page 5518-1).
5. Test tubes, 1-mL, with polyethylene stoppers.
6. Syringes, glass, 5- and 10-μL, readable to 0.1 μL.
7. Pipet, TD, 0.5-mL.
8. Volumetric flasks, low actinic, 10-mL.
9. Centrifuge.
10. Balance, analytical.
11. Test tube shaker, vortex type.

SPECIAL PRECAUTIONS: The naphthylamines are recognized human bladder carcinogens [3, 4]. Avoid all contact with them. Use a glove box for preparation of standard solutions. Dispose of all unneeded solutions in accordance with accepted procedures for carcinogens.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.8 L/min for a total sample size of 30 to 100 L.
4. Cap the samplers. Pack securely for shipment in dry ice.

SAMPLE PREPARATION:

5. Bring samples to room temperature.
6. Place glass fiber filter and 100-mg section of silica gel in a test tube. Place the 50-mg section of silica gel in a separate test tube. Desorb PTFE rings and stainless steel screens with the appropriate stages. Discard sampler caps.
7. Add 0.5 mL eluent to each vial. Cap each test tube and mix with test tube shaker.
8. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.

a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain analyte concentrations in the range 0.02 to 7 μg/mL.
b. Analyze with samples and blanks (steps 12 and 13).
c. Prepare calibration graph (peak area vs. μg analyte).

10. Determine desorption efficiency (DE) at least once for each lot of filters and sorbent used for sampling in the range of interest. Prepare three samplers at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject separate known amounts (2 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto filter and front sorbent section with a microliter syringe.
    c. Cap the sampler. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze with working standards (steps 12 and 13).
    e. Prepare graphs for filter and sorbent (DE vs. μg analytes recovered).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5518-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: For the conditions given, t_r = 6 min for α-naphthylamine and 7 min for β-naphthylamine.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of analyte found on the sample filter (W_f) and sample sorbent (W_s) and on the media blank filter (B_f) and media blank silica gel (B_s) from the calibration graph.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{W_f + W_s - B_f - B_s}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 264 was issued on August 1, 1978 [2], and evaluated with generated atmospheres containing mixtures of the two analytes produced by controlled vapor diffusion [1]. Capacity of the 100-mg front sorbent section at breakthrough (effluent = 5% of test concentration) was approximately 5 μg of α-naphthylamine and 7.5 μg β-naphthylamine at 80% RH with a sampling range of 0.8 L/min in atmospheres containing approximately 80 μg/m^3 of the analytes. Breakthrough capacity was found to be strongly influenced by relative humidity, being reduced by 50% at 95% RH compared to the values found at 80% RH.

In storage tests, quantitative recovery was obtained for 0.5-μg masses of α-naphthylamine on silica gel and filters if stored at −15 °C for up to seven days; recovery for samples stored 14 or 21 days at -15 °C was 81 to 82% for filters and 94% for silica gel. For β-napthylamine under the same conditions,

similar recoveries were observed, except that recovery from filters was quantitative at −15 °C when stored 14 or 21 days. Recovery after storage at room temperature (23 °C) for 8 days was in the range 24 to 73%.

REFERENCES:

[1] Morales, R., S. M. Rappaport, R. W. Weeks, Jr., E. E. Campbell, and H. J. Ettinger, Development of Sampling and Analytical Methods for Carcinogens, Los Alamos Scientific Laboratory, Progress Report LA-7058-PR (January 1, 1976 to September 30, 1976), NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 264, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-185 (1978).

[3] 1993-1994 Threshold Limit Values and Biological Exposure Indices, ACGIH, Cincinnati, OH 45211 (1993).

[4] NIOSH Recommendations for Occupational Safety and Health, U.S. Department of Health and Human Services (NIOSH) Publ. 92-100 (January, 1992).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

NICKEL

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

NICKEL CARBONYL 6007

$Ni(CO)_4$ MW: 170.73 CAS: 13463-39-3 RTECS: QR6300000

METHOD: 6007, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.001 ppm (as Ni)
NIOSH: 0.001 ppm; carcinogen
ACGIH: 0.05 ppm (as Ni)
(1 ppm = 6.98 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.318 g/mL @ 20 °C; BP 43 °C; MP −25 °C; VP 43 kPa (321 mm Hg; 42% v/v) @ 20 °C; lower explosive limit 2% v/v in air

SYNONYMS: nickel tetracarbonyl

SAMPLING

SAMPLER: PREFILTER + SOLID SORBENT TUBE (low-Ni charcoal, 120 mg/60 mg; 0.8-μm cellulose ester membrane)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 7 L @ 0.001 ppm
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: 95% recovered after 17 days @ room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.0007 to 0.017 ppm [1] (3- to 40-L air samples)
BIAS:	− 7% [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.099 [1]
ACCURACY:	± 26.4%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: nickel

DESORPTION: 1 mL 3% HNO_3; 30 min ultrasonic bath

INJECTION VOLUME: 20 μL

GRAPHITE FURNACE: 110 °C dry 30 sec; 800 °C char 15 sec; ≥ 2700 °C atomize 10 sec

WAVELENGTH: 232 nm, with background correction

CALIBRATION: standard solution of Ni^{2+} in 3% (w/v) HNO_3

RANGE: 0.05 to 0.6 μg Ni per sample [1]

ESTIMATED LOD: 0.01 μg Ni per sample [1]

PRECISION ($\bar{S}_r$): 0.028 @ 0.08 to 0.5 μg Ni per sample

APPLICABILITY: The working range is 0.00036 to 0.007 ppm (0.0025 to 0.05 mg/m^3) nickel carbonyl for a 20-L air sample.

INTERFERENCES: Particulate nickel compounds will give a positive interference unless a prefilter is used during sampling.

OTHER METHODS: This revises P&CAM 344 [2]. A colorimetric method has also been recommended [3].

REAGENTS:

1. Water, double-distilled (or deionized).
2. Nitric acid, 70% (w/v) HNO_3, redistilled in glass.
3. Nitric acid, 3% (w/v) HNO_3. Add 31 mL 70% HNO_3 to distilled water. Dilute to 1 L.
4. Nickel stock solution, 1000 μg Ni/mL. Dissolve 1.000 g pure Ni metal in minimum volume 70% HNO_3. Dilute to 1 L with 3% HNO_3. Commercially available.
5. Calibration stock solution, 50 μg Ni/mL. Dilute 0.500 mL nickel stock solution (1000 μg/mL) to 10 mL in a volumetric flask with 3% HNO_3. Store in a polyethylene bottle. Prepare fresh weekly.
6. Argon, high-purity purge gas in cylinder with a two-stage regulator.
   NOTE: Nitrogen cannot be used as purge gas because of the formation of UV-absorbing cyanogen.
7. Charcoal, acid-washed, activated. Acid-wash a sufficient quantity of coconut-based charcoal having an initial blank value of less than 0.02 μg Ni/200 mg, by soaking overnight in 3% nitric acid. Rinse several times with distilled water. Pour off excess water, cover with a watchglass, and activate by heating at 600 °C for 1.5 hrs in still air.

EQUIPMENT:

1. Sampler:
   a. Prefilter: 37-mm, 0.8-μm cellulose ester filter and cellulose backup pad in a plastic filter holder.
   b. Glass tube, 8 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh acid-washed activated (600 °C) coconut shell charcoal (front = 120 mg; back = 60 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: The prefilter must be used when particulate nickel is present in the air to be sampled. Connect prefilter to sorbent tube with a short section of plastic tubing.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. File, triangular.
4. Atomic absorption spectrophotometer equipped with:
   a. Heated graphite atomizing rod, tube or furnace (either non-pyrolitic or pyrolitic; better sensitivity with pyrolitic).
   NOTE: Reproducible control of times and temperatures during dry, char, and atomize cycles is essential; minimum atomization temperature 2700 °C.
   b. Readout device (recorder or digital peak height or peak area analyzer).
   c. Pipetting system (automatic or manual, 5- to 50-μL, as appropriate to atomizer size).
   d. Background correction, e.g., D_2 or H_2 lamp or non-absorbing line (231.5 nm for the 232 nm Ni line).
   e. Hollow cathode lamp for nickel.
5. Vials, 2-mL, with plastic-lined screw caps.*
6. Pipet, TD, 1-mL.*
7. Ultrasonic water bath.
8. Volumetric flasks, 10-mL and 1-L.*
9. Bottles, polyethylene, 20-mL.
10. Syringe, 25-μL, readable to 0.1 μL.

*Soak new glassware 1 h in hot, conc. nitric acid followed by thorough rinsing with distilled water. After each use, wash glassware with, in order, detergent solution, tap water, 3% nitric acid (soak $\geq$4 h) and distilled water.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach prefilter. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 7 to 80 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs. Discard prefilter or analyze for particulate Ni.
6. Add 1.0 mL 3% HNO_3 to each vial. Cap each vial.
7. Allow to stand 30 min in an ultrasonic water bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 3% HNO_3 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain Ni^{2+} concentrations in the range 0.01 to 0.6 μg/mL. Store in polyethylene bottles and prepare fresh daily.
   b. Analyze with samples and blanks (steps 11 through 13).
   c. Prepare calibration graph (absorbance vs. μg Ni^{2+}).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 through 13).
   e. Prepare a graph of DE vs. μg Ni^{2+} recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations, conditions given on page 6007-1, and the following:
    a. Inert gas flow: increased sensitivity if flow is interrupted during atomization.
    b. Wavelength: either 232 nm (more sensitive) or 341.5 nm.
    c. Dry cycle: 30 sec at 110 °C; longer time and ramp program may be needed for aliquots >20 μL.
    d. Ash (char) cycle: 15 sec at 800 °C.
    e. Atomize cycle: 10 sec at 2700 to 3000 °C; atomization is too slow for reproducible results below 2600 °C; "maximum power" feature will increase sensitivity.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak height. Analyze a series of standards before and after each set of samples and analyze one mid-range standard after each ten samples. Analyze all solutions, including sorbent tube blanks and reagent blanks, in triplicate.

    NOTE 1: Peak occurs about 3 sec after start of atomize cycle.

NOTE 2: If peak height is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with 3% HNO_3, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of Ni found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of nickel carbonyl in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.91}{V}, \text{ mg/m}^3.$$

where: 2.91 = stoichiometric conversion factor from Ni to $Ni(CO)_4$.

EVALUATION OF METHOD:

Method P&CAM 344 was issued on August 31, 1981 [2], and evaluated with generated atmospheres of $Ni(CO)_4$ containing 6 to 300 ppm added carbon monoxide. Mean recovery was 93% (24 samples) in the range 5 to 121 $\mu g/m^3$ (0.0007 to 0.017 ppm). Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.475 L/min from an atmosphere containing 34 $\mu g/m^3$ (0.005 ppm) $Ni(CO)_4$ in air at 22 °C and 19% RH. Desorption efficiency for eighteen samples containing 0.08 to 0.5 μg Ni (nickel nitrate standard solution added to 120 mg charcoal) averaged 0.934 with S_r = 0.029. Nickel carbonyl was observed to pass quantitatively through 0.8-μm cellulose ester membrane filters in these experiments.

REFERENCES:

[1] Eller, P. M. "Determination of Nickel Carbonyl by Charcoal Tube Collection and Furnace Atomic Absorption," Appl. Ind. Hyg. 1:115-118 (1986).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 344, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).
[3] Special Occupational Hazard Review and Control Recommendations for Nickel Carbonyl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-184 (1977).

METHOD WRITTEN BY:

Peter M. Eller, Ph.D., NIOSH/DPSE.

NICOTINE 2544

$C_{10}H_{14}N_2$ MW: 162.26 CAS: 54-11-5 RTECS: QS5250000

METHOD: 2544, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: liquid, BP 245.5 °C; density 1.009 g/mL (20 °C)

SYNONYMS: 3-(1-methyl-2-pyrrolidinyl) pyridine

SAMPLING

SAMPLER: SOLID SORBENT TUBE XAD-2 (100 mg/50 mg)

FLOW RATE: 1.0 L/min

VOL-MIN: 60 L @ 0.5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.3 to 1.2 mg/m^3 [1] (100-L samples)

BIAS: not determined [2]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [2]

ACCURACY: ±12%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY-NITROGEN PHOSPHOROUS DETECTOR

ANALYTE: nicotine

DESORPTION: 1 mL ethyl acetate, stand 30 min

INJECTION VOLUME: 2.0 µL

TEMPERATURE-INJECTION: 235 °C
-DETECTOR: 260 °C
-COLUMN: 165 °C

CARRIER GASES: He, 25 mL/min; fuel, H_2

COLUMN: glass, 2 m x 2-mm ID, packed with 3% OV-101 on 100/120 mesh Supelcoport

CALIBRATION: solutions of nicotine in ethyl acetate

RANGE: 0.03 - 0.13 mg per sample

ESTIMATED LOD: not determined [2]

PRECISION ($\bar{S}_r$): 0.015 [1]

APPLICABILITY: The working range is 0.3 to 2 mg/m^3 for a 100-L air sample. The probable useful range of this method is likely to extend to lower concentrations than the analytical range specified above. Desorption efficiency must be determined over the range evaluated.

INTERFERENCES: None identified.

OTHER METHODS: This is method S293 [2] in a revised format.

REAGENTS:

1. Nicotine, reagent grade.*
2. Ethyl acetate, chromatographic quality.
3. Calibration solution, 5 mg/mL:
   Add 5 mg (5 μL) of nicotine to a 1.0 mL volumetric flask. Dilute to the mark with ethyl acetate.
4. Nitrogen, purified.
5. Hydrogen, pre-purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass tube, 7 cm long, 6-mm OD, 4-mm ID; two sections of 20/50 mesh pre-extracted XAD-2 (front = 100 mg, back = 50 mg separated by a plug of silylated glass wool and held in place with plugs of silylated glass wool, flame-sealed with plastic caps. The pressure drop across the tube should be 0.133 kPa at $\leq$1.0 L/min. Tubes are commercially available.
2. Personal sampling pump, 1.0 L/min with flexible connecting tubing.
3. Gas chromatograph, NPD, integrator, and column (p-2544-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-μL and 25-μL, readable to 0.1 μL.
6. Volumetric flasks, 1.0-mL.
7. Pipets, delivery-type, 1.0-mL.
8. File.

SPECIAL PRECAUTIONS: Nicotine is a vasoconstrictor. Perform all work with these chemicals in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Before sampling, score the ends of each sampling tube with a file, and break open. Attach the sampler to personal sampling pump with flexible tubing.
3. Sample at 1.0 L/min to obtain the recommended sample volume of 60 to 400 L.
4. Cap the tubes with plastic (not rubber) caps immediately following sampling and pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the front (larger) section of XAD-2 with glass wool plug to a 2-mL vial. Transfer the backup sorbent section along with the separating section of glass wool to another vial. Discard the back glass wool plug.
6. Pipet 1.0 mL of ethyl acetate into each vial. Seal the vials with a teflon-lined crimp-cap.
7. Allow to stand 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the analytical range 0.005 to 0.13 mg nicotine per sample.
   a. Add 1 to 25 μL or other convenient aliquots of the calibration solution to 1.0 mL of ethyl acetate in separate vials. Correct the volume of ethyl acetate in each vial to account for volume of the aliquot of calibration solution added. Seal the vials with septum-lined crimp-caps.
   b. Analyze the standards together with the samples (steps 11 through 13).
   c. Prepare a calibration graph of peak area vs. mg of analyte.

9. Determine the Desorption Efficiency (DE) at least once for each batch of sorbent used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of the media blank sampler.
   b. Inject a known amount of calibration solution directly onto the front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight at ambient temperatures prior to analysis.
   d. Transfer to a sample vial and desorb (steps 5 through 7) and analyze together with the working standards (steps 11 through 13).
   e. Plot DE vs. mg of nicotine recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and the DE graph are in control.

MEASUREMENT:

11. Set the gas chromatograph to conditions given on page 2544-1. Follow manufacturer's directions for the air/fuel (H_2) mixture for the NPD.
12. Inject a 2-μL sample aliquot, using the solvent-flush technique or with autosampler. Make duplicate injections of samples and standards.
    NOTE: If the peak area is above the linear range of working standards, dilute an aliquot of the sample solution with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure the peak area.

CALCULATIONS:

16. Determine the mass (mg) of nicotine (corrected for DE) found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b \geq W_f/10$, report breakthrough and possible sample loss.
17. Calculate the concentration of nicotine in the actual air volume V (L) at the sampling site:

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S293 [2] was issued 3/26/76. Synthetic atmospheres of the analyte in dry air were generated dynamically at 22.1 to 24.5 °C and 765.4 to 767.9 torr (102 to 102.4 kPa) over the range 0.3 to 1.2 mg/m^3. The analyte was metered into dry dilution air using a calibrated syringe pump; however, there was no independent measure of analyte concentration. Collected samples were stored five days prior to analysis. A 100-mg bed of the sorbent retained at least 0.2 mg of the analyte without breakthrough to the backup section, when 200 L of a challenge atmosphere containing 1.2 mg/m^3 of analyte in dry air was sampled at 1.1 L/min. There were no statistically significant differences at the 95% confidence level in the recoveries of samples that had been spiked with 0.03 to 0.13 mg of nicotine, and stored for 1 or 5-days prior to analysis. The method was originally validated using an alkali-flame ionization detector. Owing to the high variability in the response of this detector, it was necessary to use an internal standard - diphenylamine; this may not be necessary when using an NPD. The method has not been field tested.

REFERENCES:

[1] Backup Data Report No. S-293, Nicotine. Documentation of the NIOSH Validation Tests, Department of Health, Education, and Welfare (NIOSH) Publication No. 77-185 (1977). Prepared for NIOSH under Contract #CDC-99-74-45.

[2] NIOSH Manual of Analytical Methods, 2nd Edition, Vol. 3, Method S293 DHHS (NIOSH) Publication 77-157-C (April 1977).

METHOD REVISED BY:

Robert Glaser, NIOSH/DPSE. Originally prepared under Contract # CDC-99-74-45.

NITRIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure

NITRIC OXIDE and NITROGEN DIOXIDE 6014

NO	MW: 30.01	CAS: 10102-43-9	RTECS: QX0525000
NO_2	46.01	10102-44-0	QW9800000

METHOD: 6014, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 25 ppm NO; C 1 ppm NO_2
NIOSH: 25 ppm NO; 1 ppm STEL NO_2
ACGIH: 25 ppm NO; 3 ppm TWA, 5 ppm STEL NO_2
(1 ppm NO = 1.227 mg/m^3 @ NTP)
(1 ppm NO_2 = 1.882 mg/m^3 @ NTP)

PROPERTIES: NO: gas; BP −151.7 °C; vapor density (air=1) 1.0
NO_2: gas; MP −11.2 °C; BP 21 °C; vapor density (air=1) 2.83

SYNONYMS: NO: nitrogen monoxide
NO_2: nitrogen peroxide; nitrogen tetroxide

SAMPLING

SAMPLER: SORBENT TUBE (oxidizer + triethanolamine-treated molecular sieve)

FLOW RATE: NO: 0.025 L/min
NO_2: 0.025 - 0.2 L/min

VOL-MIN: 1.5 L
-MAX: 6 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 7 days @ 25 °C [1,2]

BLANKS: 3 to 6 field blanks and 10 media blanks per set

ACCURACY

RANGE STUDIED: NO: 11-48 ppm [1]; NO_2: 2-12 ppm [2]
(1.5-L samples) (3-L samples)

BIAS: NO: 4.1% [1]; NO_2: -2% [2]

OVERALL PRECISION ($\hat{S}_{rT}$): NO:0.083 [1]; NO_2:0.063 [2]

ACCURACY: NO: ± 20.4%;
NO_2: ± 14.6%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: nitrite ion, NO_2^-

EXTRACTION SOLUTION: absorbing solution, 50 mL

WAVELENGTH: 540 nm

CALIBRATION: standard solutions of NO_2^-

RANGE: 3 to 18 μg NO_2^- per sample [1]

ESTIMATED LOD: 1 μg NO_2^- per sample [3]

PRECISION ($\bar{S}_r$): NO: 0.061 [1]; NO_2: 0.026 [2]

APPLICABILITY: The working range for NO is 1 to 50 ppm (1.3 to 61 mg/m^3) for a 1.5-L air sample. The working range for NO_2 is 0.5 to 25 ppm (1 to 47 mg/m^3) for a 3-L air sample. The lower sampling rate for NO is to allow collection of oxidized NO on the back sorbent section. At the lower rate, both NO and NO_2 may be determined simultaneously.

INTERFERENCES: Any compound that reacts with the colorimetric reagents will interfere.

OTHER METHODS: This method is based on that of Willey, et al. [4] and combines S321, S320, and P&CAM 231 in a revised format [3,5]. OSHA methods ID-182 and ID-190 use the same sampler, with measurement by ion chomatography [6].

REAGENTS:

1. Triethanolamine, TEA, reagent grade.
2. n-Butanol, reagent grade.
3. Phosphoric acid, H_3PO_4, conc., reagent grade.*
4. N-(1-naphthyl) ethylenediamine dihydrochloride, NEDA.
5. Sodium nitrite, $NaNO_2$.
6. Absorbing solution: Dissolve 15.0 g triethanolamine in ca. 500 mL deionized water, add 0.5 mL n-butanol, and dilute to 1 L.
7. H_2O_2 solution, 0.02% (v/v): Dilute 0.2 mL of 30% H_2O_2 to 250 mL with deionized water.
8. Sulfanilamide solution: Dissolve 10 g sulfanilamide in 400 mL deionized water, add 25 mL conc. H_3PO_4, and dilute to 500 mL.
9. NEDA solution: Dissolve 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride in 500 mL deionized water.
10. Calibration stock solution, 100 μg NO_2^-/mL: Dissolve 0.1500 g $NaNO_2$ in 1 L deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Three glass tubes, 7-mm OD, flame-sealed ends with plastic caps, with glass wool retainers:
   Tube A: 400 mg TEA-coated molecular sieve (type 13x, 30-40 mesh).
   Tube B: 800 mg oxidizer (chromate) to convert NO to NO_2.
   Tube C: Same as tube A.
   Connect the tubes in series with flexible tubing. Position Tube C closest to the inlet of the sampling pump. Tubes are commercially available (SKC-226-40, or equivalent).
2. Personal sampling pump, 0.025 to 0.2 L/min, with flexible connecting tubing.
3. Spectrophotometer, UV-visible (540 nm), with cuvettes, 1-cm silica cuvettes.
4. Beakers, borosilicate, 100-mL.
5. Volumetric flasks, 50-mL and other convenient sizes.
6. Pipets, 1-, 5-, 10-mL and other convenient sizes.
7. Stopwatch.

SPECIAL PRECAUTIONS: Concentrated acid is corrosive to the skin and mucous membranes. Handle it only in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler and attach to pump.
   NOTE: Nitrogen dioxide collects on the first tube (Tube A), and is thereby separated from nitric oxide, which is oxidized by Tube B and then is collected on Tube C (adjacent to the sampling pump.)
3. Sample at an accurately known flow rate of 0.025 L/min ± 5%.
   NOTE: If nitric oxide is not to be determined, a flow rate of up to 0.2 L/min may be used.
4. Cap the sampler and pack securely for shipment. Submit adequate numbers of field blanks and media blanks to the laboratory.

SAMPLE PREPARATION:

5. Transfer the sorbent from Tube A and Tube C to separate 50-mL volumetric flasks. Discard glass wool plugs and oxidizer (Tube B).
6. Add absorbing solution to sample in 50-mL volumetric and bring to the mark.
7. Stopper flask and shake vigorously for 30 sec. Allow solids to settle.
8. Pipet 10 mL of extracted sample into a 50-mL volumetric flask.
   NOTE: Start reagent blanks at this step.
9. Add 1.0 mL hydrogen peroxide solution, 10.0 mL sulfanilamide solution, and 1.4 mL NEDA solution. Mix thoroughly after each addition.
10. Allow 10 min for complete color development.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards to cover the range of 1 to 18 μg nitrite ion per 10-mL sample.
    a. Analyze the working standards together with blanks and samples (steps 8 through 10 and steps 12 through 14).
    b. Prepare a calibration graph [absorbance vs. μg NO_2^- per sample].

MEASUREMENT:

12. Set wavelength on the spectrophotometer to 540 nm.
13. Set to zero with reagent blank.
14. Transfer some of the sample solution from step 10 to a cuvette and record the absorbance.

CALCULATIONS:

15. From the calibration graph, determine the mass of NO_2^- in each Tube A, W_A (μg), and in the corresponding average blank, B_A (μg). Similarly, determine the mass of NO_2^- in each Tube C, W_C (μg) and average blank, B_C (μg).
16. Calculate the concentration, C_{NO} (mg/m^3), of NO in the air volume sampled, V (L), applying the factor 0.652 (MW NO/MW NO_2^-) and the conversion factor 0.63 (see NOTE at step 17):

$$C_{NO} = \frac{(W_A - B_A) \cdot 0.652}{0.63\ V}, \text{ mg/m}^3.$$

17. Calculate the concentration, C_{NO2} (mg/m^3) of NO_2 in the sample:

$$C_{NO_2} = \frac{(W_C - B_C) \cdot 0.652}{0.63\ V}, \text{ mg/m}^3.$$

NOTE: The conversion factor represents the number of moles of nitrite ion produced by 1 mole of nitrogen dioxide gas. For NO or NO_2, gas concentrations above 10 ppm, use 0.5 as the conversion factor [7].

EVALUATION OF METHOD:

Method S321, Nitric Oxide, was evaluated over the range of 11.1 to 47.7 ppm (13.8 to 58.5 mg/m^3) for 1.5-L samples, collected from dynamically generated test atmospheres [1,8]. The test concentration was verified with a direct reading instrument, Energetic Sciences Enolyzer. The 1.2 g oxidizer section was found adequate for a 60-min sampling time. NO samples had a mean recovery of 99.5% after 7 days storage at ambient temperature.

Method S320, Nitrogen Dioxide, was evaluated over the range 3.0 - 11.6 ppm (5.8 to 21.6 mg/m^3) using 3/9-L samples [2,7]. When an atmosphere at 84% RH containing 11.59 ppm NO_2 was sampled at 0.064 L/min, 1.0% breakthrough occurred after 60 min and 2.4% breakthrough occurred after 180 min. Quantitative recovery was obtained for samples containing 47 μg NO_2 which were stored for 12 days at ambient conditions.

REFERENCES:

[1] Backup Data Report for Nitric Oxide, S321, prepared under NIOSH Contract No. 210-76-0123.
[2] Backup Data Report for Nitrogen Dioxide, S320, prepared under NIOSH Contract No. 210-76-0123.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, Methods S320 and S321. U.S. Department of Health, Education, and Welfare. DHEW (NIOSH) Publication No. 78-175.
[4] Willey, M.A., C.S. McCammon, and L.J. Doemeny, Am. Ind. Hyg. Assoc. J. 38, 358 (1977).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1, P&CAM 231, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 77-157-A (1977).
[6] OSHA Analytical Methods Manual, 2nd ed., Part 2, Vol. 2, ID-182 and ID-190, U.S. Department of Labor, Salt Lake City, UT (1991).
[7] Gold, A., Anal. Chem. 49, 1443-1450 (1977).
[8] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

W. J. Woodfin and M. E. Cassinelli, NIOSH/DPSE; Method S321 validated under NIOSH Contract No. 210-76-0123.

p-NITROANILINE 5033

$H_2NC_6H_4NO_2$ MW: 138.14 CAS: 100-01-6 RTECS: BY7000000

METHOD: 5033, Issue 1 **EVALUATION:** FULL **Issue 1:** 15 August 1994

OSHA : 6 mg/m^3 (skin)
NIOSH: 3 mg/m^3 (skin)
ACGIH: 3 mg/m^3 (skin)

PROPERTIES: yellow crystals; MP 146 °C; BP 332 °C; VP 0.02 Pa (1.5 x 10^{-4} mm Hg) @ 20 °C

SYNONYMS: 4-nitrobenzenamine, p-aminonitrobenzene, p-nitrophenylamine

SAMPLING

SAMPLER: FILTER (0.8 µm mixed cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 16 L @ 6 mg/m^3
-MAX: 350 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3.9 to 12.9 mg/m^3 (90-L samples) [1]

BIAS: −1.7%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.054 for range studied [1]

ACCURACY: ±11.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: p-nitroaniline

EXTRACTION: 5 mL isopropanol

MOBILE PHASE: 40% isopropanol/60% hexane isocratic, 1 mL/min

COLUMN: silica (Partisil 10, 25-cm x 4.6-mm x 6.4-mm stainless steel)

DETECTOR: UV @ 375 nm

CALIBRATION: solutions of p-nitroaniline in isopropanol

RANGE: 100 to 2000 µg per sample [1]

ESTIMATED LOD: 20 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.020 [1]

APPLICABILITY: The working range is 1.1 to 22 mg/m^3 for a 90-L air sample. This method is applicable to p-nitroaniline aerosol but not for environments where vapor may be present.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S7 [2].

REAGENTS:

1. p-Nitroaniline, 99%.*
2. Isopropanol, distilled in glass.*
3. Hexane, distilled in glass.*
4. Calibration stock solution, 10 mg/mL: dissolve 0.100 g p-nitroaniline in 10 mL 2-propanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter (37-mm) and cellulose backup pad (37-mm) in a 2-piece filter holder held together by shrinkable band.
2. Personal sampling pump, calibrated, capable of operating 8 h at 1 to 3 L/min, with flexible connecting tubing.
3. HPLC with UV detector (375 nm), silica column (Partisil 10 or equivalent), injector, and electronic integrator.
4. Microliter syringes, various sizes.
5. Volumetric flasks, various sizes.
6. Squat form ointment jars with Teflon gaskets and screw caps.
7. Pipet, 5-mL, with pipet bulb.
8. Tweezers.

SPECIAL PRECAUTIONS: p-Nitroaniline is a toxic agent that may be absorbed through the skin [3]. It is an explosion risk. Hexane and isopropanol are flammable liquids.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front and rear plugs immediately before sampling and attach sampler to personal sampling pump with flexible tubing. Sample at a known flowrate between 1 and 3 L/min and collect a total smaple of 16 to 350 liters of air.
3. Cap the filters, record sample identity and all relevant sample data (duration, ambient temperature and pressure).
4. Prepare blank sample filters by handling in the same manner (open, seal, and transport) as samples except that no air is sampled through the blanks.
5. Ship in suitable container with blanks.

SAMPLE PREPARATION:

6. Open the filter holder and using tweezers, transfer each mixed cellulose ester filter to an ointment jar.
7. Add 5 mL isopropanol, cap, and swirl the jar to ensure that the filter is thoroughly wetted.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Dilute aliquots of p-nitroaniline stock solution with isopropanol in volumetric flasks to encompass the range of interest.
   b. Prepare calibration graph (peak area vs. μg p-nitroaniline per sample).
9. Determine the recovery (R) of the filters at least once for each lot of filters used in the range of interest.
   a. Using a microliter syringe, spike 6 filters at each of 3 concentration levels with p-nitroaniline in isopropanol. Allow the filters to dry overnight for solvent evaporation.
   b. Analyze the spiked filters. Prepare graph of μg recovered vs. μg spiked.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set HPLC according to manufacturer's recommendations and to conditions on page 5033-1.
12. Separation is achieved on a silica column using a mobile phase of 40% isopropanol/60% hexane at 1 mL/min. Inject 20-μL sample aliquot.
    NOTE: If peak area is above the linear range of the working standards, dilute with isopropanol and apply the appropriate dilution factor in calculations.
13. Measure peak areas.

CALCULATIONS:

14. Determine the mass of p-nitroaniline, μg (corrected for recovery), for the sample (W) and average media blank (B).
15. Calculate the concentration of p-nitroaniline, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method is not applicable to environments where p-nitroaniline vapor is present. However, experiments indicate that less than 0.04 mg/m^3 of p-nitroaniline would exist as a vapor at 40 °C [1]. Extraction efficiencies of spiked filters containing 0.278, 0.556, or 1.112 mg of p-nitroaniline were 96.6%, 94.7%, and 94.6%, respectively [1]. Samples generated to measure the filter's collection efficiency at 1.5 L/min for concentration of 3.9, 6.75, and 12.88 mg/m^3 showed recoveries of 95.9%, 98.8%, and 100.9% respectively [1]. The average recovery for 7-day-old samples was 98.6% [1].

REFERENCES:

[1] Back-up Data Report for p-Nitroaniline, S7, prepared under NIOSH Contract No. 210-76-0123, (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V 3, S7, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

Charles Neumeister, NIOSH/DPSE.

(1) Nitrobenzene: $C_6H_5NO_2$	MW: (1) 123.11	CAS: (1) 98-95-3	RTECS: (1) DA6475000
(2) Nitrotoluene: $CH_3C_6H_4NO_2$	(2) 137.14	(2) varies	(2) varies with isomer
(3) 4-Chloronitrobenzene: $C_6H_4ClNO_2$	(3) 157.56	(3) 100-00-5	(3) CZ1050000

METHOD: 2005, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1984**
Issue 2: 15 August 1994

OSHA: Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (2): o-, m- and p-methylnitrobenzene.
(3): p-nitrochlorobenzene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: (1) and (3): 0.01 to 1 L/min;
(2): 0.01 to 0.2 L/min

	(1)	(2)	(3)
VOL-MIN:	10 L	1 L	1 L
-MAX:	150 L	30 L	150 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]; unknown for m- and p-nitrotoluene

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1): 3 to 12 mg/m^3 (55 L) [1];
(2): 11 to 58 mg/m^3 (20 L) [1];
(3): 0.4 to 3 mg/m^3 (50 L) [1]

BIAS: (1) 2.37%; (2) -0.06%; (3) -0.05%

OVERALL PRECISION ($\hat{S}_{rT}$): EVALUATION OF METHOD

ACCURACY: (1) ± 12.39%; (2) ± 11.3%; (3) ± 18.43%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: nitrobenzenes

DESORPTION: 1 mL methanol; ultrasonic bath 1 h

INJECTION VOLUME: 5 µL with 3-µL backflush

GC TEMPERATURES: Table 2

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 2-mm ID stainless steel, packed with 100/120 mesh Chromosorb WHP coated with: (1) and (3) 10% FFAP or (2) 5% SE-30

CALIBRATION: nitrobenzenes in methanol

RANGE: Table 2

ESTIMATED LOD: Table 2

PRECISION ($\bar{S}_r$): EVALUATION OF METHOD

APPLICABILITY: The working ranges for 25-L air samples are 2 to 56 mg/m^3 (0.4 to 11 ppm) nitrobenzene, 0.25 to 52 mg/m^3 (0.04 to 9 ppm) nitrotoluene, and 0.2 to 40 mg/m^3 (0.03 to 6 ppm) 4-chloronitrobenzene. During sampling, high humidity may greatly decrease breakthrough volume. Short-term (15 min) samples at 0.2 L/min may be used to monitor STEL compliance.

INTERFERENCES: None identified.

OTHER METHODS: This method combines and replaces Methods S217, S218 and S223 [2].

REAGENTS:

1. Methanol, chromatographic quality.
2. Analytes: nitrobenzene,* nitrotoluene isomers (o-, m- and p-),* and 4-chloronitrobenzene.*
3. Benzene.*
4. Hexane.*
5. Calibration stock solution, 10 mg/mL. Prepare in methanol for each analyte.
6. DE stock solutions:
   a. Nitrobenzene, 60 mg/mL in hexane.
   b. Nitrotoluene, 150 mg/mL in hexane.
   c. 4-Chloronitrobenzene, 10 mg/mL in 20/80 (v/v) benzene/hexane.
7. Nitrogen, purified.
8. Hydrogen, prepurified.
9. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections (front = 150 mg; back = 75 mg) of 20/40 mesh silica gel separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at the sampling flow rate. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2005-1).
4. Vials, glass, 2-mL, with PTFE-lined crimp caps.
5. Volumetric flasks, 10-mL.
6. Pipet, 1-mL, with pipet bulb.
7. Syringes, 10- and 100-μL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: The analytes are severe poisons and irritants. Do not get in eyes, on skin or on clothing. Nitrobenzene and m-nitrotoluene are absorbed through skin and can cause methemoglobinemia [3,4]. Benzene is a suspect human carcinogen. Hexane is a severe fire hazard.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for nitrotoluene isomers. Use a flow rate of 1 L/min or less for nitrobenzene and 4-chloronitrobenzene. Observe the maximum and minimum sample volumes on page 2005-1.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL methanol to each vial. Attach crimp cap securely to each vial.
7. Allow to stand 60 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution, or a dilution thereof, to methanol in 10-mL volumetric flasks and dilute to the mark. Prepare solutions in the ranges 20 to 800 μg/mL

for nitrobenzene, 1 to 1500 μg/mL for nitrotoluene, and 0.1 to 150 μg/mL for 4-chloronitrobenzene.

b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area vs. μg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration ranges (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2005-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak is above the linear range of the working standards, dilute with methanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Methods S217 (nitrobenzene) and S218 (4-nitrochlorobenzene) were issued on November 21, 1975 [2]. Method S223 (o-nitrotoluene) was issued on December 19, 1975. The ranges studied and the precision obtained are shown below [1]. The average DE measured was 1.00 for nitrobenzene (without ultrasonic agitation) and 1.03 for o-nitrotoluene and 4-chloronitrobenzene. Breakthrough (5% on back sorbent section) capacities were greater than 2.8, 2.5, and 2.2 mg of nitrobenzene, o-nitrotoluene, and 4-chloronitrobenzene, respectively, under the conditions tested.

Compound	Range Studied		Precision		Breakthrough Volume (L)
	µg	mg/m³	Measurement ($\hat{S}_r$)	Overall ($\hat{S}_{rT}$)	
Nitrobenzene	120 to 480 (55 L)	3 to 12	0.010	0.058	>223[a]
o-Nitrotoluene	300 to 1200 (20 L)	11 to 58	0.025	0.062	>47[b]
4-Chloronitrobenzene	25 to 100 (50 L)	0.4 to 3	0.025	0.103	>216[c]

[a]Determined using a concentration of 12.4 mg/m³ in dry air and a flow rate of 0.93 L/min.
[b]Determined using a concentration of 52 mg/m³ in dry air and a flow rate of 0.19 L/min.
[c]Determined using a concentration of 9.9 mg/m³ in dry air and a flow rate of 0.90 L/min.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S217, S218 and S223, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S217, S218 and S223, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Occupational Diseases, A Guide to Their Recognition, revised ed., 235-238, 280-281, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-181 (1978).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Nitrobenzene, p-Nitrochlorobenzene and Nitrotoluene, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[5] Aldrich Catalog Handbook of Fine Chemicals, 1982-83, Milwaukee, WI 53233.
[6] Riddick, J. A. and W. B. Bunger. Organic Solvents, 3rd ed., John Wiley and Sons, New York, NY (1970).
[7] UBTL, Inc., NIOSH Sequence #3386-K (NIOSH, unpublished, March 30, 1982).

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S217, S218 and S223 validated under NIOSH Contract CDC-99-74-45.

Table 1. Properties of the analytes [4,5,6].

Compound	Personal Exposure Limits OSHA @ NTP	NIOSH	ACGIH	BP, °C	MP, °C	d, g/mL @ 20 °C	VP @ 20 °C	mg/m³ = 1 ppm Pa (mm Hg)
Nitrobenzene	1 ppm (skin)	1 ppm (skin)	1 ppm (skin)	211	5	1.204	37 (0.28) @ 25 °C	5.03
Nitrotoluene	2 ppm	2 ppm	2 ppm					
ortho-	(skin)	(skin)	(skin)	222	-4	1.161	20 (0.15)	5.61
meta-				232	16	1.158	20 (0.15)	5.61
para-				238	52	1.29	17 (0.12)	5.61
4-chloronitrobenzene	1 mg/m³ (skin)	lowest[a] feasible (skin)	0.64 mg/m³ (skin)	242	83	1.37		6.44

[a]Potential carcinogen.

Table 2. Measurement details [1,2].

Compound	t, °C Injector Detector Column	LOD, µg per sample	Measurement Range, µg per sample
Nitrobenzene	245 275 160	20 [7]	50 to 800
o-Nitrotoluene[a]	150 250 90	0.8	6 to 1500
4-Chloronitrobenzene	180 260 155	0.1	5 to 150

[a]These GC conditions will resolve o-, m-, and p-toluene.

NITROETHANE 2526

$CH_3CH_2NO_2$ MW: 75.07 CAS: 79-24-3 RTECS: CZ1050000

METHOD: 2526, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: 100 ppm
ACGIH: 100 ppm
(1 ppm = 3.07 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.051 g/mL @ 20 °C; BP 114 °C; MP −89.5 °C; VP 2.8 kPa (21 mm Hg; 2.7% v/v) @ 25 °C; lower explosive limit 3.4% (v/v) in air

SYNONYMS: None.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (XAD-2, 600 mg + 300 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1.5 L @ 100 ppm
-MAX: 3 L [1]

SHIPMENT: separate front and back sorbent tubes

SAMPLE STABILITY: stable 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 147 to 604 mg/m^3 (3-L samples) [1]

BIAS: − 1.13 [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1]

ACCURACY: ± 11.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME IONIZATION DETECTOR

ANALYTE: nitroethane

DESORPTION: 2 mL ethyl acetate; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 200 °C
-COLUMN: 120 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: stainless steel, 6-m x 4-mm ID, packed with 10% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: standard solutions of nitroethane in ethyl acetate

RANGE: 0.5 to 2 mg per sample [1]

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.02 @ 0.47 to 1.9 mg per sample [1]

APPLICABILITY: The working range is 80 to 320 ppm (250 to 1000 mg/m^3) for a 2-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S219 [2].

REAGENTS:

1. Eluent: Ethyl acetate, containing (optionally) 0.1% v/v 1-hexanol or other suitable internal standard.
2. Nitroethane, chromatographic quality.*
3. Methanol.
4. Methylene chloride.*
5. Calibration stock solution, 0.21 mg/μL. Add 2.1 g (2.0 mL) nitroethane to a 10-mL volumetric flask. Dilute to the mark with ethyl acetate.
6. Helium or nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: separate front and backup glass tubes with plastic caps, each 10 cm long, 10-mm OD, 8-mm ID, flame-sealed ends, packed with 20/50 mesh XAD-2 (front = 600 mg; back = 300 mg). The sorbent beds are held in place with silanized glass wool plugs. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (SKC Cat. No. 226-30-02, or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2526-1).
4. Vials, glass, 5-mL, PTFE-lined crimp caps.
5. Syringes, 2- to 20-μL, readable to 0.1 μL.
6. Volumetric flask, 10-mL.
7. Pipets, delivery-type, 1- and 2-mL; calibrated-type, 5-mL, readable to 0.01 mL.
8. File.

SPECIAL PRECAUTIONS: Contact with amines, strong acids, and alkalies may sensitize nitroethane so that it will readily explode [3]. Methylene chloride is a suspect carcinogen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1.5 to 3 L.
   NOTE: High pressure drop across the sampler may occur at flow rates above 0.05 L/min, giving inaccurate sample volumes.
4. Immediately following sampling, separate the front from the back sorbent tube and cap both. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool plugs.
6. Pipet 2.0 mL eluent into each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain nitroethane concentrations in the range 0.03 to 1 mg/mL.

b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of nitroethane to peak area of internal standard vs. μg nitroethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Inject a known amount (2 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section (600 mg sorbent) with a microliter syringe.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. μg nitroethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2526-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of nitroethane by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of nitroethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of nitroethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S219 was issued on January 20, 1978 [2]. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 22 °C and 777 torr over the range 143 to 614 mg/m^3 by calibrated syringe pump delivery of the neat analyte into a humidified dilution airstream [1,4]. The concentrations were monitored by total hydrocarbon analyzer. A 600-mg bed of sorbent retained 2.8 mg analyte before 5% breakthrough occurred at 5 L when a challenge atmosphere of 585 mg/m^3 analyte in humid air was sampled at 0.05 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 314 mg/m^3 nitroethane in humid air and stored for one or seven days at ambient temperatures prior to analysis. It was found necessary to separate the front and back sorbent sections immediately after sampling due to analyte migration during storage. Desorption efficiency averaged 0.88 in the range 0.47 to 1.9 mg per sample. A previous study found nitroethane to be unstable on activated charcoal [5].

REFERENCES:

[1] Backup Data Report for Nitroethane, NIOSH Contract #210-76-0123 (unpublished).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S219, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
[5] Failure report, S219, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD WRITTEN BY:

Robert Glaser, NIOSH/DPSE; S219 originally validated under NIOSH Contract No. 210-76-0123.

NITROGLYCERIN

$(CH_2ONO_2)_2CHONO_2$ MW: 227.09 CAS: 55-63-0 RTECS: QX2100000

METHOD: 2507, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : C 0.2 ppm (skin)
NIOSH: STEL 0.1 mg/m^3 (skin)
ACGIH: 0.05 ppm (skin)
(1 ppm = 9.29 mg/m^3 @ NTP)

PROPERTIES: liquid; MP 3 to 13 °C; d 1.592 g/mL @ 25 °C; VP 0.034 Pa (0.00026 mm Hg; 0.34 ppm) @ 20 °C

SYNONYMS: NG; 1,2,3-propanetriol trinitrate.

SAMPLING

SAMPLER: SOLID SAMPLER TUBE (Tenax-GC, 100 mg/50 mg)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 3 L @ 1 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 25 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.6 to 3.2 mg/m^3 [2,3] (15-L samples)

BIAS: −0.02%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.104 [2]

ACCURACY: ±20.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: nitroglycerin

DESORPTION: 2 mL ethanol; stand 30 min

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 280 °C
-COLUMN: 125 °C

CARRIER GAS: 95% argon/methane, 75 mL/min

COLUMN: glass, 1 m x 4-mm, 2-mm ID 10% OV-17 on 60/80 mesh Gas Chrom Q

CALIBRATION: solutions of NG in ethanol

RANGE: 3 to 45 µg per sample

ESTIMATED LOD: 0.6 µg per sample

PRECISION ($\bar{S}_r$): 0.051 [2]

APPLICABILITY: This method is applicable to the simultaneous determination of nitroglycerin and ethylene glycol dinitrate (EGDN). The working range for both compounds is 0.02 to 0.3 ppm (0.2 to 3 mg/m^3) for a 15-L air sample, provided that the linear range of the ECD is not exceeded.

INTERFERENCES: A high concentration of 2-hydroxyethyl nitrate (ethylene glycol mononitrate) tails into the EGDN peak but does not prevent a satisfactory determination of EGDN.

OTHER METHODS: This method combines and replaces Methods S216 [2,5] and P&CAM 203 [4].

REAGENTS:

1. Ethanol, absolute.
2. Nitroglycerin (NG)* - one of the following:
   a. pure material.
   b. standard solution in ethanol, available from dynamite manufacturer.
   c. tablets, sublingual, USP (analyzed; 80 to 112% NG).
      NOTE: to prepare solutions, weigh, crush and extract with ethanol. Filter and dilute to volume.
   d. nitroglycerin lactose trituration, available from NG tablet manufacturer.
3. Ethylene glycol dinitrate (EGDN)* - one of the following:
   a. pure material.
   b. dynamite, analyzed, available.
      NOTE: Dynamite is heterogeneous. Use care to obtain representative sample.
4. Argon/methane, 95:5 (v/v), purified.
5. DE stock solution, 3 μg/μL. Dissolve 30.0 mg NG and/or 30.0 mg EGDN in ethanol to make 10 mL solution.
6. Calibration stock solution, 0.3 μg/μL. Dilute 1 mL DE stock solution to 10 mL with ethanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends and plastic caps, containing two sections of 35/60 mesh Tenax-GC resin (front = 100 mg; back = 50 mg), separated by a urethane foam plug. Silylated glass wool plugs precede the front section and follow the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, ECD, integrator and column (page 2507-1).
4. Vials, 5-mL, with PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipets, 1- and 2-mL, delivery, glass, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Ethanol is flammable. All work should be done in an exhaust hood and away from any open flame.

Nitroglycerin and ethylene glycol dinitrate can be explosive in their pure forms and extreme caution should be used when handling the bulk material [5, 6].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 3 to 100 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL ethanol to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 1 to 45 μg NG or EGDN per sample.
   a. Add known amounts of calibration stock solution to ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg NG or EGDN).
9. Determine desorption efficiency (DE) at least once for each lot of Tenax-GC used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg NG or EGDN recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2507-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethanol, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of NG or EGDN found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of NG or EGDN in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S216 [3] was issued on November 11, 1975, and validated over the range of 0.56 to 3.2 mg/m^3 for nitroglycerin and 0.51 to 1.8 mg/m^3 for ethylene glycol dinitrate [2]. Eighteen 15-L samples for each analyte were collected from dynamically-generated test atmospheres. Eighteen additional samples for each analyte were spiked (six each at one-half, one and two times the OSHA standard) directly. The average recovery for all three levels for nitroglycerin was 97.6% and had a pooled precision ($\bar{S}_r$) of 0.051. The average recovery for the three levels for ethylene glycol dinitrate was 92.0% with a pooled precision ($\bar{S}_r$) of 0.063. Since the collection efficiency of the Tenax-GC for both compounds was established as 100%, the corrected "found" value of the generated sample was taken as the measure of the generated air concentrations. Breakthrough for each compound was evaluated at a concentration twice the OSHA standard. Duplicate samples were collected at interim periods of 60, 120, and 240 min at 1.1 L/min. Breakthrough of EGDN occurred at some point between 130 and 257 L of air sampled. No

breakthrough occurred with the NG samples up to an average sample volume of 261 L. Sample stability was evaluated with 2.6 μg EGDN per sample and 9.0 μg NG per sample for 25 days at ambient temperature. No losses were observed for either compound [1].

REFERENCES:

[1] Sampling and Analysis of Four Organic Compounds Using Solid Sorbents, Final Report, NIOSH Contract No. HSM-99-73-63, Southern Research Institute, Birmingham, AL.
[2] Documentation of the NIOSH Validation Tests, S216, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S216, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid, V. 1, P&CAM 203, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Criteria for a Recommended Standard...Occupational Exposure to Nitroglycerin and Ethylene Glycol Dinitrate, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-167 (1978).
[6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD WRITTEN BY:

Martha J. Seymour, NIOSH/DPSE; S216 validated under NIOSH Contract CDC-99-74-45.

NITROMETHANE

CH_3NO_2 MW: 61.04 CAS: 75-52-5 RTECS: PA9800000

METHOD: 2527, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: no recommended standard
ACGIH: 100 ppm
(1 ppm = 2.50 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.138 g/mL @ 20 °C; BP 101.2 °C; MP −29 °C; VP 4.9 kPa (37 mm Hg; 4.8% v/v) @ 25 °C; lower explosive limit 7.3% (v/v) in air

SYNONYMS: nitrocarbol.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Chromosorb 106, 600 mg/300 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1.2 L @ 100 ppm
-MAX: 3 L [1]

SHIPMENT: separate front and back sorbent sections

SAMPLE STABILITY: stable 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 123 to 501 mg/m³ (3-L samples) [1]

BIAS: − 0.73% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.078 [1]

ACCURACY: ± 15.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NITROGEN-SPECIFIC DETECTOR

ANALYTE: nitromethane

DESORPTION: 5 mL ethyl acetate; stand 30 min

INJECTION VOLUME: 5.0 µL

TEMPERATURE-INJECTOR: 225 °C
-DETECTOR: 300 °C
-COLUMN: 100 °C

CARRIER GAS: He or N_2, 20 mL/min

COLUMN: stainless steel, 2-m x 4-mm ID, packed with 10% SP 1000 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solution of nitromethane in ethyl acetate

RANGE: 0.3 to 2 mg per sample [1]

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.042 @ 0.34 to 1.34 mg per sample [1]

APPLICABILITY: The working range is 60 to 360 ppm (150 to 900 mg/m³) for a 2-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S220 [2].

REAGENTS:

1. Nitromethane, chromatographic quality.*
2. Ethyl acetate, chromatographic quality.
3. Calibration stock solution, 0.1138 mg/μL. Add 1.138 g (1.00 mL) nitromethane to a 10-mL volumetric flask. Dilute to the mark with ethyl acetate.
4. Helium or nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10.0-cm long, 10-mm OD, 8-mm ID; two sections of 60/80 mesh Chromosorb 106 (front = 600 mg; back = 300 mg) separated by a plug of silanized glass wool and held in place with plugs of silanized glass wool, flame-sealed at both ends; with plastic caps. Tubes are commercially available. (SKC Cat. No. ST 226-111, or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, nitrogen-phosphorus detector, integrator and column (page 2527-1).
4. Vials, glass, 5-mL, PTFE-lined septum, screw-caps.
5. Syringes, 1- to 25-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, delivery, 1- and 5-mL.
8. File.

SPECIAL PRECAUTIONS: Nitromethane vapor forms highly explosive mixtures with air. When highly confined and heated, it can detonate [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1.2 to 3 L.
   NOTE: High pressure drop across the sampler may occur at flow rates above 0.05 L/min, giving inaccurate sample volumes.
4. Immediately following sampling, remove the silanized glass wool from the end of the sampler nearer the pump and empty the 300-mg back sorbent section into a clean vial. Seal the vial with a PTFE-lined cap. Cap the tubes containing the front section. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section of the sampler tube in a separate vial from that containing the back sorbent section. Discard the glass wool plugs.
6. Pipet 5.0 mL ethyl acetate into each vial. Immediately cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to ethyl acetate in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain nitromethane concentrations in the range 0.01 to 0.4 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg nitromethane).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg nitromethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2527-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of nitromethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of nitromethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S220 was issued January 19, 1979 [2]. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 20 to 24 °C and 767 to 774 torr over the range from 123 to 514 mg/m^3 by calibrated syringe pump injection of the analyte into a dilution airstream [1,4]. The concentrations were monitored by total hydrocarbon analyzer. A 600-mg bed of the sorbent retained 2.6 mg of the analyte before 5% breakthrough occurred at 5.0 L, when a challenge atmosphere of 518 mg/m^3 of analyte in humid air was sampled at 0.05 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 236 mg/m^3 nitromethane in humid air and stored for one or seven days at ambient temperatures prior to analysis. Desorption efficiency averaged 0.971 in the range 0.34 to 1.34 mg per sample. A previous study showed that samples of nitromethane collected on activated charcoal were unstable [5].

REFERENCES:

[1] Backup Data Report for Nitromethane, prepared under NIOSH Contract 210-76-0123 (unpublished, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6., S220, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
[5] Failure report, S220, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD REVISED BY:

Robert Glaser, NIOSH/DPSE; S220 originally validated under NIOSH Contract No. 210-76-0123.

2-NITROPROPANE

$(CH_3)_2CHNO_2$ MW: 89.09 CAS: 79-46-9 RTECS: TZ550000

METHOD: 2528, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 25 ppm
NIOSH: lowest feasible; suspect carcinogen; Group I Pesticide
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 3.64 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.9821 g/mL @ 25 °C; BP 120 °C; MP −91 °C; VP 2.4 kPa (18 mm Hg; 2.4% v/v) @ 25 °C; lower explosive limit 2.6% (v/v) in air

SYNONYMS: dimethylnitromethane; sec-nitropropane.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Chromosorb 106, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 25 ppm
-MAX: 2 L [1]

SHIPMENT: routine

SAMPLE STABILITY: 100% recovered after 7 days @ 25 °C + 21 days @ 0 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3.1 to 28.3 mg/m^3 (3-L samples) [1]

BIAS: 2.8% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.05 [1]

ACCURACY: ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME IONIZATION DETECTOR

ANALYTE: 2-nitropropane

DESORPTION: 1 mL ethyl acetate; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 190 °C
-DETECTOR: 200 °C
-COLUMN: 90 °C

CARRIER GAS: He or N_2, 20 mL/min

COLUMN: stainless steel, 6-m x 4-mm ID, packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solution of 2-nitropropane in ethyl acetate

RANGE: 10 to 150 µg per sample [1]

ESTIMATED LOD: 1 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.03 @ 0.01 to 0.1 mg per sample [1]

APPLICABILITY: The working range is 1.4 to 27 ppm (5 to 100 mg/m^3) for a 2-L air sample.

INTERFERENCES: The method has been evaluated in epoxy spray paint operations with no apparent interference from methyl butyl ketone, heptane, 1-nitropropane, toluene and xylene [2]. The Chromosorb 106 must be extracted with acetone [1]; otherwise autosampler needles will be readily plugged.

OTHER METHODS: This revises P&CAM 272 [3].

REAGENTS:

1. 2-Nitropropane, chromatographic quality.*
2. Ethyl acetate, chromatographic quality.
3. Calibration stock solution, 9.82 mg/mL. Add 98.2 mg (100 μL) 2-nitropropane to a 10-mL volumetric flask. Dilute to the mark with ethyl acetate. Prepare in duplicate.
4. Helium or nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7.0-cm long, 6.0-mm OD, 4-mm ID; two section of 60/80 mesh, acetone-washed, Chromosorb 106 (front = 100 mg; back = 50 mg) separated by a 2-mm section of urethane foam and held in place with plugs of silanized glass wool, flame-sealed at both ends; with plastic caps. Tubes are commercially available (SKC Cat. No. ST 226-111, or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2528-1).
4. Vials, glass, 2-mL, PTFE-lined septum crimp caps.
5. Syringes, 1- to 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, delivery, 1.0-mL.
8. File.

SPECIAL PRECAUTIONS: 2-Nitropropane is a suspected human carcinogen [4]. Perform all work with this chemical in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 2 L.
   NOTE: High pressure drop across the sampler may occur at flow rates >0.05 L/min, giving inaccurate sample volumes.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Pipet 1.0 mL ethyl acetate into each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to ethyl acetate in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 2-nitropropane concentrations in the range 1 to 150 μg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg 2-nitropropane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg 2-nitropropane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2528-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.
    NOTE: Retention time of 2-nitropropane is ca. 20 min under these conditions.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of 2-nitropropane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 2-nitropropane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 272 was issued on August 1, 1978. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 25 °C and 745 torr over the range 3.1 to 28.3 mg/m^3 by the vapor pressure saturation/air dilution technique [1]. The concentrations were verified by total hydrocarbon analyzer. A 100-mg bed of acetone-washed sorbent retained 374 μg of analyte before 5% breakthrough occurred at 10.4 L when a challenge atmosphere of 36 mg/m^3 analyte in humid air was sampled at 0.2 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 4.7 mg/m^3 2-nitropropane in humid air and stored for 1, 7, 14 or 28 days prior to analysis. The 14- and 28-day samples were stored at 0 °C after an initial seven-day storage at ambient temperature. A previous study showed 2-nitropropane to be unstable after collection on activated petroleum-based charcoal [5].

REFERENCES:

[1] Glaser, R. and W. J. Woodfin. A Method for Sampling and Analysis of 2-Nitropropane in Air, Am. Ind. Hyg. Assoc. J., 42: 18-22 (1981).
[2] NIOSH Health Hazard Evaluation Report HHE-80-57-781 (1980).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] NIOSH Current Intelligence Bulletin 17, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-127 (1978).
[5] Failure report, S222, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD WRITTEN BY:

Robert Glaser, NIOSH/DPSE.

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 2522, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PELs; N-nitrosodimethylamine is a carcinogen
NIOSH: no RELs; N-nitrosodimethylamine is suspect carcinogen
ACGIH: no TLVs; N-nitrosodimethylamine is suspect carcinogen

PROPERTIES: Table 1

SYNONYMS: Table 1.

SAMPLING	
SAMPLER:	SOLID SORBENT TUBE (Thermosorb/N™ air sampler)
FLOW RATE:	0.2 to 2 L/min
VOL-MIN:	15 L @ 10 $\mu g/m^3$
-MAX:	1000 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 6 weeks @ 20 °C [1,2]
BLANKS:	2 to 10 field blanks per set

ACCURACY	
RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT	
TECHNIQUE:	GAS CHROMATOGRAPHY, TEA [1]
ANALYTE:	nitrosamines (Table 1)
DESORPTION:	2 mL 3:1 (v/v) methanol: dichloromethane, stand 30 min
INJECTION VOLUME:	5 μL
COLUMN:	stainless steel (10 in x ⅛ in); 10% Carbowax 20M + 2% KOH on Chromosorb W-AW
TEMPERATURE-INJECTION:	200 °C
-DETECTOR:	550 °C to 600 °C
-COLUMN:	110 °C to 200 °C programmed @ 5°/min
GASES:	N_2 carrier, 25 mL/min; oxygen, 5 mL/min; ozone, 0.2 mL/min
CALIBRATION:	standard solutions of analytes in methanol/dichloromethane
RANGE:	0.15 to 0.5 μg per sample [2]
ESTIMATED LOD:	0.05 μg per sample [2]
PRECISION ($\bar{S}_r$):	0.014 @ 0.05 to 0.4 μg per sample [2]

APPLICABILITY: The working range is 0.003 to 10 mg/m^3 for a 50-L air sample. If high ambient concentrations of nitrosamines are expected, another Thermosorb/N tube should be used as a back-up in sampling.

INTERFERENCES: When the thermal energy analyzer (TEA) is operated in the nitrosamine mode, it is highly specific for N-nitroso compounds. Because of the TEA's selectivity and sensitivity, it is possible to chromatograph and quantitate N-nitroso compounds, even in the presence of other co-eluting compounds. Therefore, there is little or no interference from other compounds.

OTHER METHODS: This replaces NIOSH methods P&CAM 252 [3] and P&CAM 299 [4].

REAGENTS:

1. Dichloromethane, reagent grade.
2. Methanol, reagent grade.
3. Nitrogen, purified.
4. Oxygen, purified, 99.99%.
5. Standard solutions of N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodibutylamine, N-nitrosodipropylamine, N-nitrosomorpholine, N-nitrosopiperidine, N-nitrosopyrrolidine.
6. Eluent, 1:3 (v/v) dichloromethane/methanol.
7. Air, filtered, compressed.
8. Ozone, purified 99.99%.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Commercially available tubes (Thermedics Detection, Inc., 220 Mill Rd., Chelmsford, MA 01824, 508/251-2000).
2. Personal sampling pump, 0.2 to 2 L/min, with flexible tubing.
3. Gas chromatograph equipped with thermal energy analyzer (TEA), integrator and column (page 2522-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Pipets, various sizes for preparing standards.
6. Syringes, 1-, 5-, 10-, 25-, and 100-μL readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Gloves for safe handling of toxic chemicals.
9. Syringe, glass, 5.0-mL, with male Luer adapter.
10. Needle, industrial blunt, 20-gauge with female luer adapters.

SPECIAL PRECAUTIONS: N-nitrosodimethylamine is an OSHA-regulated carcinogen. Other nitrosamines are suspected carcinogens and are very toxic. Handle samples and standards in a well-ventilated hood or glove box.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the Thermosorb/N tube from the foil pouch. Save the pouch.
3. Remove the red end caps from the inlet and outlet ports. Store red caps on the Thermosorb/N tube in the brackets under the "AIR IN" sign.
4. Label the Thermosorb/N tube with the peel-off "AIR SAMPLER" label provided on the foil pouch.
5. Attach the Thermosorb/N tube to the sampling pump with flexible tubing.
6. Sample at an accurately known flow rate between 0.2 and 2 L/min for a total sample size of 15 to 1000 L.
7. After sampling, detach the sampler from the pump.
8. Replace the red end caps on the inlet and outlet ports of the sampler.
9. Replace the Thermosorb/N tube in the foil pouch. Fold the pouch and seal it with the clip provided and pack securely for shipment.

SAMPLE PREPARATION:

10. Remove the sampler from the foil pouch.
11. Label analysis vial with the label from the Thermosorb/N air sampler.
12. Remove the red end-caps, store them in the bracket provided with the tube.
13. Attach a syringe needle to the male Luer fitting of the Thermosorb/N tube.
14. Attach a syringe barrel containing eluent to the female Luer fitting of the Thermosorb/N tube.
15. Elute by "backflushing" the Thermosorb/N tube with 2.0 mL of eluent. Collect the effluent in the labeled vial.
    NOTE: The optimum elution rate is 0.5 mL/min.

CALIBRATION AND QUALITY CONTROL:

16. Calibrate daily with at least six working standards over the range of 0.05 to 0.5 μg of analyte per sample (0.025 to 0.25 μg/mL).
    a. Add known amounts of the nitrosamines standard solution to eluent in 10-mL volumetric flasks and dilute to mark.
    b. Analyze together with samples and blanks (steps 19-22).
    c. Prepare calibration graph (peak area of analyte vs. μg analyte).
17. Determine desorption efficiency (DE) at least once for each batch of Thermosorb/N tubes used.
    a. Inject a known amount of nitrosamine standard solution directly onto the Thermosorb/N tube with a microliter syringe.
    b. Cap the tube. Allow to stand overnight.
    c. Desorb (steps 12 through 15) and analyze together with working standards (steps 19 through 22).
    d. Prepare a graph of DE vs. μg analyte recovered.
18. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

19. Set gas chromatograph and TEA to the conditions listed on page 2522-1.
20. Inject sample aliquot manually, using solvent flush technique or with an autosampler.
21. Approximate retention times of the seven nitrosamines at indicated column temperatures are:

COMPOUND	COLUMN TEMP. °C	RETENTION TIME (MIN)
N-nitrosodimethylamine	120	2.2
N-nitrosodiethylamine	125	3.1
N-nitrosodipropylamine	142	6.2
N-nitrosodibutylamine	145	7.4
N-nitrosomorpholine	178	13.2
N-nitrosopiperidine	169	12.0
N-nitrosopyrrolidine	166	11.2

22. Measure peak area.

CALCULATIONS:

23. Determine the mass, μg (corrected for DE) of analyte found in the sample (W) and blank (B).
24. Calculate concentration, C, analyte in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was evaluated over the range 0.05 to 0.5 μg of the seven nitrosamines per sample. Desorption efficiency was checked by spiking known amounts of the compounds on Thermosorb/N tubes and was found to be nearly 100% for all nitrosamines studied. The sampling device is small and interferences are minimal; large concentrations can be sampled (up to 1500 μg loading) with no breakthrough. Samples can be stored at room temperature for long periods of time (≥6 weeks). Some field samples were also used for evaluation of this method [2].

REFERENCES:

[1] Roundbehler, D. and Fajen J. N-Nitroso Compounds in the Factory Environment, NIOSH contract #210-77-0100 (1977).
[2] Foley, D. NIOSH/MRSB Method Development Efforts, Backup Data Report and Analysis for Nitrosamines, NIOSH, (Unpublished, 1983-1988).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 252, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid., V.5, P&CAM 299, NIOSH Publ. 79-141 (1979).

METHOD WRITTEN BY: G. David Foley, NIOSH/DPSE.

Table 1: General Information

Compounds (Synonyms)	Formula	MW	Properties
N-nitrosodimethylamine (N-Methyl-N-nitrosomethanamine; dimethylnitrosamine; DMN; DMNA; CAS #62-75-9) RTECS: IQ0525000	$(CH_3)_2N-N=O$	74.1	liquid; d 1.00 g/mL @ 20 °C; BP 151 °C; VP 0.36 kPa (2.7 mm Hg) @ 20 °C
N-nitrosodiethylamine (N-Ethyl-N-nitrosoethanamine; diethylnitrosamine; DEN; DENA; CAS #55-18-5) RTECS: IA3500000	$(C_2H_5)_2N-N=O$	102.1	liquid, d 0.94 g/mL @ 20 °C; BP 175 °C; VP 0.1 kPa (0.86 mm Hg) @ 20 °C
N-nitrosodipropylamine (N-Propyl-N-nitrosopropylamine DPN; DPNA; CAS #621-64-7) RTECS: JL9700000	$(C_3H_7)_2N-N=0$	130.2	liquid; d 0.916 g mL/@ 20 °C; BP 194.5 °C; VP 11 Pa (0.085 mm Hg) @ 20 °C
N-nitrosodibutylamine (N-Butyl-N-nitrosobutylamine; dibutylnitrosamine; CAS #924-16-3) RTECS: EJ4025000	$(C_4H_9)_2N-N=O$	158.3	liquid; d 9.901 g/mL @ 20 °C; BP 116 °C @ 14 mm Hg, VP 4 Pa (0.03 mm Hg) @ 20 °C
N-nitrosomorpholine (NMOR; 4-Nitrosomorpholine; MORNA; CAS #59-89-2) RTECS: QE7525000	$C_4H_8N_2O_2$	116.1	liquid/crystals; d unknown; BP 225 °C; MP 29 °C; VP unknown
N-nitrosopiperidine (N-NPIP; PIPNA; NPIP; CAS #100-75-4) RTECS: TN2100000	$(CH_2)_5N-N=0$	114.2	liquid; d 1.063 @ 19 °C; BP 217 °C @ 720 mm Hg; VP unknown
N-nitrosopyrrolidine (N-NPyr; NPYR, PYRNA; 1-Nitrosopynolodine; CAS #930-55-2) RTECS: UY1575000	$C_4H_8N-N=0$	100.1	liquid; d 1.09 g/mL @ 20 °C; BP 214 °C; VP 10 Pa (0.072 mm Hg) @ 20 °C

NITROUS OXIDE 6600

N_2O MW: 44.01 CAS: 10024-97-2 RTECS: QX1350000

METHOD: 6600, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : no standard
NIOSH: 25 ppm
ACGIH: 50 ppm
(1 ppm = 1.80 mg/m^3 @ NTP)

PROPERTIES: gas; BP -88.46 °C; d = 1.53 (air = 1)

SYNONYMS: hyponitrous acid anhydride; laughing gas.

SAMPLING

SAMPLER: AMBIENT AIR OR BAG SAMPLE

VOL-MIN: at least 2 spectrophotometer cell volumes
-MAX: no maximum volume

SAMPLE STABILITY: bag samples stable 2 h @ 25 °C

BLANKS: use uncontaminated air

ACCURACY

RANGE STUDIED:	10 to 1000 ppm
BIAS:	none known
OVERALL PRECISION ($\hat{S}_{rT}$):	0.013 [1] (between-instrument)
ACCURACY:	± 2.5%

MEASUREMENT

TECHNIQUE: LONG-PATHLENGTH PORTABLE INFRARED SPECTROPHOTOMETER (FIELD READOUT)

ANALYTE: nitrous oxide

OPERATION: according to manufacturer's instructions

ANALYTICAL WAVELENGTH: 4.48 μm

PATHLENGTH: 0.5 m to 40 m (function of desired concentration range)

CALIBRATION: closed-loop dilution of N_2O

RANGE: 10 ppm to > 1% N_2O in air

ESTIMATED LOD: ca. 1 ppm N_2O @ 10-m pathlength; varies with pressure and instrument

PRECISION ($\bar{S}_r$): 0.01 [1] (within-instrument)

APPLICABILITY: The working range of this method is 10 ppm (v/v) to more than 1% (v/v) N_2O. This method may be used for the sequential determination of two or more analyses by changing the analytical wavelength and pathlength.

INTERFERENCES: In common application (i.e., hospital, dental or veterinary operatory), there are no identified interferences.

OTHER METHODS: The criteria document on waste anesthetic gases [2] also describes an infrared method.

REAGENTS:

1. Nitrous oxide, 99%, compressed.*
   NOTE: Required in field for calibration.
2. Air, uncontaminated.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Spectrophotometer: infrared analyzer, transportable, long pathlength (0.5 to 40 m, as needed for concentration range measured), wavelength 4.48 μm, sample cell of known volume.
   NOTE: Readout drift should be less than 5% full-scale/8-h.
2. Pump to circulate air samples through the spectrophotometer sample cell; flow rate ca. 1 sample cell volume/min.
3. Syringes, gas-tight, 0.1-, 0.5- and 1-mL.
4. Regulator for nitrous oxide.
5. Strip chart recorder, compatible with spectrophotometer (optional).
6. Personal sampling pump, 0.1 to 4 L/min, capable of bag filling, with flexible connecting tubing; and plastic bags, inert and impermeable, clean, various sizes, capacity $\geq$2 times spectrophotometer cell volume (optional; for TWA samples).
7. Plastic tubing (optional; for remote, real-time analysis).

SPECIAL PRECAUTIONS: Nitrous oxide supports combustion. Shipment of compressed calibration gas must comply with 49 CFR 1992 regulations regarding shipment of hazardous materials.

SAMPLING:

1. Select one of the following sampling modes according to the desired form of the data:
   a. **Ambient air.** Pump ambient air at ca. 1 cell volume/min through the spectrophotometer sample cell.
      NOTE 1: Record and integrate the continuous spectrophotometer output signal if data are to be expressed as TWA concentration.
      NOTE 2: Remote air samples may be transported to the spectrophotometer with the use of plastic tubing and a vacuum pump and analyzed in the same manner as ambient air samples.
   b. **Integrated air samples for TWA determinations.**
      (1) Evacuate a clean plastic bag.
      (2) Attach the plastic bag to a personal sampling pump and pump the air to be sampled into the bag at a rate calculated to fill the bag over the duration of the sampling period. Terminate sampling before the bag is 80% full.
      NOTE: The flow rate must remain within $\pm$ 5% of the initial setting throughout the sampling period.
      (3) Analyze the bag sample within 2 h after completion of sampling to minimize loss of analyte by adsorption and permeation.

INSTRUMENT PREPARATION AND CALIBRATION:

2. Set instrument parameters as required for analysis. Allow sufficient warm-up/equilibration time.
3. Perform on-site multi-point calibration at five or more concentrations over the range 10 to 1000 ppm.
   a. Zero instrument while recirculating uncontaminated air through sample cell.
   b. Inject known volume of N_2O into the sample cell with a gas-tight syringe.
      NOTE: Inject the N_2O through tubing or a septum attached to the sample cell.
   c. Calculate concentration, C_s (ppm), of N_2O in sample cell:

$$C_s = \frac{\text{Volume of } N_2O \text{ injected } (\ \mu L\ )}{\text{Volume of cell } (\ L\ )}, \text{ ppm.}$$

   d. When instrument reading stabilizes, record meter or recorder deflection.
   e. Prepare calibration graph (C_s vs. meter or recorder deflection).
4. Practice routine instrument maintenance.
   a. Replace septa in a closed-loop system frequently in accordance with manufacturer's recommendations.
   b. Check and replace, if cloudy, the NaCl windows in the infrared spectrophotometer.
      NOTE: AgBr optics cloud less quickly.
   c. Follow manufacturer's recommendations for specific routine maintenance.

MEASUREMENT:

5. Pump air to be analyzed through sample cell to purge the sample cell. Typically, 2 to 3 cell volumes are necessary. When output stabilizes, record meter or recorder reading.
6. Read the concentration of N_2O in the unknown samples, C_v (ppm), corresponding to the meter or recorder deflection directly from the calibration graph.
7. Periodically during each day's operation recheck calibration by going to step 2 and repeating three or more points on the calibration graph.

EVALUATION OF METHOD:

This method has been successfully used in hospital, dental and veterinary operatories. Calibration curves have proven reproducible. Individual data sets have demonstrated statistical comparability in Bartlett's test for homogeneity. Relative standard deviations, s_r, as low as 0.006 have been seen in replicate calibrations of the same instrument by different individuals in the 10 to 1000 ppm range [1].

REFERENCES:

[1] Burroughs, G. E. NIOSH, Division of Physical Sciences and Engineering, unpublished data (1983).

[2] Criteria for a Recommended Standard...Occupational Exposure to Waste Anesthetic Gases and Vapors, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-140 (1977).

METHOD WRITTEN BY:

G. E. Burroughs and M. L. Woebkenberg, NIOSH/DPSE.

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NIOSH MANUAL OF ANALYTICAL METHODS

4th EDITION

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O - Z

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n-OCTANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

1-OCTANETHIOL 2510

$CH_3(CH_2)_7SH$ MW: 146.29 CAS: 111-88-6 RTECS: None

METHOD: 2510, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: C 0.5 ppm/15 min
ACGIH: no TLV
(1 ppm = 5.98 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.843 g/mL @ 20 °C;
BP 199.1 °C; MP - 49.2 °C; VP 0.026 kPa
(1.55 mm Hg; 2040 ppm) @ 37.7 °C

SYNONYMS: n-octanethiol; octyl mercaptan; 1-mercaptooctane; octylthiol.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Tenax-GC, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 0.5 ppm
-MAX: 15 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.32 to 6.55 mg/m^3 [1] (8.5-L samples)

BIAS: - 0.013 [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.083 [1]

ACCURACY: ± 17.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR-SPECIFIC FPD

ANALYTE: 1-octanethiol (sulfur)

DESORPTION: 2 mL acetone; 45 min ultrasonic agitation

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 200 °C
-COLUMN: 115 °C

CARRIER GAS: N_2 or He, 50 mL/min

COLUMN: 1.8 m x 4-mm ID glass; 3% OV-1 on 100/120 mesh Gas-Chrom Q or equivalent

CALIBRATION: 1-octanethiol in acetone

RANGE: 3 to 64 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION ($\bar{S}_r$): 0.030 [1]

APPLICABILITY: The working range is 0.05 to 1 ppm (0.3 to 6 mg/m^3) for a 10-L air sample.

INTERFERENCES: Presence of other volatile compounds may interfere with collection of 1-octanethiol or reduce capacity of sorbent tube.

OTHER METHODS: None evaluated by NIOSH.

REAGENTS:

1. Acetone*.
2. 1-Octanethiol, ≥97% purity.*
3. Calibration stock solution, 0.843 μg/μL. Dissolve 10 μL 1-octanethiol in 10 mL acetone. Prepare fresh daily.
4. Nitrogen or helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID, sealed with PTFE tape and plastic caps containing front (100-mg) and rear (50-mg) sections of 60/80 mesh Tenax-GC, separated and held in place by three silanized glass wool plugs. (Tenax-GC pretreatment: Sohxlet extraction for 6 hrs with acetone/methanol, 6 hrs with methanol, then drying under vacuum.) Typical pressure drop across tube is 2.4 kPa at 0.05 L/min flow. Similar commercially available tubes, e.g., SKC #226-35-03, are acceptable.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Gas chromatograph, sulfur-specific FPD, integrator and column (page 2510-1).
5. Vials, glass, 2- and 5-mL, crimp seals or caps, PTFE-lined silicone rubber septa.
6. Pipets, 1-, 2- and 5-mL, with pipet bulb.
7. Syringes, 10- and 100-μL.

SPECIAL PRECAUTIONS: Acetone is highly flammable (flash point = −18 °C).

Thiols are malodorous [2]. Prepare samples and standards in well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 15 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL acetone to each vial. Attach crimp cap to each vial.
7. Place vials in an ultrasonic bath for 45 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 60 μg 1-octanethiol per sample.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (square root of peak height vs. μg 1-octanethiol).

9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg 1-octanethiol recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2510-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Under these conditions, the retention time of 1-octanethiol is about 3.0 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak height.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of 1-octanethiol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1-octanethiol in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Analytical precision was determined by analyzing spiked sampling media [1]. The average desorption efficiency was 0.94. The breakthrough volume was greater than 15 L for a concentration of 14.6 mg/m^3 at 40 °C and 80% RH. Overall precision, bias and storage stability were determined by sampling and analyzing generated atmospheres. Generated concentrations were independently verified [1].

REFERENCES:

[1] Spafford, R. B., H. K. Dillon, D. H. Love, and W. K. Fowler. Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for n-Octanethiol and Benzenethiol, NIOSH Contract No. 210-79-0100, Southern Research Institute, Birmingham, AL, available from NTIS, PB 92-128-677, Springfield, VA 22161 (1982).

[2] Criteria for a Recommended Standard...Occupational Exposure to n-Alkane Mono Thiols, Cyclohexanethiol, and Benzenethiol, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-123 (1978).

METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0100.

OIL MIST, MINERAL

C_nH_{2n+2} where n ≥ 16 MW: not pertinent CAS: 8012-95-1 RTECS: PY8030000

METHOD: 5026, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 5 mg/m³
NIOSH: 5 mg/m³; STEL 10 mg/m³
ACGIH: 5 mg/m³ (as sampled by a method which does not collect vapor)

PROPERTIES: liquid; d 0.8 to 0.9 g/mL @ 20 °C; BP 360 °C; vapor pressure negligible

SYNONYMS: airborne mist of white mineral oil or the following water-insoluble petroleum-based cutting oils: cable oil; cutting oil; drawing oil; engine oil; heat-treating oils; hydraulic oils; machine oil; transformer oil.

SAMPLING

SAMPLER:	MEMBRANE FILTER (37-mm diameter, 0.8- or 5-μm pore size, PVC or MCE)
FLOW RATE:	1 to 3 L/min
VOL-MIN:	20 L @ 5 mg/m³
-MAX:	500 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	required for quantitative data

ACCURACY

RANGE STUDIED:	2.5 to 11.7 mg/m³ [1] (100-L samples)
BIAS:	− 0.84% [1,2]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.065 [1]
ACCURACY:	± 11.8%

MEASUREMENT

TECHNIQUE:	INFRARED SPECTROPHOTOMETRY
ANALYTE:	mineral oil
EXTRACTION:	10 mL $C_2Cl_3F_3$ (Freon 113)
IR SCAN:	3200 to 2700 cm^{-1} vs. blank $C_2Cl_3F_3$
CALIBRATION:	standard solutions of mineral oil in $C_2Cl_3F_3$
RANGE:	0.1 to 2.5 mg per sample
ESTIMATED LOD:	0.05 mg per sample [3]
PRECISION ($\bar{S}_r$):	0.05 [3]

APPLICABILITY: The working range is 1 to 20 mg/m³ for a 100-L air sample. This method is applicable to all trichlorotrifluoroethane-soluble mineral oil mists, but not to (nor does OSHA's standard cover) semi-synthetic or synthetic cutting fluids.

INTERFERENCES: Any aerosol (e.g., tobacco smoke) which absorbs infrared radiation near 2950 cm-1 interferes.

OTHER METHODS: This revises P&CAM 283 [3]. P&CAM 159 [4] and S272 [5] use similar samplers with measurement by fluorescence spectrophotometry. These methods have not been revised because of limited applicability (i.e., not all mineral oils contain fluorescent components and other fluorescent compounds interfere). Infrared analysis overcomes both of these limitations.

REAGENTS:

1. Trichlorotrifluoroethane ($C_2Cl_3F_3$).
2. Stock mineral oil standard, 20 mg/mL. Weigh 1.0 g of the bulk mineral oil sample into a 50-mL volumetric flask. Dilute to volume with $C_2Cl_3F_3$. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: membrane filter, PVC or MCE, 37-mm, 0.8- or 5-μm pore size; two-piece filter cassette.
   NOTE 1: High concentrations of oil mist may plug membrane filters. Glass fiber filters have a higher capacity for oil mist than membrane filters.
   NOTE 2: Handle filters carefully with tweezers to avoid contamination by skin oil.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Infrared spectrophotometer, double beam, dispersive, with scanning capability in the 3200-2700 cm^{-1} region, and two 10-mm spectrophotometer cells, infrared quartz with PTFE stoppers mounted in demountable cell holders.
   NOTE: Standard glass cells may be used if infrared quartz cells are not available.
4. Vials, scintillation, 20-mL, with foil-lined or PTFE-lined caps.*
5. Volumetric flasks, 10-, 25-, and 50-mL.*
6. Volumetric pipet or reagent dispenser, 10-mL.*
7. Pipets, 2- to 250-μL.
8. Tweezers.

* Rinse glassware with $C_2Cl_3F_3$. Air dry.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 3 L/min for a total sample size of 20 to 500 L.
   NOTE: High concentrations of oil mist may plug membrane filters creating unacceptably high pressure drops. If this occurs, terminate sampling.
3. Collect 5 to 10 mL of unused, undiluted mineral oil in a vial. Submit with samples for standard preparation.

SAMPLE PREPARATION:

4. Using tweezers, transfer each sample or blank filter to a vial. Add 10.0 mL $C_2Cl_3F_3$. Cap and shake vigorously.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards.
   a. Add known amounts of stock mineral oil standard to $C_2Cl_3F_3$ in 10-mL volumetric flasks and dilute to the mark to obtain mineral oil concentrations in the range 5 to 250 μg/mL.
   b. Analyze with samples and blanks (step 8).
   c. Prepare calibration graph (peak absorbance vs. mg mineral oil).

6. Determine recovery (R) at least once for each lot of filters used for sampling in the range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of stock mineral oil standard onto the filter. Allow solvent to evaporate.
   b. Store samples overnight in filter cassettes.
   c. Prepare and analyze with working standards.
   d. Prepare a graph of R vs. μg mineral oil recovered.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

8. Scan each standard solution and each blank or sample filter extract from 3200 to 2700 cm^{-1} in absorbance mode vs. $C_2Cl_3F_3$ in reference beam. Record absorbance at wavelength of largest absorbance near 2940 cm^{-1} ($\pm$ 11.8%).

CALCULATIONS:

9. Determine the mass, μg (corrected for R), of mineral oil found in the sample (W) and in the average media blank (B) from the calibration graph.
10. Calculate concentration, C, of mineral oil in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The sampling portion of this method was evaluated over the range 2.5 to 11.7 mg/m^3 at 22 °C and 755 mm Hg using 100-L air samples of Gulf machine cutting oil with measurement by fluorescence spectrophotometry. Mixed cellulose ester filters, 0.8-μm pore size, were used for sampling [1,5]. The overall precision was 0.065 with an average recovery of 98%. The infrared measurement method was subsequently evaluated by NIOSH [2,3]. Precision and accuracy of the infrared and fluorescence spectrophotometric techniques are similar.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as PB 274-248 from NTIS, Springfield, VA 22161.

[2] Bolyard, M. L. Infrared Quantitation of Mineral Oil Mist in Personal Air Samples, AIH Conference, Houston, TX (1980).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 283, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[4] Ibid., Vol. 1, P&CAM 159, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[5] Ibid., Vol. 3, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5600, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 3

SYNONYMS: Table 4

SAMPLING

SAMPLER: FILTER/SOLID SORBENT TUBE (OVS-2 tube: 13-mm quartz filter; XAD-2, 270 mg/140 mg)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 12 L
-MAX: 240 L; 60 L (Malathion, Ronnel)

SHIPMENT: cap both ends of tube

SAMPLE STABILITY: at least 10 days at 25 °C
at least 30 days at 0 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 5, Column A

ACCURACY: Table 5, Column B

BIAS: Table 5, Column C

OVERALL PRECISION ($\hat{S}_{rT}$): Table 5, Column D

MEASUREMENT

TECHNIQUE: GC, FLAME PHOTOMETRIC DETECTION (FPD)

ANALYTE: organophosphorus pesticides, Table 1

EXTRACTION: 2-mL 90% toluene/10% acetone solution

INJECTION VOLUME: 1-2 µL

TEMPERATURE
-INJECTION: 240 °C
-DETECTOR: 180 °C to 215 °C (follow manufacturer's recommendation)
-COLUMN: Table 6

CARRIER GAS: He at 15 psi (104 kPa)

COLUMN: fused silica capillary column; Table 6

DETECTOR: FPD (phosphorus mode)

CALIBRATION: standard solutions of organophosphorus compounds in toluene

RANGE: Table 8, Column C

ESTIMATED LOD: Table 8, Column F

PRECISION ($\bar{S}_r$): Table 5, Column E

APPLICABILITY: The working ranges are listed in Table 5. They cover a range of 1/10 to 2 times the OSHA PELs. This method also is applicable to STEL measurements using 12-L samples. This method may be applicable to the determination of other organophosphorus compounds after evaluation for desorption efficiency, sample capacity, sample stability, and precision and accuracy.

INTERFERENCES: Several organophosphates may co-elute with either target analyte or internal standard causing integration errors. These include other pesticides (see Table 7), and the following: tributyl phosphate (plasticizer), tris-(2-butoxy ethyl) phosphate (plasticizer used in some rubber stoppers), tricresyl phosphate (petroleum oil additive, hydraulic fluid, plasticizer, flame-retardant, and solvent), and triphenyl phosphate (plasticizer and flame-retardant in plastics, lacquers, and roofing paper).

OTHER METHODS: This method may be used to replace previous organophosphorus pesticide methods. See Table 10 for partial listing. The OVS-2 tube is similar in concept to the device of Hill and Arnold [11], but offers greater convenience and lower flow resistance.

REAGENTS:

1. Organophosphorus analytes listed in Table 1. and (optional) triphenyl phosphate, analytical standard grade.*
2. Toluene, pesticide analytical grade.*
3. Acetone, ACS reagent grade or better.*
4. Desorbing solution. Add 50 mL acetone to a 500-mL volumetric flask. Dilute to volume with toluene.
   NOTE: For optional internal standard, add 1 mL of a 5 mg/mL solution of triphenyl phosphate in toluene to 500 mL desorbing solution.
5. Organophosphorus stock solutions, 10 mg/mL. Prepare individual standard stock solutions of each pesticide of interest in 90/10 toluene/acetone (V/V). All pesticides in Table 1 were found to be soluble to at least 10 mg/mL.
6. Spiking solutions for calibration (step 9) and media fortification (steps 10, 11).
   NOTE: Spiking solutions may contain more than one analyte.
   a. Spiking solution SS-1: Dilute the volume of stock solution indicated in column F of Table 11 to 10 mL with toluene or 90/10 toluene/acetone.
   b. Spiking solution SS-2: Dilute 1 mL of SS-1 solution with toluene in a 10-mL volumetric flask.
7. Purified gases: Helium, hydrogen, nitrogen, dry air, and oxygen, (if required by detector).

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 11-mm ID x 13-mm OD x 50 mm long, with the outlet end drawn to a 6-mm o.d. x 25 mm long tube. The enlarged part of the tube contains a 270-mg front section of 20/60 mesh XAD-2 sorbent or equivalent held in place by a 9 to 10-mm o.d. quartz fiber filter and polytetrafluoroethylene (PTFE) retaining ring. The front section is separated from the back section of 140 mg XAD-2 sorbent or equivalent with a short plug of polyurethane foam. The back section is held in place by a long plug of polyurethane foam. The tube is available commercially as the OVS-2 sampler. See Figure 2.
   NOTE: Some OVS-2 tubes contain glass fiber filters, as specified in the OSHA methods (see Table 10). These tubes, however, did not perform as well for the more polar analytes (amides, phosphoramides, and sulfoxides; see Table 9). Low or erratic recoveries for Malathion may be encountered with glass fiber filters.
2. Personal sampling pump, 0.2 to 1 L/min. with flexible connecting tubing, preferably silicon, polyethylene, or PTFE tubing.
3. Vials, 4-mL with PTFE-lined cap; 2-mL GC autosampler vials with PTFE-lined crimp caps.
4. Gas chromatograph, flame photometric detector with 525-nm bandpass filter for phosphorus mode, integrator, and column (Table 6).
5. Syringes, 5-mL and 100-, 50-, and 10-mL for making standard solutions and GC injections.
6. Volumetric flasks, 500-, 10-, and 2-mL.
7. Tweezers.
8. GC vial crimper.
9. Small ultrasonic cleaning bath.

SPECIAL PRECAUTIONS: Organophosphorus compounds are highly toxic. Special care must be taken to avoid inhalation or skin contact through the wearing of gloves and suitable clothing when handling pure material [13-17].

Toluene is flammable and toxic. Acetone is highly flammable. Prepare all samples in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to personal sampling pump with flexible tubing. The sampler should be placed vertically with the large end down, in the worker's breathing zone in such a manner that it does not impede work performance. [4, 12]

3. Sample at an accurately known flowrate between 0.2 and 1 L/min for a total sample size of 12 to 240 L.
4. Cap both ends of the sampler with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end and remove PTFE retainer ring; transfer filter and front XAD-2 section to a 4-mL vial. Transfer the short polyurethane foam plug along with back-up XAD-2 section to a second 4-mL vial.
6. Add 2 mL of desorbing solvent to each vial using a 5-mL syringe or 2-mL pipette. Cap each vial.
7. Allow to stand 30 minutes, immerse vials approximately 15 mm in an ultrasonic bath for 30 minutes. Alternatively, place the vials in a shaker or tumbler for 1 hour.
8. Transfer 1 to 1.5 mL from each 4-mL vial to a clean 2-mL GC vial, cap and label.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes.
   a. Add known amounts of calibration spiking solution (SS-1 or SS-2 according to schedule in Table 11) to desorbing solution in 2-mL volumetric flasks and dilute to the mark.
      NOTE: If an internal standard is included in the desorbing solution, then exactly 2 mL of desorbing solution in a volumetric flask must be concentrated slightly under a gentle stream of nitrogen in order to accommodate the specified volume of the spiking solutions. After adding the spiking solutions to the slightly concentrated desorbing solution, dilute to the 2-mL mark with toluene or 90/10 toluene/acetone.
   b. Include a calibration blank of unspiked desorbing solution.
   c. Analyze together with field samples, field blanks, and laboratory control samples (steps 12 and 13).
   d. Prepare calibration graph (peak area vs. μg analyte), or if internal standard (IS) is used (peak area of analyte/peak area of IS vs. μg analyte).
10. Prepare Laboratory Control Samples (LCS) with each sample set, in duplicate.
   a. Remove cap from large end of sampler tube. Apply 30 μL of spiking solution SS-1 to face of quartz fiber filter. Cap and allow to stand for a minimum of 1 hour. Preferably, these should be prepared as soon as samples arrive and should be stored with the field samples until analyzed.
   b. Include an unspiked sampler as a media blank.
   c. Analyze along with field samples and blanks, and liquid calibration standards (steps 12 through 16).
11. When extending application of this method to other organophosphorus compounds, the following minimal desorption efficiency (DE) test may be performed as follows:
   a. Determine the NIOSH REL, OSHA PEL, or ACGIH TLV in mg/m^3.
   b. Prepare spiking solution SS-1 (refer to Table 11, or use the following formulae, which are specific for the calculation of the weight of analyte to add to 10 mL toluene/acetone 90:10).
      For REL > 1 mg/m^3 (assuming 12-L collection vol.), let W = REL x 4 m^3
      For REL $\leq$ 1 mg/m^3 (assuming 120-L collection vol.), let W = REL x 40 m^3
      where W = weight (mg) of analyte to dissolve into 10 mL of desorbing solvent.
      Let [SS-1] = W/10 mL where [SS-1] = concentration of spiking solution SS-1 in mg/mL.
      Let [SS-2] = [SS-1] x 0.1 where [SS-2] = concentration of spiking solution SS-2.
   d. Prepare three tubes at each of five levels plus three media blanks. Concentration at each level may be calculated using formulae in entry 20, part II of Table 11.
      i. Remove plastic cap from large end of sampler, apply appropriate volume of spiking solution to face of quartz fiber filter following schedule in part I of Table 11.
      ii. Cap and allow sampler to stand overnight.
   e. Prepare tubes for analysis (Steps 5 through 8).

f. Analyze with liquid standards (Steps 12 and 13).
g. Prepare a graph of desorption efficiency (DE) vs. μg of analyte.
h. Acceptable desorption criteria for 6 replicates is >75% average recovery with a standard deviation of < ±9%.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 6 and on page 5600-1. Inject sample aliquot manually using solvent flush technique or with autosampler. See Table 7 for retention times of selected analytes.
    NOTE: If peak area is greater than the linear range of the working standards, dilute with desorbing solution or with desorbing solution (containing internal standard) and reanalyze. Apply the appropriate dilution factor in calculations.
13. Measure peak area of analyte and of internal standard.

CALCULATIONS:

14. Determine the mass in μg (corrected for DE) of respective analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: The filter is combined with the front section. If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \quad mg/m^3.$$

CONFIRMATION:

16. Whenever an analyte is detected, and its identity is uncertain, confirmation may be achieved by analysis on a second column of different polarity. If primary analysis was performed using a non-polar or weakly polar column (DB-1 or DB-5), confirmation should be accomplished by reanalysis on a polar column (DB-1701 or DB-210). See Table 7 for approximate retention times for each column type. Fewer analytes co-elute on DB-210 than on DB-1701. Relative retention times are more convenient for the identification of unknown analytes. If Parathion is not used as the retention time reference compound, then another related compound such as tributyl phosphate, Ronnel, or triphenyl phosphate may be substituted.

EVALUATION OF METHOD:

This method was evaluated over the ranges specified in Table 5 at 25 °C using 240-L air samples. Sampler tubes were tested at 15% and 80% relative humidity and at 10 °C and 30 °C. In these tests, test atmospheres were not generated; instead, analytes were fortified on the face of the sampler filters. This was followed by pulling conditioned air at 1 L/min. for 4 hours. No difference in sampler performance was noted at any of these temperature/humidity combinations. Evaluations of sampler precision and stability were conducted at 30 °C and 15% relative humidity. Overall sampling and measurement precisions, bias, accuracy, and average percent recovery after long-term storage are presented in Table 5. No breakthrough was detected after 12 hours of sampling at 1 L/min with a sampler fortified with the equivalent of 4x the NIOSH REL. Malathion and Ronnel were tested at 1/40 x REL, Sulprofos at 1/20 x REL (See Table 5, note 4). All criteria [9] were met.

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METHOD WRITTEN BY:

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Table 1. Formula and Registry Numbers

Compound (alphabetically)	MW[1] (Daltons)	Empirical Formula	Structural Formula	CAS # [2,3,4]	RTECS[2]
1. Azinphos methyl	317.32	$C_{10}H_{12}N_3O_3PS_2$	$(CH_3O)_2P(=S)SCH_2(C_7H_4N_3O)$	86-50-0	TE1925000
2. Chlorpyrifos	350.58	$C_9H_{11}Cl_3NO_3PS$	$(C_2H_5O)_2P(=S)O(C_5HN)Cl_3$	2921-88-2	TF6300000
3. Diazinon	304.34	$C_{12}H_{21}N_2O_3PS$	$(C_2H_5O)_2P(=S)O(C_4HN_2)(CH_3)CH(CH_3)_2$	333-41-5	TF3325000
4. Dicrotophos	237.19	$C_8H_{16}NO_5P$	$(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)N(CH_3)_2$	141-66-2	TC3850000
5. Disulfoton	274.39	$C_8H_{19}O_2PS_3$	$(C_2H_5O)_2P(=S)S(CH_2)_2SC_2H_5$	298-04-4	TD9275000
6. Ethion	384.46	$C_9H_{22}O_4P_2S_4$	$[(C_2H_5O)_2P(=S)S]_2CH_2$	563-12-2	TE4550000
7. Ethoprop	242.33	$C_8H_{19}O_2PS_2$	$(C_3H_7S)_2P(=O)OC_2H_5$	13194-48-4	TE4025000
8. Fenamiphos	303.36	$C_{13}H_{22}NO_3PS$	$(CH_3)_2CHNHP(=O)(O[C_2H_5])O(C_6H_3)(CH_3)SCH_3$	22224-92-6	TB3675000
9. Fonofos	246.32	$C_{10}H_{15}OPS_2$	$C_2H_5OP(C_2H_5)(=S)S(C_6H_5)$	944-22-9	TA5950000
10. Malathion	330.35	$C_{10}H_{19}O_6PS_2$	$(CH_3O)_2P(=S)SCH[C(=O)OC_2H_5]CH_2C(=O)OC_2H_5$	121-75-5	WM8400000
11. Methamidophos	141.12	$C_2H_8NO_2PS$	$CH_3OP(=O)(NH_2)SCH_3$	10265-92-6	TB4970000
12. Methyl parathion	263.20	$C_8H_{10}NO_5PS$	$(CH_3O)_2P(=S)O(C_6H_4)NO_2$	298-00-0	TG0175000
13. Mevinphos (E)	224.15	$C_7H_{13}O_6P$	$(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)OCH_3$	298-01-1[2]	GQ5250100
Mevinphos (E & Z)				7786-34-7[3,4]	GQ5250000
14. Monocrotophos (Z)	223.17	$C_7H_{14}NO_5P$	$(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)NHCH_3$	919-44-8[2]	TC4981100
Monocrotophos (E)				6923-22-4[3,4]	TC4375000
15. Parathion	291.26	$C_{10}H_{14}NO_5PS$	$(C_2H_5O)_2P(=S)O(C_6H_4)NO_2$	56-38-2	TF4550000
16. Phorate	260.36	$C_7H_{17}O_2PS_3$	$(C_2H_5O)_2P(=S)SCH_2SC_2H_5$	298-02-2	TD9450000
17. Ronnel	321.54	$C_8H_8Cl_xO_3PS$	$(CH_3O)_2P(=S)O(C_6H_2)Cl_3$	299-84-3	TG0525000
18. Sulprofos	322.43	$C_{12}H_{19}O_2PS_3$	$C_2H_5OP(S[C_3H_7])(=S)O(C_6H_4)SCH_3$	35400-43-2	TE4165000
19. Terbufos	288.42	$C_9H_{21}O_2PS_3$	$(C_2H_5O)_2P(=S)SCH_2SC(CH_3)_3$	13071-79-9	TD7740000

(1) Molecular weights calculated from the empirical formula using 1979 IUPAC Atomic Weights of the Elements.
(2) RTECS = NIOSH Registry of Toxic Effects of Chemical Substances [1].
(3) Merck Index [2].
(4) Farm Chemicals Handbook [3].

Table 2. Toxicity and Maximum Exposure Limits

Compound (alphabetically)	LD_{50}, mg/Kg[1]	OSHA PEL[4] mg/m³	NIOSH REL[5] mg/m³	(ppm)	ACGIH TLV mg/m³	STEL mg/m³
1. Azinphos methyl	11 f	0.2	0.2	(0.015)	0.2 (skin)	
2. Chlorpyrifos	145	0.2	0.2	(0.014)	0.2 (skin)	0.6[5]
3. Diazinon	250 m, 285 f	0.1	0.1	(0.008)	0.1 (skin)	
4. Dicrotophos	16 f, 21 m	0.25	0.25	(0.026)	0.25 (skin)	
5. Disulfoton	2.3 f, 6.8 m	0.1	0.1	(0.009)	0.1[3] (skin)	
6. Ethion	27 f, 65 m	0.4	0.4	(0.025)	0.4 (skin)	
7. Ethoprop	61.5[2]					
8. Fenamiphos	10	0.1	0.1	(0.008)	0.1 (skin)	
9. Fonofos	3 f, 13 m[3]	0.1	0.1	(0.010)	0.1 (skin)	
10. Malathion	1000 f, 1375 m	10	10	(0.740)	10 (skin)	
11. Methamidophos	25 m, 27 f					
12. Methyl parathion	14 m, 24 f	0.2	0.2	(0.019)	0.2 (skin)	
13. Mevinphos	3.7 f, 6.1 m	0.1	0.1	(0.011)	0.1 (skin)	0.27[6]
14. Monocrotophos	17 m, 20 f	0.25	0.25	(0.027)	0.25[3] (skin)	
15. Parathion	3.6 f, 13 m	0.1	0.05	(0.004)	0.1 (skin)	
16. Phorate	1.1 f, 2.3 m	0.05	0.05	(0.005)	0.05 (skin)	0.2[5,6]
17. Ronnel	1250 m, 2630 f	10	10	(0.760)	10 (skin)	
18. Sulprofos	227	1	1	(0.076)	1[3] (skin)	
19. Terbufos	1.6-4.5 m, 9.0 f					

(1) Rat-oral; from Merck Index, unless otherwise noted, f = female, m = male [2].
(2) Farm Chemicals Handbook [3].
(3) RTECS [1].
(4) OSHA Final Rule, 1989 (unenforceable, 1992); only Malathion and Parathion had previous PELs.
(5) NIOSH Recommendations for Occupational Safety and Health [5].
(6) ACGIH [18].

Table 3. Physical Properties[1]

Compound (alphabetically)	Liquid Density (g/mL)	MP (°C)	BP °C (mm Hg)	Vapor Pressure Pascal	Vapor Pressure mm Hg	@ °C	Solubility in Water (mg/L at 20 °C)
1. Azinphos methyl	1.44	73-74	unstable >200	0.00018	$1.35x10^{-6}$	20[3]	30[6]
2. Chlorpyrifos	none found	41-42	—	0.0025	$1.87x10^{-5}$	25	—
3. Diazinon	1.116-1.118	liquid	decomp. >120	0.019	$1.4x10^{-4}$	20	40
4. Dicrotophos	1.216	liquid	400 (760)		none found		miscible
5. Disulfoton	1.144	oil	—	0.024	$1.8x10^{-4}$	20	nearly insol.
				0.0074	$5.4x10^{-5}$	20[3]	insol.[3]
6. Ethion	1.220	-12 to -13	—	0.0002	$1.5x10^{-6}$		slightly sol.
7. Ethoprop	1.094	oil	—	0.047	$3.5x10^{-4}$	26	750
8. Fenamiphos	none found	49	—	0.00012	$9x10^{-7}$	20[3]	329
9. Fonofos	1.16	liquid	—		none found		13[7]
10. Malathion	1.23	2.9	156 (0.7)[6]	0.005	$4x10^{-5}$	30[6]	145
11. Methamidophos	1.31	54.	—	0.04	$3x10^{-4}$	30	readily sol.
				0.0023	$1.7x10^{-5}$	20[3]	—
12. Methyl parathion	1.358	37-38	—	0.0002	$1.5x10^{-6}$	20[3]	50
13. Mevinphos	1.25	20.6[4]	325 (760) [4]	0.4	$3x10^{-3}$	20[4]	miscible
				0.29	$2.2x10^{-3}$	20[7]	—
14. Monocrotophos	none found	54-55[5]	—	0.0009	$7x10^{-6}$	20	miscible
15. Parathion	1.26	6	375 (760)	0.005	$3.78x10^{-5}$	20[6]	20
				0.00089	$6.7x10^{-6}$	20[3]	10[8]
16. Phorate	1.156	liquid	118-120 (2.0)[3]	0.11	$8.4x10^{-4}$	20	50
17. Ronnel	sp. gr=1.48[2]	41	—	0.1	$8.x10^{-4}$	25	40 @ 25 °C
18. Sulprofos	1.20	liquid	210 (0.1)[6]	<0.0001	$<10^{-6}$	20[3]	nearly insol.[3]
19. Terbufos	1.105	-29.2	—		none found		10-15

(1) From Merck Index, unless otherwise noted [2].
(2) NIOSH 2nd Edition Method for Ronnel, S299 [7].
(3) Farm Chemicals Handbook [3].
(4) NIOSH 3rd Edition Method 2503 for Mevinphos [8].
(5) 54-55 °C for pure material, 25-30 °C for commercial mixture.
(6) NIOSH 3rd Edition Method 5012 (EPN, Malathion, Parathion) [8].
(7) OSHA Stopgap Methods (See specific analyte Method) [4].
(8) NIOSH Pocket Guide [6].

Table 4. Synonyms

	Compound[1] (alphabetically)	Other name[2]	CAS Name
1.	Azinphos methyl	Guthion*	Phosphorodithioic acid, O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] ester[3]
2.	Chlorpyrifos	Dursban*	Phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester[3]
3.	Diazinon	Spectracide*	Phosphorothioic acid, O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester[3]
4.	Dicrotophos	Bidrin*	Phosphoric acid, 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl ester[3] Phosphoric acid, dimethyl ester, ester with cis-3-hydroxy-N,N-dimethylcrotonamide[4]
5.	Disulfoton	Di-Syston*	Phosphorodithioic acid, O,O-diethyl S-[2-(ethylthio)ethyl] ester[3]
6.	Ethion		Phosphorodithioic acid, S,S'-methylene O,O,O',O'-tetraethyl ester[3] O,O,O',O'-Tetraethyl S,S'-methylenediphosphorodithioate[4]
7.	Ethoprop	Prophos*	Phosphorodithioic acid, O-ethyl S,S-dipropyl ester[3]
8.	Fenamiphos	Nemacur*,Phenamiphos[1]	(1-Methylethyl)phosphoramidic acid, ethyl 3-methyl-4-(methylthio)phenyl ester[3] Phosphoramidic acid, isopropyl-, 4-(methylthio)-m-tolyl ethyl ester[4]
9.	Fonofos	Dyfonate*	Ethyl phosphonodithioic acid, O-ethyl S-phenyl ester[3] Phosphonodithioic acid, ethyl-, O-ethyl S-phenyl ester[4]
10.	Malathion	Cythion*	[(Dimethoxyphosphinothioyl)thio]butanedioic acid diethyl ester[3] Succinic acid, mercapto-, diethyl ester, S-ester with O,O-dimethylphosphorodithioate[4]
11.	Methamidophos	Monitor*	Phosphoramidothioic acid, O,S-dimethyl ester[3]
12.	Methyl parathion	Parathion Methyl[1]	Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl) ester[3]
13.	Mevinphos	Phosdrin*	3-[(Dimethyoxyphosphinyl)oxy]-2-butenoic acid, methyl ester[3] Crotonic acid, 3-hydroxy-, methyl ester dimethyl phosphate[4]
14.	Monocrotophos	Azodrin*	Phosphoric acid, dimethyl [1-methyl-3-(methylamino)-3-oxo-1-propenyl] ester[3] Phosphoric acid, dimethyl ester, ester with (E)-3-hydroxy-N-methylcrotonamide[4]
15.	Parathion	Ethyl Parathion[1]	Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl) ester[3]
16.	Phorate	Thimet*	Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)methyl] ester[3]
17	Ronnel	Fenchlorphos[1]	Phosphorothioic acid, O,O-dimethyl O-(2,4,5-trichlorophenyl) ester[3]
18.	Sulprofos	Bolstar*	Phosphorodithioic acid, O-ethyl O-[4-(methylthio)phenyl] S-propyl ester[4]
19.	Terbufos	Counter*	Phosphorodithioic acid, O,O-diethyl S-[[(1,1-dimethylethyl)thio]methyl] ester[4]

(1) Common name as given in Farm Chemicals Handbook [3].
(2) *=Trade name (Trademark or Registered Name) as given in Farm Chemicals Handbook [3].
(3) Merck Index [2].
(4) RTECS [1] or alternate CAS name in Merck Index [2].

Table 5. Method Evaluation[1]

Compound (alphabetically)	A. Range Studied[2] mg/m³	mg/sample	B. Accuracy	C. Bias Ave.	Range	D. Precision Overall, $\hat{S}_{rT}$	E. Measurement, $\hat{S}_r$	G. % Recovery at 30 days 25 °C (0 °C)
1. Azinphos methyl	0.02-0.4	0.0048-0.096	± 0.178	-0.038	(-0.120 - +0.028)	0.070	0.030	97 (105)
2. Chlorpyrifos	0.02-0.4	0.0048-0.096	± 0.163	-0.027	(-0.054 - +0.017)	0.068	0.018	92 (90)
3. Diazinon	0.01-0.2	0.0024-0.048	± 0.162	-0.032	(-0.057 - -0.005)	0.065	0.020	94 (93)
4. Dicrotophos	0.025-0.5	0.006-0.120	± 0.169	-0.037	(-0.102 - -0.032)	0.066	0.025	89 (92)
5. Disulfoton	0.01-0.2	0.0024-0.048	± 0.196	-0.064	(-0.081 - -0.032)	0.066	0.024	87 (89)
6. Ethion	0.04-0.8	0.0096-0.192	± 0.165	-0.029	(-0.056 - -0.003)	0.068	0.018	96 (95)
7. Ethoprop[3]	0.01-0.2	0.0024-0.048	± 0.157	-0.025	(-0.058 - +0.025)	0.066	0.024	97 (93)
8. Fenamiphos	0.01-0.2	0.0024-0.048	± 0.155	-0.029	(-0.066 - +0.002)	0.063	0.022	94 (96)
9. Fonofos	0.01-0.2	0.0024-0.048	± 0.168	-0.036	(-0.076 - +0.008)	0.066	0.023	95 (92)
10. Malathion[4]	0.025-0.5	0.006-0.120	± 0.172	-0.038	(-0.064 - -0.014)	0.067	0.019	93 (93)
11. Methamidophos[5]	0.02-0.4	0.0048-0.096	± 0.156	-0.018	(-0.046 - +0.011)	0.069	0.026	88 (95)
12. Methyl parathion	0.02-0.4	0.0048-0.096	± 0.160	-0.034	(-0.082 - +0.016)	0.063	0.018	95 (95)
13. Mevinphos	0.01-0.2	0.0024-0.048	± 0.176	-0.042	(-0.061 - -0.004)	0.067	0.028	89 (91)
14. Monocrotophos	0.025-0.5	0.006-0.120	± 0.185	-0.043	(-0.047 - -0.020)	0.071	0.026	88 (92)
15. Parathion	0.005-0.1	0.0012-0.024	± 0.163	-0.021	(-0.045 - +0.011)	0.071	0.019	92 (92)
16. Phorate	0.005-0.1	0.0012-0.024	± 0.202	-0.070	(-0.097 - -0.047)	0.066	0.025	91 (91)
17. Ronnel[4]	0.025-0.5	0.006-0.120	± 0.172	-0.040	(-0.076 - +0.021)	0.066	0.018	95 (94)
18. Sulprofos[4]	0.01-0.2	0.0024-0.048	± 0.181	-0.047	(-0.054 - -0.031)	0.067	0.017	94 (94)
19. Terbufos[3]	0.01-0.2	0.0024-0.048	± 0.188	-0.054	(-0.091 - -0.024)	0.067	0.022	92 (91)

(1) NIOSH Back-up Data Report [9]
(2) The ranges studied were 1/10 to 2x the NIOSH REL (except as noted) sampling at 1 L/min for 4 hours.
(3) No NIOSH REL or OSHA PEL available; used 0.1 mg/m³.
(4) Malathion and Ronnel were studied at 1/400 to 1/20 the NIOSH REL, Sulprofos at 1/200 to 1/10 the NIOSH REL.
(5) No NIOSH REL or OSHA PEL available; used 0.2 mg/m³.

Table 6. Recommended Gas Chromatographic Columns and Conditions[1]

Parameter	Wide Bore Fused Silica Capillary Column			
Stationary Phase[2]	DB-1	DB-5	DB-1701	DB-210
Polarity	non-polar	weakly polar	mod. polar	mod. polar
Length (meters)	30	30	30	30
I.D. (millimeters)	0.32	0.32	0.32	0.32
Film thickness (mm)[3]	0.25	1.0	.1.0	0.25
Injection (vol., mode)[4][5]	1 µL, SPL	1 µL, DIR	1 µL, DIR	1 µL, SPL
Oven Temperatures				
Initial (°C)	100	125	125	100
Final (°C)	275	275	275	250
Max. Recommended (°C)[5]	325	325	280	240/260
Program (°C/min.)	3.0	4.0	4.0	3.0
Carrier Gas (Helium)				
Head pressure (p.s.i.)	15	15	15	15

(1) Actual conditions may vary depending on column and analytical objectives. The conditions given above are those corresponding to the RT data in Table 7.

(2) DB-1, 100% methyl silicone; DB-5, 5% phenyl, 95% methyl silicone; DB-1701, 14% cyanopropylphenyl, 86% methyl silicone; DB-210, 50% trifluoropropyl, 50% methyl silicone. Other phase types may also work well.

(3) Thinner films give faster separations at lower temperatures promoting analyte stability.

(4) Use 2-mm i.d. injection port lines for 0.5-µL injection and 4-mm i.d. injection port liners for 1-to-2-µL injections with 0.32-mm i.d. capillary columns.

(5) SPL = splitless mode, initial oven temperature 5-10 °C < BP of desorption solvent;
DIR = direct mode, initial oven temperature 5-10 °C > BP of desorption solvent.
In both modes, split-vent off time should be 60 sec for 1-2 µL injections with 4-mm ID injection port liners, and 20-30 sec for 0.5-µL injections with 2-mm ID injection port liners. Use 2-mm ID injection port liners for 0.5-µL injection and 4-mm ID injection port liners for 1-2 µL injections with 0.32-mm ID capillary columns.

(6) J & W Scientific Catalog, p. 21. [10]

Table 7. Approximate Retention Times of Selected Organophosphorous Compounds[1]

Compound (by RT on DB-1)	Capillary Column[2]					
	DB-1			DB-5	DB-1701	DB-210
	RT min	RRT[3]	Elution T, °C[4]	RT, min	RT, min	RT, min
1. TEPP	3.71	0.128	111	5.47	7.18[B]	7.88
2. Triethylphosphorothioate	4.37	0.151	113	6.34	7.14[B]	4.93
3. Methamidophos	5.12	0.177	115	7.64	13.61	12.03
4. Dichlorvos	5.81	0.200	117	8.24	10.67	10.54
5. Mevinphos	10.45	0.360	131	12.92	16.69	19.20
6. Ethoprop	17.15	0.592	151	19.09	21.52	20.10
7. Naled	17.61	0.608	153	no data	23.17[C]	21.46[H]
8. Dicrotophos	18.00	0.621	154	19.94	25.84[E]	31.43
9. Monocrotophos	18.27	0.630	155	20.12	28.11	31.60
10. Sulfotepp	19.06	0.658	157	no data	23.09[C]	21.11
11. Phorate	19.18	0.662	158	20.94	23.10[C]	18.92
12. Dimethoate	19.44	0.671	158	21.84	no data	29.33[I]
13. Demeton-S	20.15	0.695	160	21.70	25.06[D]	24.97
14. Dioxathion	21.30	0.735	164	23.04	26.33[F]	23.46
15. Fonofos	22.04	0.760	166	23.57	25.87[E]	22.20
16. Terbufos	22.22	0.767	168	23.80	25.02[D]	21.52[H]
17. Disulfoton	23.09	0.797	169	24.19	26.43[F]	22.78
18. Diazinon	23.37	0.806	170	23.75	25.00[D]	20.99
19. Methyl parathion	25.37	0.875	176	26.48	31.37	33.21
20. Oxydemeton methyl	26.[5]	0.90	179	no data	no data	no data
21. Ronnel	26.86	0.927	181	27.39	29.30	26.27
22. Pirimiphos methyl	28.13	0.971	184	27.90	29.72	26.77
23. Malathion	28.53	0.984	186	28.33	31.78[G]	33.08[J]
24. Fenthion	28.74	0.992	186	28.93	31.78[G]	29.35[I]
25. Parathion	28.98	1.000	187	29.10[A]	33.28	35.60
26. Chlorpyrifos	29.11	1.004	187	29.10[A]	30.79	27.72
27. Crufomate	29.64	1.023	189	29.54	34.00	35.34
28. Isofenphos	31.91	1.101	196	31.17	33.81	33.02[J]
29. Tetrachlorvinphos	33.26	1.148	200	32.60	35.96	37.01
30. Fenamiphos	34.09	1.176	202	33.03	37.14	38.95
31. Merphos	35.19	1.214	206	no data	30.57	23.89
32. Fensulfothion	36.61	1.263	210	35.78	42.41	46.98
33. Ethion	37.88	1.307	214	36.30	39.30	37.96
34. Sulprofos	38.49	1.328	216	36.96	39.54	37.11
35. Triphenyl phosphate	40.88	1.411	223	39.06	no data	no data
36. EPN	42.64	1.471	228	41.06	47.83	47.13
37. Azinphos methyl	44.16	1.524	232	43.67	no elution	49.24
38. Leptophos	45.12	1.557	235	43.91	47.38	41.68
39. Azinphos ethyl	46.55	1.606	240	46.50	47.43	50.40
40. Coumaphos	49.31	1.702	248	50.10	67.86	60.88

(1) Actual retention times (RT) will vary with individual columns and chromatographic conditions. See Table 9 for chromatographic performance notes. Capillary Column conditions given in Table 6. Data from Backup Data Report [9].

(2) Sets of co-eluting or nearly co-eluting peaks are identified by letters: (A), (B), (C), (D), (E), (F), (G), (H), (I), and (J)

(3) Retention times relative to Parathion.

(4) Elution temperature (°C) for DB-1 column (see Table 6 for column conditions.) Elution temperatures are provided for convenience in selecting approximate GC oven temperatures for isothermal analyses of single or several closely eluting analytes.

(5) Broad, tailing peak.

Table 8. Applicable Working Range and Estimated LOD

Compound (alphabetically)	A. Applicable Working Range Atmospheric[1] mg/m³	B. Applicable Working Range Atmospheric[1] ppm[3]	C. Sample[4] µg/sample	D. Instrument[6] ng on column	E. Estimated LOD Instrument ng on column	F. Estimated LOD Sample[4] µg/sample	G. Estimated LOD Atmospheric[4] mg/m³	Margin of Sensitivity[2] REL/LOD
1. Azinphos methyl	0.02-0.6	0.0015-0.046	2.4 to 72	1.2-36	0.06	0.12	0.0012	167
2. Chlorpyrifos	0.02-0.6	0.0014-0.042	2.4 to 72	1.2-36	0.02	0.04	0.0004	500
3. Diazinon	0.01-0.3	0.0008-0.024	1.2 to 36	0.6-18	0.02	0.04	0.0004	250
4. Dicrotophos	0.025-0.75	0.0026-0.077	3.0 to 90	1.5-45	0.1	0.2	0.002	125
5. Disulfoton	0.01-0.3	0.0009-0.027	1.2 to 36	0.6-18	0.02	0.04	0.0004	250
6. Ethion	0.04-1.2	0.0025-0.076	4.8 to 144	2.4-72	0.02	0.04	0.0004	1000
7. Ethoprop	0.01-0.3	0.0010-0.030	1.2 to 36	0.6-18	0.02	0.04	0.0004	(7)
8. Fenamiphos	0.01-0.3	0.0008-0.024	1.2 to 36	0.6-18	0.07	0.14	0.0014	71
9. Fonofos	0.01-0.3	0.0010-0.030	1.2 to 36	0.6-18	0.02	0.04	0.0004	250
10. Malathion	1.0-30	0.074-2.2	12. to 360[5]	6.-180[5]	0.05	0.1	0.001	10,000
11. Methamidophos	0.02-0.6	0.0035-0.10	2.4 to 72	1.2-36	0.3	0.6	0.005	(7)
12. Methyl parathion	0.02-0.6	0.0019-0.056	2.4 to 72	1.2-36	0.02	0.04	0.0004	500
13. Mevinphos	0.01-0.3	0.0011-0.033	1.2 to 36	0.6-18	0.06	0.12	0.0012	83
14. Monocrotophos	0.025-0.75	0.0027-0.082	3.0 to 90	1.5-45	0.2	0.4	0.004	63
15. Parathion	0.005-0.15	0.0004-0.013	0.6 to 18	0.3-9	0.02	0.04	0.0004	125
16. Phorate	0.005-0.15	0.0005-0.014	0.6 to 18	0.3-9	0.02	0.04	0.0004	125
17. Ronnel	1.0-30	0.076-2.3	12. to 360[5]	6.-180[5]	0.02	0.04	0.0004	25,000
18. Sulprofos	0.1-3.0	0.0076-0.23	12. to 360	6.-180	0.03	0.06	0.0005	2000
19. Terbufos	0.01-0.3	0.0008-0.026	1.2 to 36	0.6-18	0.02	0.04	0.0004	(7)

(1) To cover range of 1/10 to 3x NIOSH REL.
(2) REL in mg/m³ (Table 2) ÷ Atmospheric LOD (Column G, Table 8).
(3) Calculated for 25 °C and 760 mm Hg (NTP).
(4) Calculated for a collection volume of 120 L (2 h @ 1 L/min, 4 h @ 0.5 L/min, or 10 h @ 0.2 L/min).
(5) Calculated for a collection volume of 12 L (12 min @ 1 L/min, 24 min @ 0.5 L/min, or 1 h @ 0.2 L/min).
(6) Desorbing sample in 2.0 mL solvent and injecting 1 µL into gas chromatograph.
(7) No REL

Table 9. Notes on Analytical Characteristics of Organophosphorous Compounds[1]

Compound (Alphabetically)	Analytical Characteristics		
	A Chemical and Physical	B Desorption and Solution	C Gas Chromatography
1. Azinphos methyl (Guthion*)			3,5,6
2. Azinphos ethyl (Guthion ethyl)			5
3. Chlorpyrifos (Dursban*)			
4. Coumaphos (Co-Ral*)			5
5. Crufomate (Ruelene*)	1	1,4	1
6. Demeton (Systox*)	2,6	5	3
7. Diazinon (Spectracide*)			
8. Dichlorvos (DDVP, Vapona*)	7		4
9. Dicrotophos (Bidrin*)			
10. Dimethoate (Cygon*)	1	1,4	1
11. Dioxathion (Delnav*)			
12. Disulfoton (Di-Syston*)	2		2
13. EPN (Santox*)			5
14. Ethion			
15. Ethoprop (Prophos*)			
16. Fenamiphos (Nemacur*)	1	1,4	1
17. Fensulfothion (Dasanit*)	3	4	
18. Fenthion (Baytex*)		5	
19. Fonofos (Dyfonate*)			
20. Isofenphos (Oftanol*)	1	1	1
21. Leptophos (Phosvel*)		5	5
22. Malathion (Cythion*)			
23. Merphos (Folex*)	4	5	2
24. Methamidophos (Monitor*)	1	1,3,4	1,4
25. Methyl parathion (Parathion methyl)			
26. Mevinphos (Phosdrin*)	6,7		3,4
27. Monocrotophos (Azodrin*)	1	1,2,4	1
28. Naled (Dibrom*)	5	5	2
29. Oxydemeton methyl (Metasystox-R)	3	1,5	1,2
30. Parathion (Ethyl parathion)			
31. Phorate (Thimet*)	2,7		2
32. Pirimiphos methyl (Actellic*)			4
33. Ronnel (Fenchlorphos)			
34. Sulfotepp (TEDP)			
35. Sulprofos (Bolstar*)			
36. TEPP	7	5	4
37. Terbufos (Counter*)	2		2
38. Tetrachlorvinphos (Gardona*)			
39. Tributyl phosphate			7
40. Triphenyl phosphate			7

* = Trade name, Registered name, or Trademark (Farm Chemicals Handbook [3]).

(1) Observations made during selection and validation of selected analytes [9]; refer to notes on the following page.

Table 9 (Continued) - Notes on ANALYTICAL CHARACTERISTICS

A. CHEMICAL AND PHYSICAL

1. Amide or phosphoramide, some slightly acidic, very polar chemically.
2. Alkyl thioether, easily oxidized to sulfone and sulfoxide.
3. Sulfoxides, easily oxidized to sulfone. Also very polar chemically.
4. Phosphite, easily air oxidized to phosphate (Merphos → DEF).
5. Vicinal dibromide, easily debrominated (Naled → Dichlorvos).
6. Two or more isomers commonly exist (e.g. Demeton-O and Demeton-S; cis- and trans- mevinphos).
7. Relatively volatile, can be lost if media or vials are left uncapped for even a short period of time.

General: Organophosphorous compounds are easily destroyed at mildly alkaline conditions (pH ≥ 8). Loses can occur for trace levels of compounds on alkaline glass surfaces. Glassware should be neutralized after washing, if alkaline detergent is used.

B. DESORPTION AND SOLUTION

1. Solubility of concentrated solutions in toluene enhanced by the addition of 1% methanol or 10% acetone. Solubility in hexane very unfavorable even for dilute solutions.
2. Changing from 100% toluene to 90/10 toluene/acetone, desorption from glass fiber filters improved from 62% to 98%, desorption from quartz fiber filters improved from 30% to 101%.
3. Changing from glass fiber filters to quartz fiber filters, desorption in toluene improved from 16% to 88% and desorption in 90/10 toluene/acetone improved from 70% to 99%.
4. These compounds are more chemically polar than the other listed organophosphorous compounds; desorption from XAD-2 or from glass or quartz fiber filters in hexane was incomplete or non-existent. Desorption in toluene was adequate except as noted in 2 and 3 above. The use of toluene containing 10% acetone improved recoveries for all analytes to satisfactory levels.
5. The desorption characteristics of these compounds were not evaluated.

General:
a. The presence of acidic hydrogen or double bonded oxygen anywhere in the molecular structure greatly decreases solubility in non-polar solvents and increases the difficulty of desorption from polar surfaces and sorbents.
b. While glass fiber filters and toluene desorbant were adequate for most compounds in preliminary tests, the method was given wider application for the more polar compounds by the use of quartz fiber filters and 90/10 toluene/acetone desorbant.
c. Solvents with lower boiling points (e.g., methylene chloride, chloroform, methyl-t-butyl ether, and ethyl acetate) had good desorption power nearing equivalent to 90/10 toluene acetone, but rendered less satisfactory gas chromatographic responses for the analytes. This effect may be due to better analyte mass-transfer from the injection port to the capillary column with higher boiling solvents using splitless or direct injection techniques.

C. GAS CHROMATOGRAPHY

1. Poor chromatography may be encountered with dirty or undeactivated columns or injection ports. Clean quartz wool plugs stuffed in the injection port liner are better than silanized glass wool at reducing losses within the injection port.
2. Multiple, shifted, irregular, or severely tailing peaks may be observed in the chromatogram if degradation or oxidation of the analytes occur prior to injection, within the injection port, or during chromatographic separation on-column.
3. Multiple peaks may be observed due to presence of isomers.
4. Short elution time, compound may co-elute with solvent if oven temperature is too high.
5. Long elution time, compound may be lost if run time is too short, column or injection port is too cool, or split-vent-valve opens too soon when injected in splitless or direct injection mode.
6. Azinphos methyl did not elute from DB-1701 even though Azinphos ethyl did elute.
7. Potential internal standards: Triphenyl phosphate is more favorable if multiple analytes are expected because it is less volatile and elutes in an area of the chromatogram having fewer competing analytes.

Table 10. Other Methods of Analysis for Organophosphorous Compounds in Air

Document	Method Number	Organophosphorous Compound(s)
Hill & Arnold[1]		Chlorpyrifos, Demeton-O, Demeton-S, Diazinon, Dimethoate, Malathion, Paraoxon, and Parathion
NMAM, 2nd ed.[2]	v. 1 P&CAM 158	Parathion
	v. 5 P&CAM 295	Dichlorvos (DDVP)
	v. 6 P&CAM 336	TEPP
	v. 3 S 208	Tributyl phosphate
	v. 3 S 209	Triorthocresyl phosphate
	v. 3 S 210	Triphenyl phosphate
	v. 6 S 280	Demeton
	v. 3 S 285	EPN
	v. 3 S 295	Parathion
	v. 6 S 296	Mevinphos
	v. 6 S 299	Ronnel
	v. 3 S 370	Malathion
NMAM, 3rd ed.[3]	2503	Mevinphos
	2504	TEPP
	5012	EPN, Malathion, and Parathion
	5514	Demeton
OSHA[4]	62	Chlorpyrifos, Diazinon, Parathion, DDVP, and Malathion
OSHA Stopgap[5]	Each method is separate and unnumbered. Refer to by name.	Azinphos ethyl, Azinphos methyl, Coumaphos, Crufomate, Demeton, Dicrotophos, Dioxathion, Disulfoton, EPN, Ethion, Ethoprop, Fenamiphos, Fensulfothion, Fenthion, Fonofos, Isofenphos, Leptophos, Methamidophos, Methyl dematon, Methyl parathion, Mevinphos, Monocrotophos, Oxydemeton methyl, Phorate, Pirimiphos methyl, Sulprofos, TEDP (sulfotepp), TEPP, Terbufos

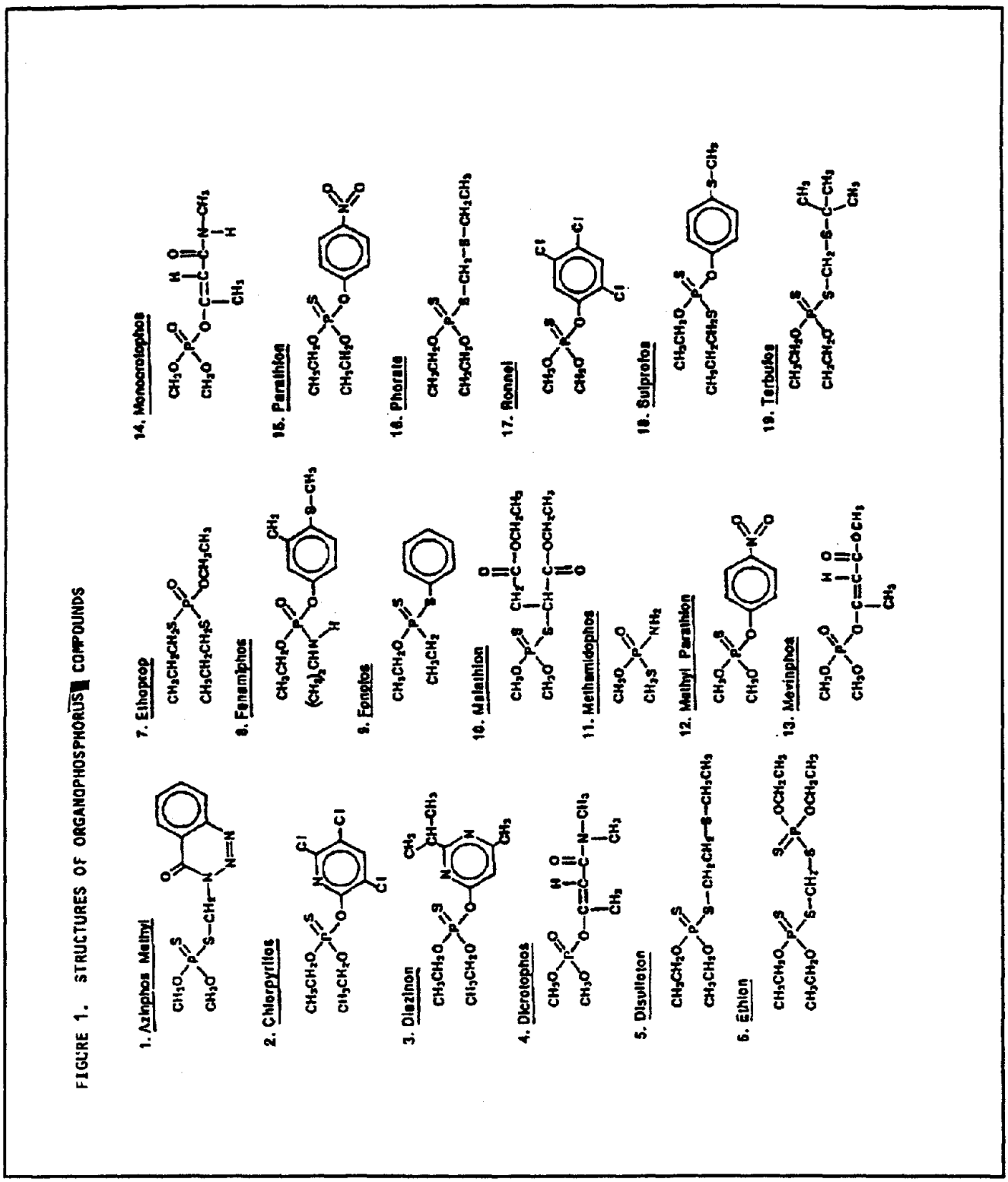
(1) Hill and Arnold [11]
(2) NMAM, 2nd ed. [7]
(3) NMAM, 3rd ed. [8]
(4) OSHA Analytical Methods Manual [12]
(5) OSHA Stopgap Methods [4]

Table 11. Preparation of Spiked Media and Liquid Calibration Standards

	Spiked Concentration					Solutions
	A.	B.	C.	D.	E.	F.
Spiking Levels (Fraction of REL)[1]	1/30x REL	1/10x REL	1/3x REL	1x REL	3x REL	
I. Spiking of Media or Liquid						
1. Spiking Solution to use:	SS-2	SS-2	SS-1	SS-1	SS-1	Dilute this
2. Preferred Syringe Size:	50 µL	50 µL	50 µL	50 µL	100 µL	volume (mL) of
3. Spiking Volume[2] to use:	10 µL	30 µL	10 µL	30 µL	90 µL	10 mg/mL stock solution to prepare 10 mL of solution SS-1
II. Total µg spiked[3]						
1. Azinphos methyl	0.8	2.4	8	24	72	0.8
2. Chlorpyrifos	0.8	2.4	8	24	72	0.8
3. Diazinon	0.4	1.2	4	12	36	0.4
4. Dicrotophos	1.0	3	10	30	90	1.0
5. Disulfoton	0.4	1.2	4	12	36	0.4
6. Ethion	1.6	4.8	16	48	144	1.6
7. Ethoprop	0.4	1.2	4	12	36	0.4
8. Fenamiphos	0.4	1.2	4	12	36	0.4
9. Fonofos	0.4	1.2	4	12	36	0.4
10. Malathion[5]	4	12	40	120	360	4.0
11. Methamidophos	0.8	2.4	8	24	72	0.8
12. Methyl parathion	0.8	2.4	8	24	72	0.8
13. Mevinphos	0.4	1.2	4	12	36	0.4
14. Monocrotophos	1.0	3	10	30	90	1.0
15. Parathion	0.2	0.6	2	6	18	0.2
16. Phorate	0.2	0.6	2	6	18	0.2
17. Ronnel[5]	4	12	40	120	360	4.0
18. Sulprofos	4	12	40	120	360	4.0
19. Terbufos	0.4	1.2	4	12	36	0.4
20. General (for 120L)[4,5]	x/30	x/10	x/3	x	3x	4y

(1) For a collection volume of 120 L. Range corresponds to values within column C, Table 8.
(2) For liquid calibration standard preparations, add specified volume to 2 mL desorption solution in 2-mL volumetric flask. For laboratory control samples spiked at the REL, apply volume specified in column D to front section of sampler; in duplicate. For Desorption Efficiency determination, apply specified volume to front section of sampler; do each of five levels in triplicate.
(3) Total µg per sample, for spiked media, or per 2 mL desorption solution for liquid calibration standards.
(4) Where x, µg/sample = REL, µg/L x 120 L/sample; and y, mg/mL = REL, mg/m^3 x 4 m^3/mL.
(5) For all REL > 1 mg/m^3, use 1/10 x REL in the calculations (assumes that collection volume in these cases would be 12 L instead of 120 L).

FIGURE 1. STRUCTURES OF ORGANOPHOSPHORUS COMPOUNDS



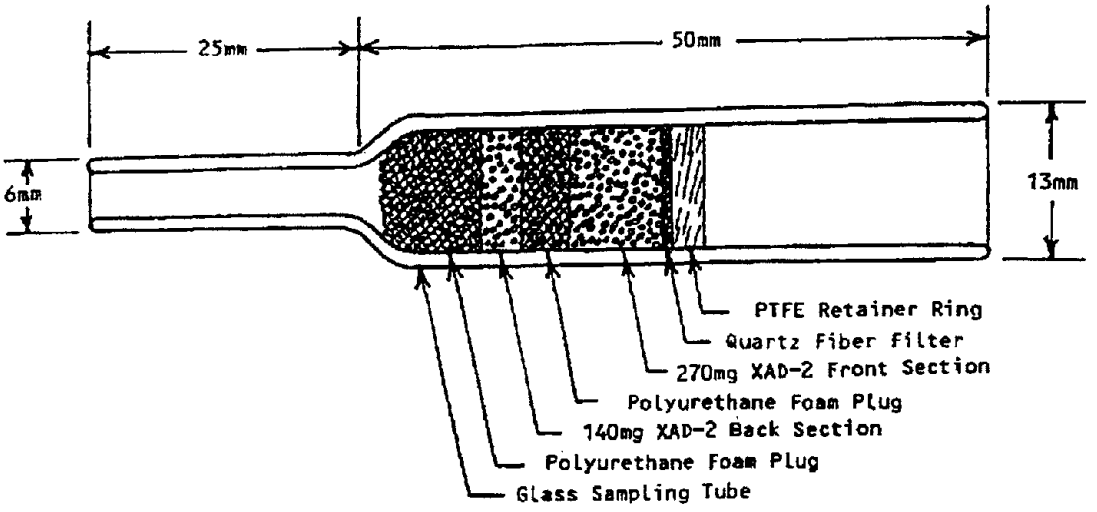


FIGURE 2. OVS-2 SAMPLER

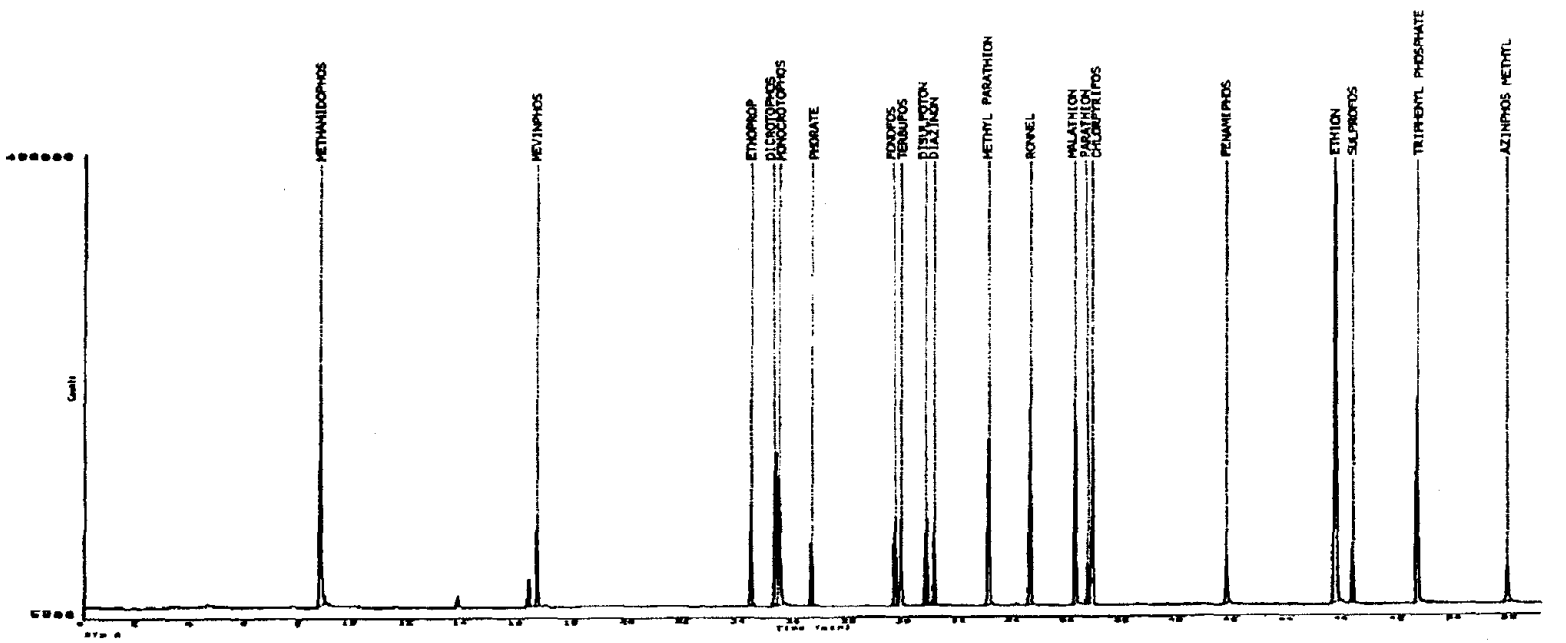


FIGURE 3. TYPICAL CHROMATOGRAM OF ORGANOPHOSPHOROUS COMPOUNDS

COLUMN: DB-1 FUSED SILICA CAPILLARY COLUMN, 30 METERS X 0.32 MM I.D. X 0.25 UM FILM THICKNESS
TEMPERATURE PROGRAM: 80°C TO 275°C AT 3.0°C/ MINUTE

CONCENTRATION OF ANALYTES: 0.6 X NIOSH REL, EXCEPT SULPROFOS (0.06X), MALATHION, AND RONNEL (BOTH 0.006X).

1.8 UG/ML	PARATHION AND PHORATE
3.6 UG/ML	ALL OTHER COMPOUNDS
7.2 UG/ML	AZINPHOS METHYL, CHLORPYRIFOS, METHAMIDOPHOS, AND METHYL PARATHION
9.0 UG/ML	DICROTOPHOS AND MONOCROTOPHOS
14. UG/ML	TRIPHENYL PHOSPHATE
14.4 UG/ML	ETHION

ORGANOTIN COMPOUNDS (as Sn) 5504

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5504, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3
NIOSH: 0.1 mg/m^3 (skin)
ACGIH: 0.1 mg/m^3 (skin)

PROPERTIES: Table 1

SYNONYMS: Table 1.

SAMPLING

SAMPLER: FILTER + SORBENT (glass fiber + XAD-2, 80 mg/40 mg)

FLOW RATE: 1 to 1.5 L/min

VOL-MIN: 50 L
-MAX: 500 L

SHIPMENT: ship assembled sampler in dry ice

SAMPLE STABILITY: stable 7 days @ 0 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 12 per sample set

ACCURACY

RANGE STUDIED: 0.07 to 0.2 mg/m^3 [1] (300-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 to 0.10 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: HPLC/ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: tin

DESORPTION: 10 mL 0.1% acetic acid/CH_3CN; ultrasonic, 30 min

SEPARATION: HPLC (cation exchange)

GRAPHITE FURNACE: dry 30 sec @ 80 °C; atomize 5 sec @ 2750 °C (gas interrupt mode)

INJECTION VOLUME: 20 µL

WAVELENGTH: 286.3 nm, with background correction

CALIBRATION: standard solutions of organotin compounds in acetic acid/CH_3CN

RANGE: 5 to 50 µg Sn per sample

ESTIMATED LOD: 1 µg Sn per sample [1]

PRECISION ($\bar{S}_r$): 0.07 to 0.08 [1]

APPLICABILITY: The working range is 0.015 to 1 mg/m^3 (as Sn) for a 300-L air sample. The method was validated using TeBT, TBTC, TCHH, and BuIOMA as surrogates for the most important classes of organotin compounds [1]. If speciation of organotin compounds is not required and if inorganic tin compounds are absent, the HPLC separation may be deleted. Use special care to avoid losses of TeBT and other volatile tetra-substituted organotin compounds.

INTERFERENCES: Organotin compounds not separated chromatographically will mutually interfere. Other compounds with similar retention times will not interfere unless they contain tin.

OTHER METHODS: This replaces the colorimetric criteria document method [2].

REAGENTS:

1. Zirconium acetate oxide, reagent grade.
2. Ammonium acetate, reagent grade.
3. Diammonium citrate, reagent grade.
4. Acetonitrile, chromatographic grade.
5. Deionized water.
6. Acetic acid, glacial, reagent grade.
7. Methanol, chromatographic grade.
8. Acetic acid, 0.1% (v/v) in acetonitrile.
9. Acetate buffer solution (v/v) 70% methanol, 27% deionized water, 3% aqueous 1 M ammonium acetate.
10. Citrate buffer solution (v/v) 70% methanol, 26.8% deionized water, 3% aqueous 1 M diammonium citrate in 0.2% (v/v) glacial acetic acid.
11. Organotin standard solutions, 1000 μg/mL (as Sn), prepared from pure organotin compounds in 0.1% (v/v) acetic acid in acetonitrile.
12. Calibration stock solution, 10 μg/mL (as Sn). Prepare a standard mixture of the organotin compounds of interest. Pipet 0.1 mL of each organotin standard solution into a 10-mL volumetric flask. Dilute to the mark with 0.1% (v/v) acetic acid in acetonitrile. Prepare fresh daily.

EQUIPMENT:

1. Sampler: glass fiber filter, 37-mm (Gelman Type AE or equivalent) in cassette filter holder followed by XAD-2 sorbent tube, 80 mg front section/40 mg back section separated and retained by silanized glass wool (SKC, Inc., Eighty-Four, PA 15330, Cat. No. 226-30).
2. Personal sampling pump, 1 to 1.5 L/min, with flexible connecting tubing.
3. Shipping container, refrigerated, with dry ice.
4. High performance liquid chromatograph (HPLC), interfaced with autoinjection system (Fig. 1), with binary solvent capability, solvent gradient capability and columns:
   a. non-tetraorganotin species: cation exchange column (Whatman, Inc., Partisil-10 Strong Cation Exchange Column and Solvecon Pre-Column Kit).
   b. tetraorganotin compounds: C_{18} column, (Whatman, Inc., Lichrosorb).
5. Atomic absorption spectrophotometer (AAS) having recorder output proportional to absorbance units, graphite furnace accessory (pyrolytic with Zr coating, coated L'vov platform may be required; see APPENDIX), sample autoinjection system with moving sample tube rack or carrousel (Fig. 1), automatic micropipettor for accurately injecting 20-μL sample aliquots into graphite furnace, background correction (e.g., D_2 or H_2 lamp) capability, and tin electrodeless discharge lamp or hollow cathode lamp.
6. Bath, ultrasonic.
7. Volumetric flasks, 10-mL.
8. Syringe, 20-μL, readable to 0.5 μL.
9. Beakers, Phillips, 125-mL.
10. Pipets, 5- and 10-mL; 10- and 100-μL.
11. Oven or muffle furnace, 200 °C.
12. Plastic film.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sorbent tube immediately before sampling and connect to the filter with a short piece of tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 1.5 L/min for a total sample size of 50 to 500 L.
4. Cap the samplers. Pack securely for shipment in dry ice.
   NOTE: The cassette and sorbent tube should remain connected for storage. Store samples at less than 0 °C. Analyze within seven days after collection.

SAMPLE PREPARATION:

5. Open the cassette filter holder. With tweezers, carefully transfer the filter to a 125-mL beaker.
6. Place the front sorbent section and front glass wool plug into a second beaker. Place the back sorbent section and remaining glass wool plugs into a third beaker.
7. Pipet 10.0 mL acetonitrile and 10 μL acetic acid into each beaker. Cover with plastic film.
8. Agitate beakers in ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 0.1% (v/v) acetic acid in acetonitrile in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain concentrations of each organotin compound in the range 0.1 to 5 μg/mL (as Sn).
   b. Analyze with samples and blanks (steps 12 through 15), alternating samples and standards with similar responses.
   c. Prepare calibration graphs (peak height vs. μg Sn) for each organotin compound.
10. Determine recovery (R) in the range of interest. Prepare three samplers at each of three levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (2 to 20 μL) of organotin standard solution directly onto front sorbent section and a separate aliquot onto the filter, with a microliter syringe.
    c. Cap the sampler. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze with working standards (steps 12 through 15).
    e. Prepare a graph of R vs. μg Sn recovered for each organotin compound.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs and recovery graphs are in control.

MEASUREMENT:

12. Set the AAS and graphite furnace according to manufacturer's recommendations and to conditions on page 5504-1. Adjust the sample injection/dry/atomize cycle so that it occurs exactly once every 60 sec.
13. Operate the HPLC according to manufacturer's recommendations and the following conditions:
    a. For non-tetraorganotin compounds:
       (1) Column: strong cation exchange (EQUIPMENT, 4.a).
       (2) Flush column with 50 to 60 mL acetate buffer prior to sample injection.
       (3) Eluent: flowrate = 2 mL/min
       (4) Eluent Gradient:

Time (min)	% Acetate Buffer	% Citrate Buffer
0 - 15	100	0
15 - 18	100 - 0	0 - 100
18 - 40	0	100

       (5) After the chromatogram is complete, re-equilibrate the HPLC system to initial conditions by pumping acetate buffer through the column for 15 min.
       (6) Inject 100-μL sample aliquot.
    b. For tetraorganotin compounds:
       (1) Column: C_{18}.
       (2) Flush column with 50 to 60 mL of 100% acetonitrile prior to sample injection.
       (3) Eluent: flowrate = 2 mL/min, isocratic, 100% acetonitrile.
       (4) Inject a 100-μL aliquot of sample solution.

14. Collect HPLC eluent at the rate of 1 fraction (2 mL) per minute in AAS autosampler (Fig. 1).
    NOTE: In this example system, the column effluent is fed directly into one of the sample cups. After 1 min, the sample holder rotates and the eluted sample is in a position to be sampled for AA measurement. The furnace injection device withdraws a portion of the sample and places it in the furnace while the next sample is being eluted and collected.
15. Measure total AAS peak area for each organotin compound.
    NOTE 1: The recorder output will consist of AA peaks which form a chromatographic peak for each organotin compound if a line is drawn connecting the highest points of the AA peaks. Determine total absorbance for a species by the sum of the absorbencies of the corresponding AA peaks.
    NOTE 2: The characteristics of the graphite tube can influence the results drastically. Pay careful attention to the response of the standards and replace the graphite tube if erratic results and non-reproducible peak areas occur.

CALCULATIONS:

16. Read the mass, μg Sn (corrected for R), for each organotin compound found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blanks [filter (B) and front sorbent (B_f) and back sorbent (B_b) sections] from the calibration graphs.
17. Calculate concentration, C (mg/m^3), for each organotin compound as Sn in air as the sum of the particulate concentration and the vapor concentration in the air volume sampled, V (L):

$$C = \frac{W - B + W_f + W_b - B_f - B_b}{V}, \ mg/m^3.$$

NOTE: W_f and W_b will include any analyte originally collected on the filter as particulate, then volatilized during sampling or storage.

EVALUATION OF METHOD:

The method was validated with tetrabutyltin (TeBT), tributyltin chloride (TBTC), tricyclohexyltin hydroxide (TCHH), and dibutyltin bis(isooctylmercaptoacetate) (BuIOMA) [1]. The working ranges, validation ranges, and estimated linear working ranges (as tin) for 300-L air samples of these organotin species at an atmospheric temperature and pressure of 20 °C and 756 mm Hg, respectively, appear below:

Species	Validation Range (mg/m^3)	Estimated Linear Working Range (mg/m^3)	Estimated Linear Working Range ($\mu g/mL$)	Measurement Precision (% $\hat{S}_r$)	Bias (%)	Overall Precision (% $\hat{S}_{rT}$)	Accuracy (± %)
TeBT	0.027-0.112	0.02-0.17	0.05-5.0	8.1	+1.8	10.0	21.4
TBTC	0.042-0.191	0.01-0.34	0.3-10	5.9	−6.7	9.9	26.1
TCHH	0.071-0.218	0.01-0.34	0.3-10	6.9	−2.3	7.1	16.2
BuIOMA	0.070-0.220	0.01-0.34	0.3-10	7.7	−1.2	7.4	15.7

REFERENCES:

[1] Gutknecht, W.F., P.M. Grohse, C.A. Homzak, C. Tronzo, M.H. Ranade, and A. Damle. Development of a Method for the Sampling and Analysis of Organotin Compounds, NIOSH Contract 210-80-0066, Research Triangle Institute, Research Triangle Park, NC 27709, available through NTIS, Springfield, VA 22161, as PB83-180737 (May, 1982).

[2] Criteria for a Recommended Standard...Occupational Exposure to Organotin Compounds, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157 (1976).

METHOD REVISED BY:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

PREPARATION OF Zr-COATED GRAPHITE FURNACE TUBE AND PLATFORM

1. Zirconium coating: soak pyrolytic graphite tubes and platforms overnight in 4.5% (w/v) zirconium acetate oxide solution; then dry in a muffle furnace for 2 h at 200 °C.
2. Pyrolytic zirconium-coated graphite furnace tubes are acceptable for measurements of all organotin compounds. However, a pyrolytic zirconium-coated graphite platform (e.g., L'vov platform) is recommended for better precision at low levels and improved atomization response for volatile species such as TeBT. Platforms may be purchased commercially or prepared from pyrolytic graphite tubes, as shown in Fig. 2. Special care must be exercised during placement of the platform in the tube (Fig. 3) and in optical alignment.

Table 1. Formulae and physical properties [3].

Compound RTECS	Formula	M.W.	% Sn	Synonyms
Dibutyltin bis(isooctyl mercaptoacetate) WH6719000	$C_{28}H_{56}O_4S_2Sn$	639.57	18.6	BuIOMA; CAS #25168-24-5
Tetrabutyltin WH8605000	$C_{16}H_{36}Sn$	347.16	34.2	Stannane, tetrabutyl-; TEBT; CAS# 1461-25-2
Tributyltin chloride WH6820000	$C_{12}H_{27}ClSn$	325.49	36.5	Stannane, chlorotributyl-; TBTC; CAS #1461-22-9
Tricyclohexyltin hydroxide WH8750000	$C_{18}H_{34}OSn$	385.16	30.8	Stannane, tricyclohexylhydroxy-; TCHH; Plictran; Dowco-213; CAS #13121-70-5

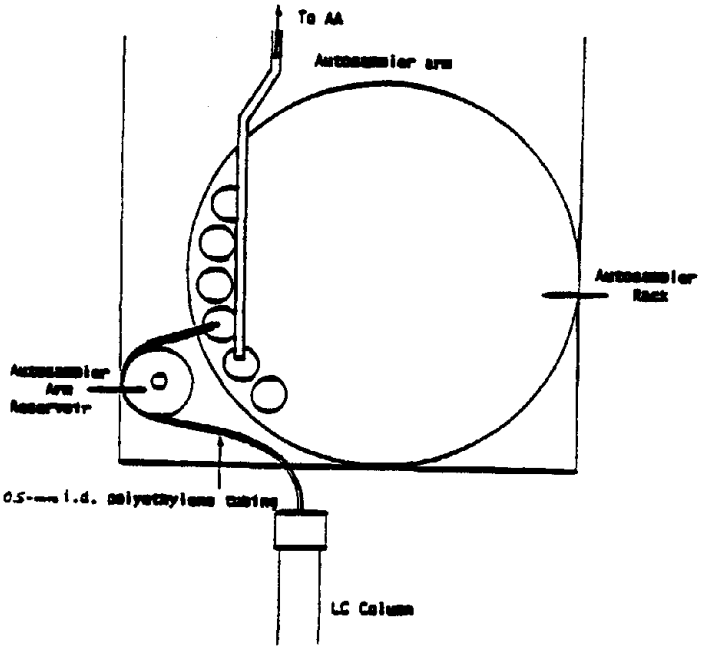


Figure 1. HPLC/AAS interface system.

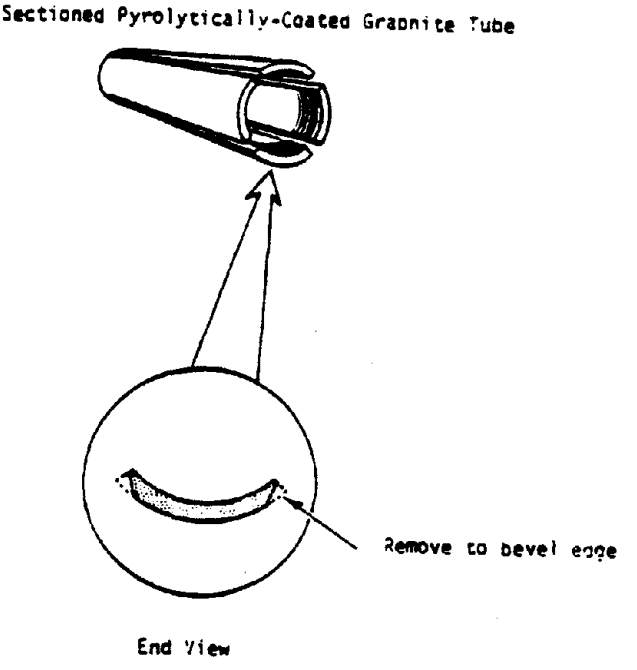


Figure 2. Construction of a laboratory-made platform.

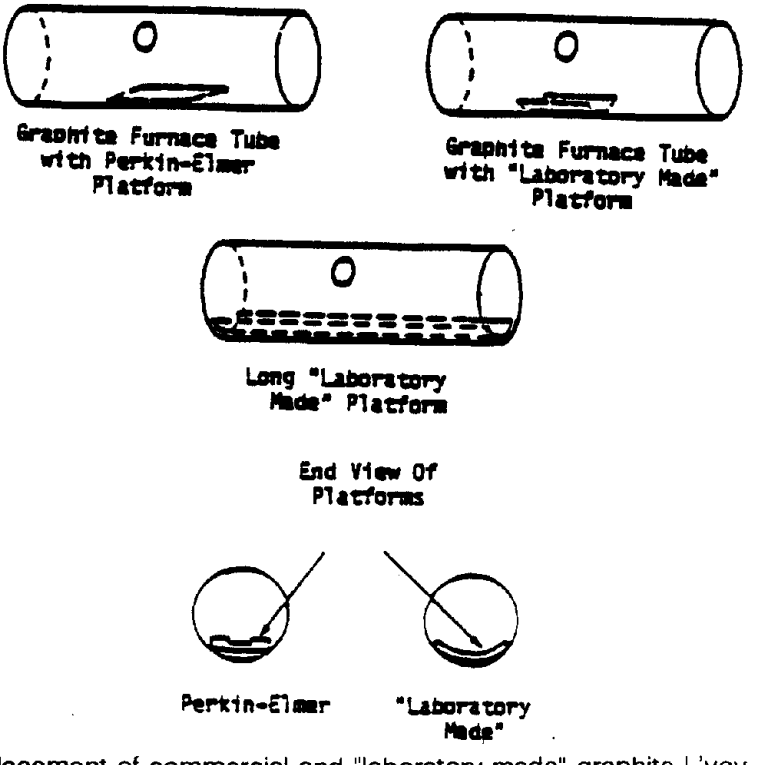


Figure 3. Placement of commercial and "laboratory-made" graphite L'vov platforms in furnace tubes.

OXYGEN

O_2 MW: 32.00 CAS: 7782-44-7 RTECS: EL9450000

METHOD: 6601, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 19.5% (v/v) minimum
NIOSH: 19.5 to 25% (v/v) @ 760 mm Hg
ACGIH: no standard

PROPERTIES: gas; d 1.331 g/L @ 20 °C; partial pressure 21.23 kPa (159.22 mm Hg, 20.9% v/v) @ sea level

SYNONYMS: None.

SAMPLING

SAMPLER: PORTABLE DIRECT-READING OXYGEN MONITOR

FLOW RATE: samples by diffusion; no pump needed

VOL-MIN: 1 L
-MAX: none

SHIPMENT: routine shipment of instrumentation

SAMPLE STABILITY: bag samples stable 4 h

BLANKS: fresh air or compressed synthetic air from cylinders

ACCURACY

RANGE STUDIED: 15 to 21% (v/v) O_2 in air [1]

BIAS: none [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.096 [1]

ACCURACY: ± 19%

MEASUREMENT

TECHNIQUE: ELECTROCHEMICAL SENSOR

ANALYTE: oxygen

RESPONSE TIME: 5 to 25 sec for step change from 21% (v/v) O_2 to 19.5% (v/v) O_2 [1]

CALIBRATION: fresh air or compressed gas tank calibration standards

RANGE: 0 to 25% (v/v) O_2 in N_2 (linear response)

SENSITIVITY: 0.1% (v/v) O_2

PRECISION ($\hat{S}_r$): 0.096 [1]

APPLICABILITY: The working range is 0 to 25% (v/v) O_2. For some monitors, the working range is 0 to 100%. This method may be used in work atmospheres to determine available O_2 levels and is particularly useful for determining safe entry conditions into confined work spaces. Many units are small enough to be worn on the person and may be used to obtain personal breathing zone samples.

INTERFERENCES: Levels of up to five times the TLV of many common industrial chemicals did not adversely affect the studied sensors [1]. Pressure and temperature changes do affect the sensors. Most units are equipped with temperature-compensating circuitry, but some take up to 1 h to equilibrate. Several models include pressure-compensating circuitry.

OTHER METHODS: None studied by NIOSH. This method was written as a result of evaluation of 18 commercially available oxygen monitors [2].

REAGENTS:

1. Fresh air or 20.9% O_2, 79.1% N_2 in compressed gas cylinder.*
2. 16% O_2, 84% N_2 in compressed gas cylinder for calibration.*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Oxygen monitor with electrochemical sensor with the following performance specifications: linear response between 15 and 21% O_2 in nitrogen; span and zero drift $\leq$0.2% O_2 for 8 h; response time $\leq$0.5 min for a 1% change in oxygen concentration.
2. Air pump, 0.2 to 2 L/min, and plastic tubing to sample remote locations (optional).
3. Sample bags to collect samples (optional).
4. Sensor cap with inlet and outlet fittings to calibrate from compressed standard cylinders in contaminated atmospheres.
5. Air line adaptor for sampling oxygen-enriched air.

SPECIAL PRECAUTIONS: Shipments of compressed calibration gases must comply with 49 CFR 1992 regulations.

SAMPLING AND MEASUREMENT:

1. Start monitor as manufacturer recommends. Allow sufficient warm up/equilibration time if monitor has been in a different environment. If a remote sensor is used in an area different from the monitor electronics, allow extra time to reach thermal equilibrium.
   NOTE: Instrument warm-up time is typically 10 min or less, but may increase to as long as 1 h if sampled atmosphere varies 5 °C or more from present ambient temperature.
2. Select one of the following sampling modes as appropriate:
   a. **Ambient air or oxygen-deficient air:**
      (1) Place monitor in atmosphere to be analyzed. Allow to equilibrate.
      (2) Record % O_2. Read and record frequently. Observe any downward trends in % O_2 levels. If a concentration of 19.5% O_2 is approached, ventilate with fresh air if possible.
      WARNING: EVACUATE THE AREA WHEN THE O_2 CONCENTRATION FALLS BELOW 19.5% [3].
   b. **Oxygen-enriched air:**
      (1) Place sensor in air line adaptor. Allow to equilibrate.
      NOTE: If line is pressurized, bleed off a stream to the sensor at atmospheric pressure in order to not pressurize the sensor.
      (2) Record % O_2.

CALIBRATION AND QUALITY CONTROL:

3. Perform on-site calibration at 20.9% O_2 several times each shift by exposing sensor to fresh air or to standard tank air. Replace sensor cell when the instrument can no longer be adjusted to read 20.9% O_2 in fresh air.
   WARNING: DO NOT PRESSURIZE THE SENSOR WITH CYLINDER MIXTURES AS THIS WILL CAUSE HIGH READINGS AND COULD DO IRREPARABLE DAMAGE TO THE SENSOR CELL.
4. Perform down-scale calibration by exposing sensor to 16 to 19% O_2 in N_2 at least once per day.
5. Check for alarm function (if included) by exposing to 16 to 19% O_2 in N_2 from a cylinder or by blowing self-exhaled breath directly onto the sensor. Following manufacturer's instructions for this procedure, adjust readout meter to agree with the calibration standard.

6. Practice routine instrument maintenance.
   a. Check sensor cell diffusion barrier for dirt and moisture. Clean with a soft cloth or tissue if needed.
   b. Replace sensor cell every six to nine months with average use.
      NOTE 1: Store cell in nitrogen when not in use to prolong life.
      NOTE 2: Some models use non-disposable, user-rechargeable sensors which require recharging every two to four weeks.
   c. Check batteries and replace when needed.
      NOTE: Battery life is two to six months for replaceable battery models. Some are equipped with nickel-cadmium batteries which require periodic recharging. Most operate at least 16 hrs without recharging. Some units have low-battery indicators.

EVALUATION OF METHOD:

Oxygen monitors have been used successfully in numerous industries for pre-entry checks of areas where oxygen levels may be low and for continuous monitoring during the time workers occupy these areas [3]. They have also been used in hospitals for monitoring oxygen levels in oxygen-enriched atmospheres supplied for medical purposes. This method has undergone extensive laboratory evaluation for use in oxygen-deficient atmospheres and has been shown to be stable and reproducible [1]. The relative standard deviation, S_r, for 15 different instruments monitoring the same atmosphere (under laboratory conditions) was 0.52% for over 100 readings over an 8-h period. The relative standard deviation, S_r, for 18 different instruments monitoring the same atmosphere in field situations was 1.22% for 126 readings taken over a two-day testing period with calibration at the beginning of each day [1].

REFERENCES:

[1] Woodfin, W. J. and M. L. Woebkenberg. An Evaluation of Portable Direct-Reading Oxygen Deficiency Monitors (NIOSH, unpublished, 1984).

[2] Katz, Morris, Ph.D., Ed. Methods of Air Sampling and Analysis (Second Edition), Library of Congress Cat. No. 77-6876, American Public Health Association (1977).

[3] Criteria for a Recommended Standard...Working in Confined Spaces, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-106 (1979).

METHOD WRITTEN BY:

William J. Woodfin and Mary Lynn Woebkenberg, NIOSH/DPSE.

$C_{12}H_{14}N_2Cl_2$ MW: 257.16 CAS: 4685-14-7 (ion) RTECS: DW1960000 (ion)
$(C_{12}H_{14}N_2)^{2+}$ (M.W. Paraquat = 186.26)

METHOD: 5003, Issue 2 EVALUATION: FULL Issue 1: 15 February 1984
Issue 2: 15 August 1994

OSHA : 0.5 mg/m^3 (skin; respirable)
NIOSH: 0.1 mg/m^3 (skin; respirable)
ACGIH: 0.1 mg/m^3 (respirable; 0.5 mg/m^3 total)

PROPERTIES: (dichloride salt) solid; decomposes @ 300 °C; VP not significant

SYNONYMS: 1,1'-dimethyl-4,4'-bipyridinium dichloride; methyl viologen; CAS # 1910-42-5; 1,1'-dimethyl-4,4'-bipyridinium bis methyl sulfate (CAS #2074-50-2).

SAMPLING

SAMPLER: FILTER (1-μm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 40 L @ 0.5 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.26 to 1.03 mg/m^3 [1] (90-L samples)

BIAS: − 0.97%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.088 [1]

ACCURACY: ± 17.1%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 1,1-dimethyl-4,4'-bipyridium cation

DESORPTION: 5 mL water

INJECTION VOLUME: 20 μL

MOBILE PHASE: 25% acetonitrile; 75% 0.01 M heptane-sulfonic acid, sodium salt (pH 3.2); 1.5 mL/min

COLUMN: 30 cm x 4-mm ID stainless steel packed with μ-Bondapak C_{18} or equivalent

DETECTOR: UV absorption @ 254 nm

CALIBRATION: Paraquat dichloride in water

RANGE: 20 to 500 μg/sample [2,3]

ESTIMATED LOD: 10 μg/sample [2]

PRECISION ($\bar{S}_r$): 0.048 [1]

APPLICABILITY: The working range is 0.1 to 10 mg/m^3 for a 200-L air sample. The paraquat cation is the analyte for this method; therefore, either salt, the dichloride or bismethyl sulfate, can be quantitated. The standards are prepared from a solution of the dichloride salt with appropriate stoichiometric factor applied.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S294 [2].

REAGENTS:

1. Water, deionized, distilled.
2. Acetonitrile, HPLC grade.
3. 1-Heptanesulfonic acid, sodium salt.
4. Paraquat dichloride.* Dry at 50 °C to remove water of hydration.
5. Calibration stock solution, 0.002 mg paraquat cation/μL.* Dissolve 27.6 mg anhydrous paraquat dichloride in distilled water to make 10 mL solution. Prepare in duplicate.
6. LC mobile phase, 25% acetonitrile in 0.01 M aqueous 1-heptanesulfonic acid, sodium salt. Add glacial acetic acid to bring pH to 3.2 ± 0.3.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 1-μm PTFE filter, 37-mm diameter with backup pad in a two-piece filter cassette held together with tape or shrink bands.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. HPLC, UV absorption detector at 254 nm, integrator and column (page 5003-1).
4. Vials, 20-mL, scintillation.
5. Pipets, 5-mL.
6. Microliter pipets or syringe, 1- to 250-μL.
7. Syringe, 20-μL, or fixed sample loop or autosampler for injections.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Paraquat is listed as a severe poison. Use care in handling [4,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 40 to 1000 L. Do not exceed 2 mg total dust on filter.

SAMPLE PREPARATION:

3. Carefully transfer the filter from the cassette to a vial using tweezers.
4. Add 5 mL deionized, distilled water to each vial. Cap the vial and gently swirl it to dissolve the sample completely.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards covering the range 10 to 500 μg paraquat per sample.
   a. Add calibration stock solution with a microliter syringe to 5 mL water in a vial.
   b. Analyze together with samples and blanks (steps 7 through 9).
   c. Prepare calibration graph (response vs. μg paraquat).
6. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

7. Set HPLC to conditions given on page 5003-1.
8. Inject sample aliquot using a syringe, a fixed volume sample loop or an autosampler.
9. Measure peak response.

   NOTE 1: Retention time under these conditions is ca. 6 to 6.5 min.

   NOTE 2: If peak response is above the range of the working standards, dilute with deionized, distilled water, reanalyze, and apply the appropriate dilution factors in calculations.

CALCULATIONS:

10. Read the mass, μg, of Paraquat found on the filter, W, and the average media blank, B, from the calibration graph.
11. Calculate concentration of Paraquat cation, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S294 was issued on March 16, 1979, and validated over the range 0.256 to 1.03 mg/m^3 using a 90-L sample [1,6]. The overall precision, $\hat{S}_{rT}$, was 0.088 with an average recovery of 98.2%, representing a non-significant bias. The concentration of Paraquat in the generation system was verified by an independent method [7]. Recovery was 101% in the range 23.7 to 94.6 μg per sample; another study found 79% recovery of 25 μg per sample and 98% recovery in the range 77 to 463 μg per sample [3]. Collection efficiency of the filter was determined by collecting six filter samples at about 1.8 mg/m^3 for a 90-L sample. The sampler consisted of two filters per cassette arranged so that the back filter was supported by the backup pad and the front filter was separated from the back filter. The overall collection efficiency was 100%. Samples were stored at room temperature for one week and found to be stable.

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METHOD REVISED BY:

Jerome Smith, Ph.D., NIOSH/DPSE; S294 originally validated under NIOSH Contract 210-76-0123.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-μm median cut point

CAS: None RTECS: None

METHOD: 0600, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: no REL
ACGIH: 10 mg/m^3

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates the non-ciliated portions of the lung

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm cyclone or Higgins-Dewell (HD) cyclone + tared 5-μm PVC membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 L/min

VOL-MIN: 20 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m^3 (lab and field)

BIAS: depends on dust size distributions [1]

OVERALL PRECISION ($\hat{S}_{rT}$): depends on size distributions [1,2]

ACCURACY: depends on dust size distributions [1]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.03 mg per sample

PRECISION: <10 μg with 0.001 mg sensitivity balance
<68 μg with 0.01-mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. Besides inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust (e.g., $\approx$ +7% bias for non-diesel, coal mine dust)[5].

INTERFERENCES: Larger than respirable particles (over 10 μm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in the sample are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 5.0-μm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD)[7], or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone or 2.2 ± 5% L/min for HD cyclone, with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Static neutralizer, e.g., Po-210; replace nine months after the production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance, e.g., 20 °C ± 1 °C and 50% ± 5% RH.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry, and mark with the same number as the backup pad.
4. Remove the cyclone's grit cap and vortex finder before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
   NOTE: Because of its square inlets, the nylon cyclone must be calibrated within a large vessel with inlet and outlet ports. The vessel inlet is connected to a calibrator (e.g., a bubble meter); whereas the outlet is connected to the sampling pump. The HD cyclone, on the other hand, can have the calibrator connected directly to the cyclone inlet. Note that even if the flowrate shifts by a known amount between calibration and use, the nominal flowrates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed approximately 2 mg dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3, \ mg/m^3.$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = mean tare weight of blank filters (mg).
B_2 = mean post-sampling weight of blank filters (mg)
V = volume as sampled at the nominal flowrate (i.e., 1.7 L/min or 2.2 L/min)

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust criterion. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international criterion for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as −0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias is less than -0.02 for most dust size distributions encountered in the workplace.

Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.029 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [7] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [13] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

REFERENCES:

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METHOD REVISED BY:

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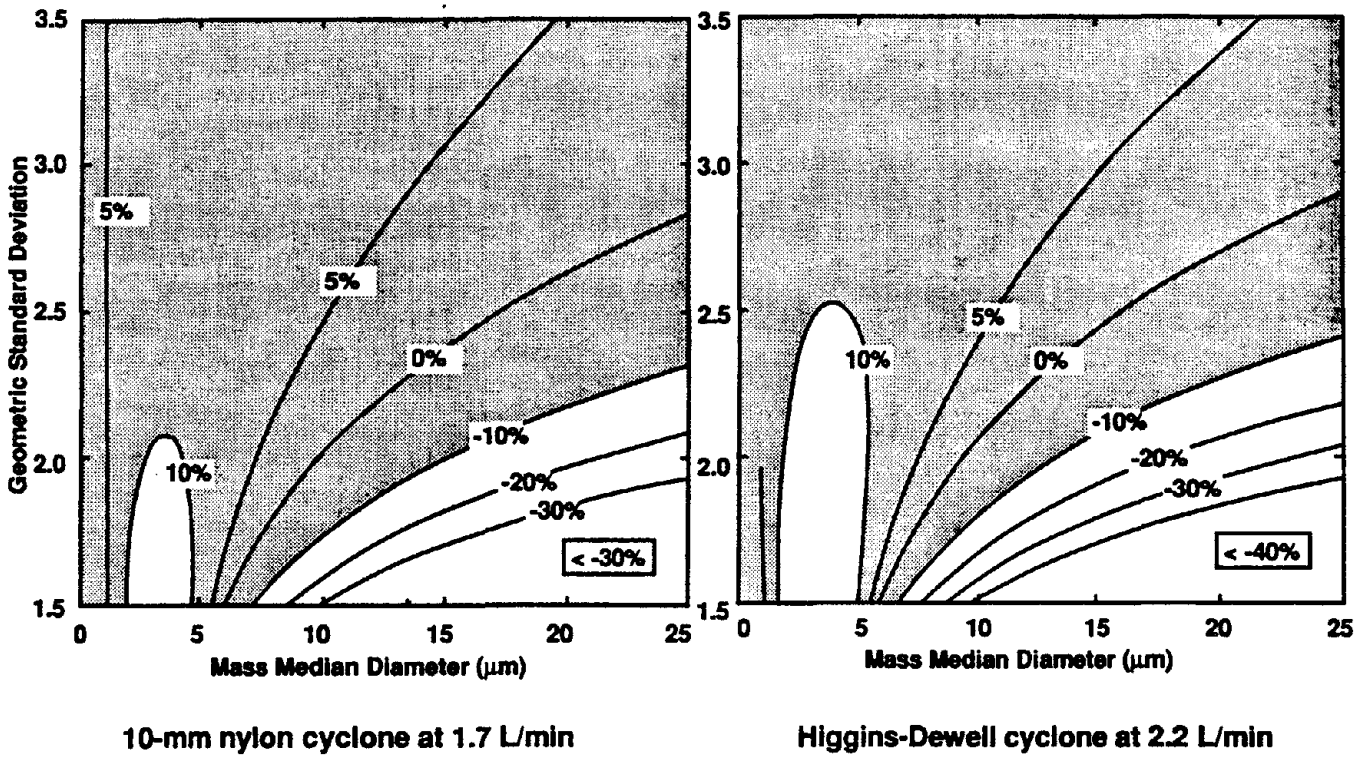

Figure 1. Bias in respirable dust determination.

PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500

DEFINITION: total aerosol mass CAS: NONE RTECS: NONE

METHOD: 0500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 15 mg/m^3
NIOSH: 10 mg/m^3
ACGIH: 10 mg/m^3, total dust less than 1% quartz

PROPERTIES: contains no asbestos and quartz less than 1%

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (tared 37-mm, 5-μm PVC filter)	**TECHNIQUE:**	GRAVIMETRIC (FILTER WEIGHT)
FLOW RATE:	1 to 2 L/min	**ANALYTE:**	airborne particulate material
VOL-MIN:	7 L @ 15 mg/m^3	**BALANCE:**	0.001 mg sensitivity; use same balance before and after sample collection
-MAX:	133 L		
SHIPMENT:	routine	**CALIBRATION:**	National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights
SAMPLE STABILITY:	indefinitely	**RANGE:**	0.1 to 2 mg per sample
BLANKS:	2 to 10 field blanks per set	**ESTIMATED LOD:**	0.03 mg per sample
BULK SAMPLE:	none required	**PRECISION ($\bar{S}_r$):**	0.026 [2]

ACCURACY

RANGE STUDIED:	8 to 28 mg/m^3
BIAS:	0.01%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.056 [1]
ACCURACY:	± 11.04%

APPLICABILITY: The working range is 1 to 20 mg/m^3 for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [3] in addition to the other ACGIH particulates not otherwise regulated [4].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [3].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [3] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

EQUIPMENT:

1. Sampler: 37-mm PVC, 2- to 5-μm pore size membrane or equivalent hydrophobic filter and supporting pad in 37-mm cassette filter holder.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Microbalance, capable of weighing to 0.001 mg.
4. Static neutralizer: e.g., Po-210; replace nine months after the production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance (e.g., 20 °C ± 1 °C and 50% ± 5% RH).

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
   NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 7 to 133 L. Do not exceed a total filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust.
   NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.

11. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control [7].

MEASUREMENT:

12. Weigh each filter, including field blanks. Record the post-sampling weight, W_2 (mg). Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)

CALCULATIONS:

13. Calculate the concentration of total particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1) \cdot 10^3}{V}, \ mg/m^3.$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = mean tare weight of blank filters (mg)
B_2 = mean post-sampling weight of blank filters (mg)

EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28 mg/m^3 [2,6]. Precision and accuracy data are given on page 0500-1.

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METHOD REVISED BY:

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PENTACHLOROETHANE

$CHCl_2CCl_3$ MW: 202.30 CAS: 76-01-7 RTECS: KI6300000

METHOD: 2517, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1985 **Issue 2:** 15 August 1994

OSHA : no standard
NIOSH: handle with caution
ACGIH: no standard
(1 ppm = 8.27 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.671 g/mL @ 25 °C; BP 162 °C; VP 450 Pa (3.4 mm Hg; 4500 ppm) @ 20 °C

SYNONYMS: Pentalin; ethane pentachloride.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Porapak R, 70 mg/35 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 0.1 mg/m^3
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: stable ≥ 7 days @ 25 °C; ≥ 21 days @ 0 °C in the dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.014 to 5.37 mg/m^3 [1] (3-L samples)

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.075 [1]

ACCURACY: ± 15%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: pentachloroethane

DESORPTION: 2 mL hexane; 30 min ultrasonic

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

INJECTION VOLUME: 5 µL

CARRIER GAS: 5% methane, 95% argon; 30 mL/min

DETECTOR PURGE GAS: 5% methane, 95% argon if required; 80 mL/min

COLUMN: nickel, 2-mm ID x 2 m, packed with 3% OV-17 on 100/120 mesh Chromosorb WHP

CALIBRATION: standard solutions of pentachloroethane in hexane

RANGE: 0.04 to 40 µg per sample

ESTIMATED LOD: 0.004 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.019 [1]

APPLICABILITY: The working range is 0.01 to 20 mg/m^3 (0.001 to 2.4 ppm) for a 5-L air sample.

INTERFERENCES: 1,2,2,3-Tetrachloropropane interferes with the analyte GC peak but is not likely to be present in most samples. Large concentrations of 1,1,2,2-tetrachloroethane may obscure the analyte GC peak.

OTHER METHODS: This revises P&CAM 335 [2].

REAGENTS:

1. Hexane, distilled in glass.*
2. Pentachloroethane, 96% pure.*
3. Mixture of 5% methane, 95% argon.
4. Calibration stock solution, 2 mg/mL. Dissolve 0.2 g pentachloroethane in hexane to make 100 mL solution. Stable indefinitely at room temperature.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 50/80 mesh Porapak R (front = 70 mg; back = 35 mg) separated by a urethane foam plug. A glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 0.2 L/min airflow must be less than 1.2 kPa (5 inches H_2O). Tubes are commercially available, e.g., SKC, Inc. ST226-59-04.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni ECD, integrator, and column (page 2517-1).
4. Vials, 2-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Ultrasonic bath.
7. Pipets, 2-mL.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Hexane is flammable (flash point = −21 °C) and toxic; all work with it must be done in a hood.

Pentachlorothenae causes CNS effects, with possible liver and kidney effects [3]. Technical grade pentachloroethane (containing 4.2% hexachloroethane, a known carcinogen in mice) was carcinogenic for B6C3F$_1$ mice, causing hepatocellular carcinomas in males and females, and adenomas in females [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with PTFE tape and plastic caps. Pack securely for shipment.

SAMPLE PREPARATION:

5. Refrigerate the samples upon receipt.
6. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section and the foam plugs to the back sorbent section.
7. Add 2.0 mL hexane to each vial. Attach crimp cap to each vial.
8. Allow to stand 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.004 to 40 μg pentachloroethane per sample (0.002 to 20 μg/mL).
   a. Add known amounts of calibration stock solution, or serial dilutions thereof, to hexane in 10-mL volumetric flasks and dilute to the mark.
      NOTE: The working standards are stable indefinitely at room temperature if kept in airtight containers.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area or height vs. μg pentachloroethane).
10. Determine desorption efficiency (DE) at least once for each lot of Porapak R used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution, or serial dilutions thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13).
   e. Prepare a graph of DE vs. μg pentachloroethane recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2517-1. Inject sample aliquot manually using solvent flush technique or with autosampler. t_r = 3.5 min at these conditions.
    NOTE: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area or height.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of pentachloroethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
15. Calculate concentration, C, of pentachloroethane in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 335 was issued on August 29, 1980, and validated over the range 0.014 to 5.4 mg/m^3 with samples from dynamically generated test atmospheres [1]. A gas chromatograph with gas sampling loop was used to monitor pentachloroethane concentration of the atmospheres. To study sample stability, four sets of six 3-L samples of 0.014 mg/m^3 pentachloroethane at 80% relative humidity were obtained. The samples were stored at room temperature for the first 7 days, and at 0 °C for the remainder of the period. These sets were analyzed at day 1, 7, 14, and 28. The mean recoveries were, respectively, 104, 105, 101.4, and 97.0%. The respective relative standard deviations were 7.4, 6.2, 9.0, and 16.7%. The breakthrough volume for the 70-mg bed of Porapak R was 14 L, when an atmosphere at 40 °C containing 126 mg/m^3 pentachloroethane and >80% relative humidity was sampled at 0.2 L/min.

REFERENCES:

[1] Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds - Research Report for Pentachloroethane, Contract No. 210-78-0012, Southern Research Institute for the Department of Health and Human Services, NIOSH (August, 1980).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 335, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] NIOSH Current Intelligence Bulletin 27. Chloroethanes: Review of Toxicity, U.S. Dept. of Health, Education & Welfare (NIOSH), Publ. 78-181 (1978).

[4] Carcinogenesis Bioassay of Pentachloroethane (CAS #76-01-7) in F344/N Rats and B6C3F$_1$ Mice (Gavage Study), Technical Report Series #232, NTP, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-1788 (April, 1983) and the National Toxicology Program, Box 12233, Research Triangle Park, NC 27709.

METHOD REVISED BY:

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PENTACHLOROPHENOL 5512

C_6Cl_5OH MW: 266.35 CAS: 87-86-5 RTECS: SM6300000

METHOD: 5512, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: solid; MP 190 °C; d 1.978 g/mL @ 22 °C; VP 16 Pa (0.12 mm Hg; 1700 mg/m^3) @ 100 °C

SYNONYMS: penta; PCP

SAMPLING

SAMPLER: FILTER + BUBBLER (mixed cellulose ester membrane with stainless steel backup screen/ethylene glycol)

FLOW RATE: 0.5 to 1.0 L/min

VOL-MIN: 48 L @ 0.5 mg/m^3
-MAX: 480 L

SHIPMENT: place filter in bubbler containing 15 mL ethylene glycol after sampling

SAMPLE STABILITY: at least 8 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.265 to 1.130 mg/m^3 [1] (180-L samples)
BIAS:	3.0%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.072
ACCURACY:	± 15% (12-28%)

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: pentachlorophenol

EXTRACTION: 10 mL methanol

INJECTION VOLUME: 20 µL

MOBILE PHASE: 60% methanol/40% water, 1.5 mL/min

COLUMN: µ-Bondapak C_{18}, 10-µm particle size, 30 cm x 3.9-mm ID

DETECTOR: UV @ 254 nm

CALIBRATION: standard solutions of pentachlorophenol in ethylene glycol and methanol

RANGE: 24 to 270 µg per sample [1]

ESTIMATED LOD: 8 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.051 @ 45 to 180 µg per sample [1]

APPLICABILITY: The working range is 0.13 to 11 mg/m^3 for a 180-L air sample. This method is also applicable to STEL measurements using a 15-L sample. The method has been used to sample for pentachlorophenol in the presence of 2,3,4,6-tetrachlorophenol at a lumber yard [3].

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S297 [2]. An independent analytical method provided by Vulcan Materials Co. [4] using a sampling train consisting of Zefluor filter and silica gel tube and HPLC analysis was used by a NIOSH contractor [5] for analyzing samples containing pentachlorophenol.

REAGENTS:

1. Pentachlorophenol*, ACS reagent grade.
2. Ethylene glycol, ACS reagent grade.*
3. Methanol, distilled in glass.
4. Isopropanol, distilled in glass.
5. Water, deionized and distilled.
6. Calibration stock solution, 5 mg/mL. Dissolve 50 mg pentachlorophenol in 10 mL isopropanol.

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm cellulose ester membrane filter (0.8-μm pore size) supported by stainless steel screen in three-piece filter holder followed by a 25-mL bubbler with 15 mL ethylene glycol.
2. Personal sampling pump, 0.5 to 1 mL/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 20-mL with PTFE-lined caps.
5. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5512-1).
6. Tweezers.
7. Syringes, 50- and 100-μL.
8. Volumetric flasks, 25-mL.
9. Pipets, 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 25-mL.

SPECIAL PRECAUTIONS: Pentachlorophenol can irritate the eyes, can be absorbed through the skin, and can cause liver damage [6]. Ethylene glycol is very toxic. It may be harmful or fatal if absorbed through the skin or swallowed, may cause kidney damage, and is a suspect reproductive hazard [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL ethylene glycol to a bubbler.
3. Attach outlet of filter holder to inlet arm of bubbler. Connect outlet arm of bubbler to a second empty bubbler and then to the sampling pump.
4. Sample 48 to 480 L (15 L for STEL) of air at an accurately known rate between 0.5 and 1.0 L/min.
5. Transfer filter carefully using tweezers to the bubbler. Seal bubbler for shipment in a suitable container in order to prevent damage during transit. Seal the inlet and outlet of the bubbler stem by connecting a piece of PTFE tubing between them or by inserting PTFE plugs in the inlet and outlet.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Transfer the liquid from the bubbler, quantitatively, to a graduated cylinder.
8. Bring volume to 15 mL with ethylene glycol. (If volume is greater than 15 mL, as would be the case when H_2O is scrubbed from humid air, record the volume and make an appropriate correction in the final calculations).
9. Just before analysis, add 10 mL methanol and mix gently but thoroughly.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards in the range 8 to 270 μg/25 mL.
    a. Add appropriate aliquots of calibration stock solution to a 60/40 (v/v) mixture of ethylene glycol and methanol.
    b. Analyze working standards together with samples and blanks (steps 13 through 15).

c. Prepare a calibration graph of peak area vs. amount (μg) of pentachlorophenol per 25 mL of sample.

11. Determine recovery for each lot of filters used for sampling in the concentration range of interest. Prepare four filters at each of five levels plus three media blanks.
    a. Spike aliquot of calibration solution onto each filter.
    b. After air-drying, extract filters in 15 mL ethylene glycol.
    c. Just before analysis, add 10 mL methanol and analyze (steps 13 through 15).
    d. Prepare graph of recovery vs. μg pentachlorophenol.
12. Check recovery at two levels for each sample set. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

13. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5512-1.
14. Inject 20-μL sample aliquot.
    NOTE: If sample peak area exceeds the linear calibration range, dilute, and apply appropriate dilution factor in calculations.
15. Measure peak area.

CALCULATIONS:

16. Determine mass, μg (corrected for recovery), of pentachlorophenol (W) found in the sample and the average media blank (B).
17. Calculate concentration of pentachlorophenol in the air volume sampled, V (L):

EVALUATION OF METHOD:

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

This method was validated over the range 0.265 to 1.31 mg/m^3 at 24 °C and pressure of 761 mm Hg using 180-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.072, with average recovery of 105%, representing a non-significant bias. The concentration of pentachlorophenol was independently verified by direct UV analysis of sample solutions. Recovery of pentachlorophenol from filters was 101% in the range 45 to 180 μg per sample. Sample stability during storage was evaluated at 100 μg pentachlorophenol per sample. Samples showed 95.3% recovery after eight days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S297, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Analysis of NIOSH Samples for Pentachlorophenol and Tetrachlorophenol, NIOSH/MRSB Sequence #4492, Utah Biomedical Research Laboratory, Salt Lake City, UT (unpublished, 1984).
[4] Vulcan Materials Co. Analytical Backup Report #1. Determination of Pentachlorophenol in Air, Birmingham, AL 35255 (1982).
[5] Analysis of NIOSH Samples for Pentachlorophenol, NIOSH/MRSB Sequence #4065, Southern Research Institute, Birmingham, AL 35255 (1984).

[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[7] CCINFO Database, Release 93-3, Record No. 41. Canadian Centre for Occupational Health and Safety, Hamilton, Ontario, Canada (1993).

METHOD REVISED BY:

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PENTACHLOROPHENOL in blood 8001

C_6HCl_5O MW:266.34 CAS: 87-86-5 RTECS: SM6300000

METHOD: 8001, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to pentachlorophenol.

SYNONYMS: PCP; Penta

SAMPLING	MEASUREMENT
SPECIMEN: whole blood in 5-mL tubes	**TECHNIQUE:** GAS CHROMATOGRAPHY, ECD
VOLUME: 5 mL	**ANALYTE:** pentachloroanisole (PCP methyl ether)
PRESERVATIVE: none	**INJECTION VOLUME:** 5 µL
SHIPMENT: polyethylene shippers with sample container kept at 10 °C	**COLUMN:** 1.8 m x 4-mm ID glass, 4% SE-30, 6% OV-210 on 80/100 mesh silanized support
ANTICOAGULANT: EDTA	**CARRIER GAS:** 5% methane in argon, 60 mL/min
SAMPLE STABILITY: unknown	**TEMPERATURE-INJECTOR:** 220 °C **-COLUMN:** 190 °C **-MANIFOLD:** 250 °C **-DETECTOR:** 300 °C
CONTROLS: collect at least 3 blood specimens from unexposed individuals per study or one control per 10 samples for studies exceeding 30 samples	**CALIBRATION:** solutions of pentachloroanisole in hexane
	QUALITY CONTROL: spiked pooled blood
	RANGE: 0.01 to 1 µg PCP/mL blood
	ESTIMATED LOD: 0.001 to 1 µg PCP/mL blood
	RECOVERY: 90%
	PRECISION ($\bar{S}_r$): 0.02
	ACCURACY: ± 13.9%

APPLICABILITY: This procedure measures free PCP. It is useful for monitoring PCP exposures via skin contact, inhalation, and ingestion. Blood PCP exposures are good indicators of acute short-term exposures because blood PCP values reach maximum 4 h after exposure [1]. Chronic exposures can best be monitored using Method 8303, Pentachlorophenol in urine.

INTERFERENCES: Chloronaphthalenes, polychlorinated biphenyl and Diuron are also hexane-extractable but are separated from PCP by column chromatography.

OTHER METHODS: This method is based on that of Borsetti [2].

REAGENTS:

1. Hexane, acetone, and benzene* (pesticide grade).
2. 20% benzene in hexane (v/v); 10% benzene in hexane (v/v).
3. Sulfuric acid, 6 M.
4. Sodium bisulfite.
5. Sodium sulfate, anhydrous.
6. Alumina (acid-washed), Brockman Activity I, 80/200 mesh
7. Pentachloroanisole (available from EPA Analytical Reference Lab).
8. Calibration stock solution equivalent to 100 mg/L PCP. Weight 0.0105 g pentachloroanisole; dilute to 100 mL with hexane in a volumetric flask. Stable 2 months if stored in refrigerator.
9. Diazomethane* prepared from Diazald kit according to manufacturer's instructions [3].
10. 5% methane in argon.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Blood-sampling tubes, 5-ml, with 7.5 mg Na_2EDTA anticoagulant (e.g., "lavender-top" tubes).
2. Gas chromatograph with a ^{63}Ni electron capture detector, electronic integrator, and column (page 8001-1).
3. Culture tubes, 16 x 150-mm and 16 x 125-mm, with PTFE-lined screw caps.**
4. Mixer, rotary, variable speed.
5. Centrifuge (refrigerated, optional).
6. Chromatography column, 7-mm ID x 200 mm, with a 50-mL reservoir and PTFE stopcock.**
7. Syringe, 10-µL, glass.
8. Pipets, 10- to 1000-µL.**
9. Flasks, volumetric, 10-, 25-, and 100-mL.**
10. Pipets, Pasteur, disposable.
11. Tubes, centrifuge, graduated, glass-stoppered, 15-mL.**
12. Waterbath, 100 °C.

**Wash with detergent; clean with chromic acid; rinse with distilled water, acetone, and hexane.

SPECIAL PRECAUTIONS: Samples of blood collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. Benzene is a documented human carcinogen and must be handled in compliance with 29 CFR 1910.1005.

Diazomethane and its precursor, n-Methyl-n-nitroso-p-toluene sulfonamide, are potent mutagens. Handle the bulk precursor in a glove box. Generate diazomethane behind an explosion shield in a hood.

SAMPLING:

1. Collect 5-mL whole blood samples by venipuncture in tubes containing 7.5 mg Na_2EDTA anticoagulant, about 4 h after suspected exposure.
2. Ship the blood samples in an insulated container with refrigerant to keep the temperature at about 10 °C. Do not freeze.

SAMPLE PREPARATION:

3. Add 2 mL whole blood to a 16 x 150-mm culture tube. Add cautiously and slowly 5 mL 6 M sulfuric acid. Cool to room temperature.
4. Add 6 mL hexane to the culture tubes in a hood; cap and place in a boiling waterbath for 45 min with shaking every 15 min.
5. Cool the culture tubes to room temperature and centrifuge at 2000 to 2500 rpm.
6. Remove the hexane layer into a 16 x 125-mm culture tube.

7. Extract twice more with 2 mL hexane for 2 min. Combine the extracts.
8. Concentrate the combined extracts to approximately 0.6 mL under a gentle stream of nitrogen.
9. Add 10 mL diazomethane reagent to the culture tube in a hood. Let stand in a hood for 1 h.
10. Concentrate to approximately 0.6 mL under a gentle stream of nitrogen in a hood.
11. Add 4 mL hexane. Evaporate the hexane solution to approximately 0.6 mL.
12. Add 4 g acid-washed alumina to a 7-mm ID x 200 mm chromatography column. Cap with 1.6 g anhydrous sodium sulfate. Rinse the column with 20% benzene in hexane. Let the column air dry and place it in an oven overnight at 130 °C. Cool the column to room temperature before use.
13. Wet the column with 5 mL hexane in a hood.
14. Add the concentrated derivatized extract when the solvent layer reaches the top of the sodium sulfate layer.
15. Rinse the culture tube three times with 0.5 mL hexane. Add the rinsings to the column.
16. Add 3.5 mL hexane to the column. Discard the hexane eluate.
17. Elute pentachloroanisole, the PCP derivative, with 20 mL 10% benzene in hexane.
18. Concentrate the sample to 2.0 mL in a graduated centrifuge tube.

CALIBRATION AND QUALITY CONTROL:

19. Prepare at least 6 working standards in the range 0.01 to 1 μg/mL PCP by dilution of the calibration stock solution with hexane.
20. Prepare a calibration graph (peak area vs. μg/mL PCP).
21. Maintain standardization by injecting a working standard after each five sample injections.
22. Run a spiked pooled control blood sample every ten samples, or if less than ten determinations are required, run at least three spiked pooled blood samples per study.
    NOTE: All blood that will be utilized for spiked pooled control blood samples must be analyzed for PCP before use because PCP is ubiquitous.

MEASUREMENT:

23. Set up the gas chromatograph according to manufacturer's instructions and to the conditions on page 8001-1.
24. Inject 5 μL sample extract (from step 18). Measure peak area of analyte.
    NOTE: The retention time for pentachloroanisole is about 4.7 to 5.0 min.

CALCULATIONS:

25. Determine the concentration, C (μg/mL), of PCP in blood by comparison of peak areas of samples with the calibration graph.

GUIDES TO INTERPRETATION:

Blood PCP levels for unexposed populations range between 0.016 to 0.32 μg/mL PCP [4,5,6]. The Biological Exposure Index is 5 mg/L for free PCP in end-of-shift plasma [7].

EVALUATION OF METHOD:

The precision for three sets of three samples of spiked whole blood was 2% relative standard deviation at levels of 0.05 to 1 μg/mL PCP whole blood, with 88 to 93% recovery.

REFERENCES:

[1] Brauan, W.H., G.E. Blau, M.B. Chenoweth. The Metabolism/Pharmacokinetics of Pentachlorophenol in Man, and a Comparison with Rat and Monkey, Toxicology Research Laboratory, Dow Chemical, Midland, MI 48640.

[2] Borsetti, A.P. Determination of Pentachlorophenol in Milk and Blood of Dairy Cattle, J. Agric. Food Chem., 28, 710-714 (1980).

[3] Diazald, Cat. No. 02800-0, Aldrich Chem. Co. Inc., Milwaukee, WI.

[4] Dougherty, R.C. Human Exposure to Pentachlorophenol in Human Blood and Urine, Dept. of Chemistry, Florida State University, Tallahassee, FL.

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[6] Klemmer, H.W., Wang, L., Sato, M.M., Reichert, E.L., Korsak, R.J. and Rashad, N.M. Clinical Findings in Workers Exposed to Pentachlorophenol, Arch. Environ. Contam. Toxicol, 9, 715-725 (1980).

[7] 1993-1994 Threshold Limit Values and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1993).

METHOD REVISED BY:

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PENTACHLOROPHENOL in urine 8303

C_6Cl_5OH MW: 266.33 CAS:87-86-5 RTECS: SM6300000

METHOD: 8303 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to pentachlorophenol.

SYNONYMS: PCP; Penta.

SAMPLING	MEASUREMENT
SPECIMAN: urine end of shift, mid to late in work week	**TECHNIQUE:** GAS CHROMATOGRAPHY, ECD
VOLUME: 100 mL in polyethylene bottle	**ANALYTE:** pentachloroanisole (PCP methyl ether)
PRESERVATIVE: 2 to 3 drops concentrated HCl added after collection	**INJECTION VOLUME:** 5 µL
SHIPMENT: ship frozen in dry ice	**COLUMN:** 1.8 m x 4-mm ID glass, 4% SE-30, 6% OV-210 on 80/100 mesh silanized support
SAMPLE STABILITY: 40 days if kept frozen	**CARRIER GAS:** 5% methane in argon, 60 mL/min
CONTROLS: collect 3 urine specimens from unexposed workers per study or 1 control urine per 10 samples	**TEMPERATURE-INJECTOR:** 220 °C **-COLUMN:** 190 °C **-MANIFOLD:** 250 °C **-DETECTOR:** 300 °C
	CALIBRATION: solutions of pentachloroanisole in hexane
	QUALITY CONTROL: spike urine pools; corrected for creatinine content
	RANGE: 5 to 1000 µg/L
	ESTIMATED LOD: 1 µg/L [1]
	RECOVERY: 0.947
	PRECISION ($\bar{S}_r$): 0.03 [1]
	ACCURACY: ± 10.3%

APPLICABILITY: This method measures free and conjugated PCP after hydrolysis and is useful when monitoring chronic PCP exposure via skin contact, ingestion or inhalation. Maximum urine levels are found 42 h after exposure [2]. Acute exposures are best monitored using Method 8001 (Pentachlorophenol in blood). Urine contains about 82% free PCP and 13% PCP glucuronide [1].

INTERFERENCES: Numerous potential interferences that can be extracted from urine include chloronaphthylenes, polychlorinated biphenyls and Diuron; these are eliminated by sample cleanup.

OTHER METHODS: This method combines and replaces P&CAM 230 [3] and P&CAM 358 [1].

REAGENTS:

1. Hexane, acetone, and benzene* (pesticide grade).
2. 20% benzene in hexane (v/v).
3. 10% benzene in hexane (v/v).
4. Hydrochloric acid (conc.).
5. Sodium bisulfite.
6. Sodium sulfate.
7. Alumina (acid-washed), Brockman Activity I, 80/200 mesh.
8. Pentachloroanisole (available from EPA Analytical Reference Lab).
9. Calibration stock solution equivalent to 100 mg/L PCP. Weigh 0.0105 g pentachloroanisole; dilute to 100 mL in a volumetric flask with hexane. Stable 2 months if stored in refrigerator.
10. Diazomethane*. Prepared from Diazald kit according to manufacturer's instructions [4].
11. 5% methane in argon.

* See Special Precautions.

EQUIPMENT:

1. Bottles, polyethylene, 125-mL, screw cap.**
2. Gas chromatograph with ^{63}Ni electron capture detector.
3. Culture tubes, 16 x 150-mm and 16 x 125-mm, with PTFE-lined screw caps.**
4. Mixer, rotary, variable speed.
5. Centrifuge (refrigerated, optional).
6. Chromatography column, 7-mm ID x 200 mm, with 50-mL reservoir and PTFE stopcock.**
7. Syringes, 10-μL, glass.
8. Pipets, 1000-, 500-, 250-, 100-, 50-, 25- and 10-μL.**
9. Flasks, volumetric, 10- and 100-mL.**
10. Pipets, Pasteur, disposable.
11. Tubes, centrifuge, graduated, glass-stoppered, 15-mL.**
12. Waterbath, 100 °C.

** Wash with detergent; clean with chromic acid; rinse with distilled water, acetone, and hexane.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. Benzene is a documented human carcinogen and must be handled in compliance with 29 CFR 1910.1005.

Diazomethane and its precursor, N-methyl-N-nitroso-p-toluene sulfonamide are potent mutagens. Handle the bulk precursor in a glove box. Generate diazomethane behind an explosion shield in a hood.

SAMPLING:

1. Collect a spot urine sample of 100 mL in a 125-mL polyethylene bottle.
2. Add two or three drops conc. HCl to the sample as a preservative.
3. Freeze the samples and pack them in an insulated shipper (e.g., styrofoam with dry ice).

SAMPLE PREPARATION:

4. Perform a creatinine determination on an aliquot of the urine (e.g., [5]).
5. Transfer a 4-mL aliquot of each urine sample to a 16 x 150-mm culture tube.
6. Add 1.0 mL conc. HCl and 100 mg sodium bisulfite to each culture tube.
7. Cap and place the culture tubes in a boiling waterbath for 1 h. Shake gently at 15-min intervals.
8. Cool the culture tubes to room temperature.
9. Add 5 mL benzene to each culture tube. Extract on a rotary mixer at 60 rpm for 1 h.
10. Centrifuge at 3000 rpm. Transfer benzene layer to a 16 x 125-mm culture tube. Repeat the extraction with an additional 5 mL benzene. Combine extracts.
11. Concentrate the extract to approximately 0.6 mL under a gentle stream of nitrogen.

12. Add 10 mL of diazomethane reagent (use hood). Let stand under hood for 1 h.
13. Concentrate under a hood to 0.6 mL under a gentle stream of nitrogen.
14. Add 4 mL hexane. Evaporate the solution to approximately 0.6 mL.
15. Add 4 g acid-washed alumina to a 7-mm ID x 200 mm chromatography column. Cap with 1.6 g anhydrous sodium sulfate. Rinse the column with 20% benzene in hexane. Air-dry. Place the column in a 130 °C oven overnight. Cool the column to room temperature before use.
16. Wet the column with 5 mL hexane (use fume hood).
17. Add the concentrated derivatized extract when the solvent layer reaches the top of the sodium sulfate layer.
18. Rinse the culture tube three times with 0.5 mL hexane. Add the rinsings to the column.
19. Add 3.5 mL hexane to the column. Discard the hexane eluate.
20. Elute pentachloroanisole, the PCP derivative, with 20 mL 10% benzene in hexane.
21. Concentrate the sample to 2.0 mL in a graduated centrifuge tube.

CALIBRATION AND QUALITY CONTROL:

22. Prepare at least six working standards in the range 5 to 1000 μg/L PCP by dilution of the calibration stock solution with hexane.
23. Prepare a calibration graph (peak area of analyte vs. μg/L PCP).
24. Maintain standardization by injecting a working standard after each five sample injections.
25. Run a spiked urine every ten samples or if less than ten determinations are required, run at least three spiked urines per run or study.
    NOTE: Urine used for spikes must be analyzed before use to determine background levels.

MEASUREMENT:

26. Set the gas chromatograph according to manufacturer's instructions and to conditions on page 8303-1.
27. Inject 5-μL sample extract from step 21. Measure peak area of analyte.
    NOTE: The retention time for pentachloroanisole is about 4.7 to 5.0 min.

CALCULATIONS:

28. Use the analyte peak area from the samples and the calibration graph to determine the PCP concentration in the extract analyzed, C_e (μg/L PCP).
29. Calculate the urine PCP concentration, C (μg/L PCP), by applying the extract concentration factor 2 (4 mL urine yields 2 mL extract):

$$C = 0.5C_e, \mu g/L \text{ PCP}.$$

30. Express PCP concentration as μg PCP/g creatinine.

GUIDES TO INTERPRETATION:

Urine pentachlorophenol levels for unexposed populations are reported to be between 20 and 40 μg/L PCP [6,7,8]. Symptoms have been reported at 200 μg/L PCP and levels in excess of 20 mg/L are fatal [7,9]. Lauwerys suggests an upper limit of 1 mg/g creatine [10]. The ACGIH Biological Exposure Index is 2 mg PCP/g creatinine [11].

EVALUATION OF METHOD:

The recovery of PCP from spiked urine samples was 93 to 96% for specimens containing 5 to 1000 μg PCP/L urine. The recovery of PCP from frozen urine samples spiked with 100 ng PCP/L urine and stored up to 36 days ranged from 85 to 91%.

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METHOD REVISED BY:

Anthony W. Smallwood, William P. Tolos, and Karl E. DeBord, NIOSH/DBBS; and Robert Kurimo, NIOSH/DPSE.

PENTAMIDINE ISETHIONATE

$C_{23}H_{36}N_4S_2O_{10}$ MW: 592.75 CAS: 140-64-7 RTECS: CV6500000

METHOD: 5032, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solid; MP 192.3 - 193.7 °C; soluble in water and ethanol

SYNONYMS: 4,4'-[1,5-pentanediylbis(oxy)]bisbenzenecarboximidamide bis(2-hydroxyethanesulfonate); Pentam 300

SAMPLING

SAMPLER: FILTER (37-mm, PVC in opaque cassette)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 50 L @ 1 $\mu g/m^3$
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 27 days @ 25 °C in the dark

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: none

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, FLUORESCENCE DETECTION

ANALYTE: pentamidine isethionate

RECOVERY: 3 mL of 50:50 ethanol:water, 0.085% H_3PO_4 and 0.04% TMAC; ultrasonic bath 10 min

INJECTION VOLUME: 100 μL

MOBILE PHASE: 19.6:80.4 CH_3CN: water, 0.085% H_3PO_4 and 0.04% TMAC; 1 mL/min

COLUMN: Ultrasphere C-8, 5-μm particles, 25 cm x 4.6-mm; ultrasphere C-8 guard

DETECTOR: fluorescence excitation/emission: 270/340 nm

CALIBRATION: pentamidine isethionate in eluent

RANGE: 50 to 3,000 ng per sample

ESTIMATED LOD: 18 ng per sample

PRECISION ($\bar{S}_r$): 0.065

APPLICABILITY: The working range is 0.5 to 30 $\mu g/m^3$ for a 100-L air sample. This method has been used to measure pentamidine isethionate in air in a hospital [1].

INTERFERENCES: None identified.

OTHER METHODS: None published for air samples. The method for measurement in solution is a variation of the method of Lin et al. [2].

REAGENTS:

1. Pentamidine isethionate, 99+% pure.
2. Water, deionized.
3. Ethanol, undenatured, chromatographic quality.
4. Acetonitrile, chromatographic quality.
5. Phosphoric acid, 42.5% solution. Dilute 85% solution 1:1 with water.
6. Tetramethylammonium chloride (TMAC), 10% solution. Dissolve 10.3 g of 97% pure reagent in water to make 100 mL of solution.
7. Eluent. Place 1 L of ethanol, 4 mL of 42.5% H_3PO_4, and 8 mL of 10% TMAC solution into a 2-L flask. Add water to make 2 L of solution.
8. Mobile phase. Place 4 mL of 42.5% H_3PO_4 and 8 mL of 10% TMAC into a 2-L flask. Add 1608 mL of water and 392 mL of acetonitrile.
9. Recovery solutions, 1.5, 35, and 1000 ng/μL. Dissolve 25 mg of pentamidine isethionate in ethanol to make 25 mL of solution. Make serial dilutions with ethanol. Recovery solutions are stable at least 6 days in the dark at 0 °C.
10. Disinfectant. 70% Ethanol or 70% isopropanol in water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two-piece filter cassette holder (opaque), 37-mm PVC membrane filter, 5-μm pore size.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph with a guard column packed with Ultrasphere C8, an analytical column (Beckman Instruments) (page 5032-1), and a fluorescence detector.
4. Volumetric flasks, 2-L and 25-mL.
5. Syringes, 1- and 0.5-mL, readable to 10 μL; 10 μL, readable to 0.2 μL.
6. Beakers, 50-mL.
7. Film, plastic, flexible, water-resistant.
8. Pipets, disposable.
9. Forceps.
10. Ultrasonic bath.
11. Biological safety cabinet [3].
12. Gloves, disposable.
13. Gauze pads.

SPECIAL PRECAUTIONS: This method includes safety steps to minimize exposure of the analyst to tuberculosis bacteria (Mycobacterium tuberculosis). A fraction of the patients with acquired immunodeficiency syndrome (AIDS) have tuberculosis. Consequently, live tuberculosis bacteria may be collected during air sampling.

Inhalation of tuberculosis bacteria in aerosols is the only notable means of transmission which results in infection. Infection does not result from skin contact. Thus, the analyst is safe as long as aerosols are not produced. The use of alcohol to kill tuberculosis bacteria simply increases the degree of safety.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach the sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 50 to 1500 L. Limit the loading of particulate matter on the filter to a maximum of about 1 mg.
4. Seal the inlet and outlet of the sampler with plugs.
5. Wet a gauze pad with disinfectant, and wipe the exterior surface of the sampler.
6. Pack the sampler securely for shipment.

SAMPLE PREPARATION:

NOTE: Sample preparation should be performed in a biological safety cabinet. Gloves should be worn.

7. Place the 37-mm PVC filter with the exposed side facing upward into a 50-mL beaker.
8. Add 3.0 mL of eluent to the beaker. Seal the mouth of the beaker with plastic, flexible, water-resistant film.
9. Place beaker into ultrasonic bath for 10 min. Use disinfectant as medium in ultrasonic bath.
10. Transfer solution to a sample vial with a disposable pipet.
    NOTE: Filtration of the sample solution is not recommended because fluorescent material could be leached from the filter or the housing for the filter, causing interference during analysis. Filtration is unnecessary because the guard column protects the analytical column from particulate matter.
11. Recover pentamidine isethionate from the interior surface of the front piece of the cassette filter holder.
    a. Add 3.0 mL of eluent to this cassette piece (original plug remains in the inlet).
    b. Wet much (about 80%) of the interior surface by tilting the cassette piece. Avoid bringing eluent into contact with glove being worn. Complete this step in about 15 seconds to minimize evaporation.
    c. Transfer solution to a sample vial with a disposable pipet.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least eight working standards over the range 2 to 1000 ng of pentamidine isethionate per mL of solution.
    a. Prepare a series of working standards in eluent by serial dilution.
       NOTE: Working standards in eluent are stable for more than 3 months when stored in the dark at 0 °C.
    b. Analyze together with samples and blanks (steps 15 through 17).
    c. Prepare a calibration graph (peak height or area versus concentration of pentamidine isethionate).
13. Determine recovery (R) at least once for each lot of PVC membrane filters used for sampling in the calibration range (step 12). Prepare three filters at each of five levels plus three media blanks.
    a. Place filters into 50-mL beakers.
    b. By means of a 10-μL syringe, fortify each filter with recovery solution.
    c. Seal the mouth of each beaker with plastic, flexible, water-resistant film.
    d. Store each sample overnight in the dark at 25 °C.
    e. Prepare samples (steps 7 through 10) and analyze with working standards (steps 15 through 17).
    f. Prepare a graph of R vs. ng of pentamidine isethionate recovered.
14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

15. Set liquid chromatograph to manufacturer's recommendations and to conditions given on page 5032-1.
16. Inject 100-μL sample aliquot manually or with autosampler.
17. Measure peak area or peak height.

CALCULATIONS:

18. Determine the mass, ng (corrected for R), of pentamidine isethionate found on the filter (W_f), on the average media blank (B_f), and the mass, ng, of pentamidine isethionate found on the interior surface of the cassette filter holder (W_c) and on the interior surface of a blank cassette filter holder (B_c).
19. Calculate concentration, C, of pentamidine isethionate in the air volume sampled, V (L):

$$C = \frac{(W_f + W_c - B_f - B_c)}{V}, \mu g/m^3.$$

EVALUATION OF METHOD:

Average recoveries after fortification of 37-mm PVC membrane filters with 50-, 99.9-, 300-, and 8816-ng quantities of pentamidine isethionate were 0.76, 0.81, 0.84, and 0.91, respectively; precision ($\bar{S}_r$) was 0.065 (24 samples, pooled). The average recovery of 324-ng quantities of pentamidine isethionate from PVC filters after 27 days of storage at room temperature in the dark was 0.97; s_r was 0.045 (6 samples). This method was not evaluated with generated atmospheres in a laboratory. However, the method was employed for measurement of pentamidine isethionate in air in a hospital [1]. Significant quantities [10 - 3,810 ng (3 - 11% of the totals)] of pentamidine isethionate were found on interior surfaces of the front pieces of eight cassette filter holders.

The LOD of pentamidine isethionate in solution was 7 ng per 3 mL. According to a curve of average recovery of pentamidine isethionate from PVC filters versus average concentration in solution, a conservative estimate of recovery was 0.40 when the concentration in solution was at the LOD. Thus, the LOD for pentamidine isethionate on a PVC filter was 18 ng (7 ng divided by 0.4). The LOQ for pentamidine isethionate on a PVC filter (50 ng) was the lowest level at which recovery was acceptable (>75%).

The LOD and LOQ for pentamidine isethionate on the interior surface of the front piece of a cassette filter holder were 7 and 24 ng, respectively.

A standard solution of pentamidine isethionate in eluent at a concentration of 100 ng/mL was stable for a period of more than 3 months during storage at 0 °C in the dark.

Smith states that for killing wet and dry tuberculosis bacteria, 95% ethanol and 50% ethanol, respectively, are most active . Also, perhaps 70% ethanol would be the best single solution for all purposes [4]. However, injection of a solution of pentamidine isethionate in 70% ethanol resulted in poor chromatography. Consequently, a 50% ethanol solution was selected for recovery of pentamidine isethionate from PVC filters.

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METHOD WRITTEN BY:

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n-PENTANE

See HYDROCARBONS, BP 36 to 126 °C (Method 1500) for procedure

2-PENTANONE

See KETONES I (Method 1300) for procedure

PHENOL and p-CRESOL in urine

(1) C_6H_5OH	MW: 94.11	CAS: 108-95-2	RTECS: SJ3325000
(2) $CH_3C_6H_4OH$	MW: 108.14	CAS: 106-44-5	RTECS: GO6475000

METHOD: 8305, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to phenol, benzene, and p-cresol.

SYNONYMS: (1) phenol: carbolic acid
(2) p-cresol: 4-methylphenol

SAMPLING		MEASUREMENT	
SPECIMEN:	two spot urine samples (before and after exposure)	**METHOD:**	GAS CHROMATOGRAPHY, FID
VOLUME:	50 to 100 mL in polyethylene screw-cap bottle containing preservative	**ANALYTE:**	phenol and p-cresol
PRESERVATIVE:	few crystals of thymol	**TREATMENT:**	acid hydrolysis; extraction
SHIPMENT:	freeze urine; ship in dry ice in an insulated container	**INJECTION VOLUME:**	5 µL
SAMPLE STABILITY:	stable for 4 days @ 25 °C and for 3 months @ −4 °C	**TEMPERATURE-INJECTION:** **-DETECTOR:** **-COLUMN:**	180 °C 200 °C 4 min @ 120 °C; 16 °C/min; 4 min @ 190 °C
CONTROLS:	collect urine from unexposed workers; pool and freeze the control urine	**COLUMN:**	3 m x 2-mm ID glass, 2% diethylene glycol adipate/Anakrom Q, 60/80 mesh
		CARRIER GAS:	N_2, 25 mL/min
		CALIBRATION:	analyte in control urine; nitrobenzene internal standard
		RANGE:	2 to 300 µg phenol/mL urine; 2 to 500 µg p-cresol/mL urine
		ESTIMATED LOD:	0.5 µg/mL urine
		RECOVERY:	(1) 94% @ 15 mg/mL; (2) 95% @ 50 µg/mL
		PRECISION ($\bar{S}_r$):	(1) 0.128; (2) 0.091
		ACCURACY:	(1) ± 31.0%; (2) ± 22.8%

APPLICABILITY: Phenol and p-cresol occur normally in urine. This method is useful in screening workers exposed to phenol, p-cresol, and benzene. The chief metabolite of benzene is phenol [1]. Workers exposed 8 h to 25 ppm benzene excreted about 150 mg phenol/L urine [2].

INTERFERENCES: o-Phenylphenol has a GC retention time similar to that of phenol. A careful work history/questionnaire is suggested.

OTHER METHODS: This method replaces P&CAM 330 [3]. A nonspecific colorimetric method yields 50% higher phenol concentrations with normal urine than does this method [4].

REAGENTS:

1. Phenol calibration stock solution, 2 mg/mL. Accurately weigh 200 mg phenol* and dissolve in distilled water. Dilute to 100 mL. Stable 14 days at 25 °C.
2. p-Cresol calibration stock solution, 5 mg/mL. Accurately weigh 500 mg p-cresol* and dissolve in methanol.* Dilute to 100 mL. Stable 14 days at 25 °C.
3. Diethyl ether.*
4. HCl, concentrated, or perchloric acid, 70%.*
5. Sodium sulfate, granular, anhydrous.
6. Thymol, USP.
7. Internal standard, 0.6 mg/mL. Dissolve 30 mg nitrobenzene* in 50 mL methanol.
8. Methanol.*
9. Nitrogen, purified.
10. Hydrogen, purified.
11. Air, filtered.
12. Dry ice.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Bottles, polyethylene, screw-top, 125-mL.
2. Gas chromatograph with FID, integrator and column (page 8305-1).
3. Centrifuge tubes, 15-mL, graduated, glass-stopper.
4. Syringe, 10-µL, readable to 0.1 µL.
5. Volumetric flasks, 100-mL.
6. Pipets, Pasteur.
7. Pipets, 1-, 2- and 5-mL.
8. Mixer, vibration.
9. Culture tubes, disposable, 10 x 75-mm.
10. Water bath, 95 °C.
11. Ice bath or freezer.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided. Diethyl ether and methanol are fire risks. Phenol, p-cresol, methanol and nitrobenzene are toxic and can be absorbed through the skin. Hydrochloric acid and perchloric acid can damage the skin. Wear gloves and eye protection. Work in a fume hood. Handle perchloric acid only in a perchloric acid hood.

SAMPLING:

1. Collect 50 to 100 mL urine in a 125-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Collect two urine samples for each worker, one prior to exposure and one after exposure. Also, collect and pool control urine samples from unexposed workers.
2. Close the bottle immediately after sample collection and swirl gently to mix.
3. Freeze the urine and ship in dry ice in an insulated container.

SAMPLE PREPARATION:

4. Thaw urine sample.
5. Determine creatinine (g/L urine) in an aliquot of the urine [5].
6. Pipet 5.0 mL urine into a 15-mL centrifuge tube.
7. Add 1 mL conc. HCl or 5 drops 70% perchloric acid. Mix well.
8. Stopper loosely. Heat in a water bath at 95 °C for 1.5 h.
9. Remove from water bath. Add 10 µL internal standard. Adjust volume in the centrifuge tube to 10 mL with distilled water.
10. Pipet 2 mL diethyl ether into the tube. Stopper and shake vigorously for 1 min. Cool the tube to 0 °C and allow the phases to separate.

11. Transfer ca. 0.5 mL of the clear ether layer to a culture tube. Add a few milligrams of Na_2SO_4 and mix. Cap the tube and keep it at 0 °C prior to measurement to avoid evaporation.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with combined working standards containing 0.5 to 300 μg phenol/mL solution and 0.5 to 500 μg p-cresol/mL solution.
    a. Add known amounts of phenol and p-cresol calibration stock solutions to pooled control urine in 100-mL volumetric flasks and dilute to the mark with pooled control urine.
    b. Process 5 mL of each working standard using the same procedure as for the samples (steps 6 through 11).
    c. Analyze working standards with urine samples and pooled control urines.
    d. Plot separate calibration graphs for phenol and p-cresol (ratio of peak area of analyte to peak area of nitrobenzene vs. μg analyte/mL solution).

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 8305-1. Inject an aliquot of the extract from step 11 using solvent flush technique.
14. Measure peak areas. Divide the peak areas of phenol and p-cresol by the peak area of nitrobenzene on the same chromatogram.

CALCULATIONS:

15. Determine the phenol and p-cresol concentrations (μg/mL) in the urine sample from the calibration graphs.
16. Calculate the concentrations of phenol and p-cresol per gram of creatinine in the urine sample by dividing by the creatinine value obtained in step 5. Compare the results obtained on the pre- and post-shift samples for each worker.

GUIDES TO INTERPRETATION:

The normal range for phenol found in this laboratory for human controls not exposed to benzene, phenol, or p-cresol was 4.5 to 20.7 mg phenol/g creatinine. The normal range found for p-cresol was 5.5 to 65 mg/g creatinine. It must be emphasized that laboratories should establish their own normal ranges using urine specimens from personnel not exposed to benzene, phenol, p-cresol or excessive amounts of dietary sodium benzoate (used as a preservative in some foods). Lauwerys [6] reported "tentative maximum permissible values" of 45 mg phenol/g creatinine for benzene exposures and 300 mg phenol/g creatinine for phenol exposures. No values were reported for p-cresol. The ACGIH Biological Exposure Index is 250 mg phenol/g creatinine [7].

EVALUATION OF METHOD:

Ten spiked urine specimens containing phenol and p-cresol at concentrations of 10 and 50 μg/mL urine, respectively, were analyzed for each analyte. Precision ($\bar{S}_r$) for the ten spiked replicate urine samples was 0.128 for phenol and 0.091 for p-cresol.

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METHOD REVISED BY:

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PHENYL ETHER

$(C_6H_5)_2O$ MW: 170.22 CAS: 101-84-8 RTECS: KN8970000

METHOD: 1617, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: STEL 2 ppm
(1 ppm = 6.96 mg/m^3)

PROPERTIES: solid, geranium-like odor; MP 27 °C; BP −257 °C; d 1.072 g/mL @ 22 °C; VP 2.7 Pa (0.02 mm Hg) @ 25 °C; vapor density 5.86 (air = 1); flash pt. 115 °C; flammable limits in air

SYNONYMS: diphenyl ether; diphenyl oxide; 1,1'-oxybisbenzene.

SAMPLING

SAMPLER: CHARCOAL TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 1 ppm
-MAX: 50 L

SHIPMENT:

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3.0 to 13.0 mg/m^3 [1] (10-L samples)

BIAS: 0.06%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 [1,2]

ACCURACY: ± 13.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: phenyl ether

EXTRACTION: 0.5 mL carbon disulfide, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 265 °C
-COLUMN: 215 °C

COLUMN: 10 ft x 1/8-in. ID stainless steel column packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W

DETECTOR: flame ionization detector

CALIBRATION: standard solutions of phenyl ether in hexane

RANGE: 7 to 210 µg per sample [1,2]

ESTIMATED LOD: 0.7 µg per sample [1,2]

PRECISION ($\bar{S}_r$): 0.048 [1,2]

APPLICABILITY: The working range is 0.1 to 9 ppm (0.7 to 60 mg/m^3) for a 10-L air sample. Better sensitivity may be achieved with a capillary column with appropriate adjustment in the instrumental conditions. A DB-wax (polyethelyene glycol) or equivalent is similar to the FFAP packed column.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S72 [3].

REAGENTS:

1. Phenyl ether*, ACS reagent grade.
2. Carbon disulfide*, ACS reagent grade.
3. Hexane, distilled in glass.
4. Calibration stock solution, 17.3 mg/mL, of phenyl ether in hexane.
5. Prepurified nitrogen.
6. Prepurified hydrogen.
7. Filtered compressed air.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tubes, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg)separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube a 1 L/min airflow must be less than 4.3 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 1-mL with PTFE-lined caps.
5. Gas chromatograph with a flame ionization detector, recorder, integrator and column (page 1617-1).
6. Tweezers.
7. Syringes, 5-, 10- and 100-μL; other sizes as needed.
8. Volumetric flasks, 10- and 25-mL.
9. Pipets, 0.5-, 1-, and 10-mL glass, delivery, with pipet bulb, graduated to 0.1-mL increments.
10. Graduated cylinders, glass, 25-mL.
11. File.

SPECIAL PRECAUTIONS: Phenyl ether is toxic by inhalation. All work with carbon disulfide should be performed in a hood because of its high toxicity and flammability (flash point = −30 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm). Attach sampler to personal sampling pump with flexible tubing.
3. Sample 1 to 50 L of air at an accurately known flow rate between 0.01 and 0.2 L/min.
4. Record the humidity temperature, and pressure of the atmosphere being sampled, if pressure reading is not available, record the elevation.
5. Cap each tube with plastic plugs and pack securely for shipment.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Place front and back sections of the sampler in separate 1-mL vials. Discard the glass wool and foam plugs.
8. Add 0.5 mL carbon disulfide to each sample vial and attach the crimp cap.
9. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of 7 to 210 μg per sample.
    a. Add known amounts of calibration stock solution to carbon disulfide in 10-mL volumetric flasks and dilute to the mark.
    b. Analyze working standards together with samples and blanks (steps 13 and 14).
    c. Prepare a calibration graph of area vs. μg of analyte per sample.
11. Determine desorption efficiency (DE) for each lot of charcoal tubes used for sampling in the concentration range of interest. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of phenyl ether (or a solution of phenyl ether in hexane) directly onto front (100 mg) sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 7 through 9) and analyze together with standards (steps 13 and 14).
    e. Prepare a graph of desorption efficiency vs. μg phenyl ether per sample.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set instrument according to manufacturer's recommendations and to conditions given on page 1617-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above linear range of the working standards, dilute an aliquot with carbon disulfide, reanalyze, and apply the appropriate dilution factor in calculations.
14. Measure peak area.

CALCULATIONS:

15. Determine mass, μg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blanks front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration (C) of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - W_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 3.0 to 13.3 mg/m^3 with 10-L samples collected from dry (0% RH) air [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.07, with average recovery of 100.6%. The test atmosphere concentration of phenyl ether was monitored with a Beckman model 402 total hydrocarbon analyzer. Desorption efficiency (DE) at 7 μg per sample was 80% and approximately 90% in the range 32 to 120 μg per sample. Sample recovery (corrected for DE) was 100.2% over the range 32 to 120 μg. No breakthrough was seen after 4 h when a concentration of 13.1 mg/m^3 was sampled at a flow rate of 0.185 L/min. Sample stability was not determined.

REFERENCES:

[1] Backup Data Report, Phenyl Ether, No. S72, prepared under NIOSH Contract CDC-99-74-45.
[2] Documentation of NIOSH Validation Tests, NIOSH Contract. CDC-99-74-45.
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S72, U. S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE.

PHENYL ETHER-DIPHENYL MIXTURE

$(C_6H_5)_2O$ & $C_6H_5C_6H_5$ MW: 166 (average) CAS: not assigned RTECS: not assigned

METHOD: 2013, Issue 1 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1994

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: no TLV
(1 ppm = 6.79 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 257 °C; MP 12 °C; d = 1.06 g/mL @ 25°C; VP = 10 Pa (0.08 mm Hg) @ 25 °C; vapor density (air = 1) 5.7.; flammable limits in air 0.5 to 6.2% v/v

SYNONYMS: None. This is a liquid eutectic, prepared by dissolving 26.5 parts by weight solid diphenyl in 73.5 parts melted phenyl ether.

SAMPLING

SAMPLER: SORBENT TUBE (silica gel, 150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 1 ppm
-MAX: 40 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 3.86 to 15.7 mg/m^3 [1] (10-L samples)

BIAS: − 0.35%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089 [1]

ACCURACY: ± 17.2%

MEASUREMENT

TECHNIQUE: gas chromatography, FID

ANALYTE: phenyl ether-diphenyl mixture

EXTRACTION: 0.5 mL benzene for 30 min

INJECTION VOLUME: 5 µL

CARRIER GAS: nitrogen, 50 mL/min

COLUMN: 10-ft x 1/8-in stainless steel column packed with 5% OV-17 on 80/100 mesh, acid washed DMCS Chromosorb W

DETECTOR: flame ionization detector

CALIBRATION: standard solutions of eutectic mixture in hexane

RANGE: 7 to 210 µg per sample [1]

ESTIMATED LOD: 4 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.073 @ 38 to 156.7 µg per sample [1]

APPLICABILITY: The working range is 0.1 to 10 ppm (0.7 to 70 mg/m^3) for a 10-L air sample. Better sensitivity may be achieved with a capillary column in place of a packed column; a DB-17 column (50% methyl, phenyl-50% dimethyl-polysiloxane) with appropriate instrumental conditions is recommended.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S73 [2] in fourth edition format.

REAGENTS:

1. Diphenyl*, reagent grade.
2. Phenyl ether*, reagent grade.
3. Phenyl ether-biphenyl mixture: dissolve 2.65 g solid diphenyl in 7.35 g melted phenyl ether (10 g mixture, liquid eutectic).
4. Benzene*, reagent grade.
5. Hexane, reagent grade.
6. Calibration stock solution, analyte mixture in hexane, 17.5 mg/mL.
7. Hydrogen, prepurified.
8. Air filtered, compressed.
9. Nitrogen, purified.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; with plastic caps; containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg; back = 75 mg). A silylated glass wool plug proceeds the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.20 L/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 1-mL with PTFE-lined crimp caps.
5. Gas chromatograph, flame ionization detector, recorder, integrator and column (page 2013-1).
6. Tweezers.
7. File.
8. Syringes, 5-, 50- and 100-μL, other sizes if needed.
9. Volumetric flasks, 10-mL.
10. Pipets, 0.5-, and 1.0-mL glass, delivery, graduated in 0.1-mL increments, with pipet bulb.
11. Graduated cylinders, glass, 10-mL.

SPECIAL PRECAUTIONS: Benzene is a carcinogen, toxic and is flammable. Phenyl ether is toxic by inhalation. Diphenyl is toxic. Work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2-mm). Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample volume of 1 to 40 L.
4. After the sample is collected, cap each tube with plastic plugs and pack securely for shipment.
5. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

6. Place front and back sorbent sections of the sampler tube in separate vials. Discard the glass wood and foam plugs.
7. Add 0.5 mL benzene to each sample vial and attach the crimp cap.
8. Allow to stand for 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 0.5 mL benzene.
   b. Analyze with samples and blanks (steps 12 and 13).

c. Prepare calibration graph (peak area vs. μg phenyl ether-diphenyl mixture.

10. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze with working standards (steps 12 and 13).
    e. Prepare a graph of DE vs. μg mixture recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2013-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with benzene, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area for each analyte peak and sum together for each sample or standard.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of phenyl ether-diphenyl mixture found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of mixture in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 3.86 to 15.7 mg/m^3 using 10-L samples collected from dry air (0% RH) [2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.089, with average recovery of 100.1%, representing a non-significant bias. Recovery of analyte from silica gel tubes was 100.0% in the range 4.0 to 15.7 μg per sample after desorption efficiency correction. Desorption efficiency ranged from 89 to 101% over 7 to 102 μg/sample. No breakthrough was seen when a concentration of 14.9 mg/m^3 was collected at 0.18 L/min for 4 hours. Sample storage stability was not determined.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
[2] NIOSH Manual of Analytical Methods, 2nd. ed. V. 2, S73, U. S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

Y.T. Gagnon, NIOSH/DPSE.

PHENYL GLYCIDYL ETHER

$C_6H_5OCH_2CH(O)CH_2$ MW: 150.18 CAS: 122-60-1 RTECS: TZ3675000

METHOD: 1619, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 10 ppm
NIOSH: C 1 ppm/15 min; carcinogen
ACGIH: 1 ppm
(1 ppm = 6.14 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.109 g/mL @ 20 °C; BP 245 °C; VP 1 Pa (0.01 mm Hg, 13 ppm) @ 25 °C

SYNONYMS: glycidyl phenyl ether; 1,2-epoxy-3-phenoxypropane; phenyl 2,3-epoxypropyl ether; (phenoxymethyl)oxirane; PGE

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 80 L @ 1 ppm
-MAX: 150 L

SHIPMENT: routine (refrigerate at lab)

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 31 to 121 mg/m^3 [1] (50-L samples)

BIAS: − 7.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 16.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: phenyl glycidyl ether

DESORPTION: 0.5 mL CS_2, 30 min

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 265 °C
-COLUMN: 90 °C

INJECTION VOLUME: 5 µL

CARRIER GAS: N_2, 50 mL/min

COLUMN: stainless steel, 3.2-mm ID x 3 m, packed with 10% FFAP on 80/100 mesh Chromosorb W-AW DMCS

CALIBRATION: standard solutions of phenyl glycidyl ether in CS_2

RANGE: 0.5 to 6 mg per sample

ESTIMATED LOD: not determined

PRECISION ($\bar{S}_r$): 0.022 [1]

APPLICABILITY: The working range is 1 to 33 ppm (6 to 200 mg/m^3) for an 80-L air sample. An appropriate capillary column may be used for better resolution and sensitivity. The sorbent's capacity for the analyte has not been determined under conditions of high relative humidity.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S74 [2] in a revised format.

REAGENTS:

1. Carbon disulfide* (CS_2), chromatographic quality.
2. Phenyl glycidyl ether*, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, purified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate tubes, 7.0 cm long, 6-mm OD, 4-mm ID; flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut charcoal (front = 100 mg; back = 50 mg) separated by a urethane foam plug. A silanized glass wool plug held in place with a metal spring precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1.0 L/min air flow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1619-1).
4. Vials, 2-mL, with PTFE-lined crimp caps.
5. Microliter syringes, 10-μL and convenient sizes for making dilutions.
6. Flasks, volumetric, 10-mL.
7. Pipets, 0.5-mL, with bulb.

SPECIAL PRECAUTIONS: Both phenyl glycidyl ether and CS_2 are toxic [3]. In addition, CS_2 is a serious fire and explosion hazard (flash point = −30 °C). All work with these compounds must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 80 to 150 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 0.5 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.01 to 6 mg phenyl glycidyl ether per sample.
   a. Add a known amount of phenyl glycidyl ether to CS_2 in 10-mL volumetric flask and dilute to the mark. Use serial dilutions as needed for smaller concentrations.
   b. Analyze with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (phenyl glycidyl ether peak area vs. mg phenyl glycidyl ether per 0.5 mL).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three medial blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject known amount (1 to 20 μL) of phenyl glycidyl ether or standard solution of phenyl glycidyl ether in CS_2 directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg phenyl glycidyl ether recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1619-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of phenyl glycidyl ether found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of phenyl glycidyl ether in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

S74 was issued on February 14, 1975 [2] and validated over the range 31 to 121 mg/m^3 for 50-L air samples from dynamically generated test atmospheres [1]. The average recoveries ranged from 91.2 to 93.7%. The phenyl glycidyl ether concentrations were independently measured by means of a total hydrocarbon analyzer. Breakthrough was not observed after sampling 220 L from a test atmosphere containing 112 mg/m^3 of phenyl glycidyl ether. The average desorption efficiency was 98% over the range of 1.5 to 6 mg per sample. Sample stability was not determined; however, refrigeration of the samples upon receipt by the labortory is recommended.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S74, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977). Available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S74, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

R.A. Glaser, NIOSH/DPSE. Method S74 was originally validated under NIOSH Contract CDC-99-74-45.

$C_6H_5NHNH_2$ MW: 108.14 CAS: 100-63-0 RTECS: MV8925000

METHOD: 3518, Issue 1 **EVALUATION:** **Issue 1: 15 August 1994**

OSHA : 5 ppm (skin)
NIOSH: C 0.14 ppm/120 min (skin)
ACGIH: 5 ppm, STEL 10 ppm, suspect carcinogen
(1 ppm = 4.42 mg/m^3 @ NTP)

PROPERTIES: solid; MP 19.5 °C; d 1.098 g/mL @ 20 °C; VP 5 Pa (0.04 mm Hg; 50 ppm) @ 25 °C

SYNONYMS: hydrazinobenzene, hydrazine-benzene

SAMPLING

SAMPLER: GLASS MIDGET BUBBLER (containing 15 mL 0.1 M hydrochloric acid)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 25 L @ 5 ppm
-MAX: 120 L

SHIPMENT: hand delivery or use of bubbler shipping cases

SAMPLE STABILITY: at least 5 days at room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 10.4 to 44.8 mg/m^3 [1] (100-L samples)

BIAS:

OVERALL PRECISION ($\hat{S}_{rT}$): 0.060 [1]

ACCURACY:

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: phenylhydrazine hydrochloride/ phosphomolybdic acid complex

SAMPLE WORKUP: transfer bubbler solution, two 5-mL rinses, and 10 mL phosphomolybdic acid to 50-mL volumetric flask

DILUTION: 3-mL aliquot diluted to 10 mL

COLORIMETRY: absorbance @ 730 nm

CALIBRATION: phenylhydrazine hydrochloride in 0.1 M hydrochloric acid

RANGE: 0.5 to 4.4 mg per sample [1]

ESTIMATED LOD: 0.2 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.023 [1]

APPLICABILITY: The working range is 1.1 to 11 ppm (5 to 45 mg/m^3) for a 100-L air sample.

INTERFERENCES: Other hydrazines may interfere in the analysis; reducing agents such as ferrous salts may interfere also [2].

OTHER METHODS: This is Method S160 [2] in a revised format. Feinsilver et al. [3] provided the basis for this method. Murty et al. [4] used photometry and photometric titrations with cacotheline as a reagent to determine phenylhydrazine in the range of 0.1 to 2 mg. Hasan [5] determined phenylhydrazine spectrophotometrically over a range of 0.1 to 3.0 mg using copper (II) nitrate.

REAGENTS:

1. Phenylhydrazine hydrochloride*.
2. Hydrochloric acid, concentrated*.
3. Phosphomolybdic acid.
4. Distilled water.
5. Collection medium, 0.1 M HCl. Fill a 1-L volumetric flask with approximately 300 mL distilled water, add 8.6 mL concentrated HCl, mix and dilute to the mark.
6. Phosphomolybdic acid solution (PMA). Dissolve 15 g PMA in 500 mL distilled water, allow to stand one day, and filter before use through a fluted paper filter.
7. Phenylhydrazine hydrochloride stock solution. Weigh accurately 0.1 g phenylhydrazine hydrochloride into a 100-mL volumetric flask and fill to the mark with 0.1 M HCl.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass, standard midget bubbler with a stem that has a fritted glass end. The fritted end should have a maximum pore diameter of approximately 170 to 220 μm.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm ID and 8-mm OD) glass tube loosely packed with glass wool and inserted between the exit arm of the bubbler and the pump.
3. Spectrophotometer, visible, 730 nm, with cuvettes, 1-cm.
4. Volumetric flasks, 1000-, 100-, 50-, and 10-mL.
5. Pipets, glass, 1-, 2-, 3-, 6-, 9-, and 10-mL, delivery, with pipet bulb.
6. Graduated cylinders, glass, 10- and 25-mL.

SPECIAL PRECAUTIONS: Concentrated hydrochloric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron, and full face shield with goggles. Phenylhydrazine is viewed as a potential carcinogen [6,7] and should be handled in a hood. Exposure to phenylhydrazine has caused hemolytic anemia [6,7]. Phenylhydrazine is a highly reactive reducing agent, and contact with oxides of copper or iron and manganese, lead, copper, or their alloys can cause fires and explosions [7]. Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL 0.1 M HCl into each bubbler. Connect the bubbler to trap and trap to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 25 to 120 L.
4. After sampling, tap bubbler stem gently against inside wall of bubbler bottle to recover as much sampling solution as possible. Wash stem with 5 mL distilled water and add wash to bubbler. Prior to shipping, seal bubblers with a hard, non-reactive stopper (preferably PTFE or glass).

SAMPLE PREPARATION:

5. Transfer liquid from bubbler to a 50-mL volumetric flask.
6. Rinse bubbler twice with 5 mL distilled water. Add rinses to volumetric flask.
7. Add 10 mL phosphomolybdic acid solution to volumetric flask and dilute to mark with distilled water.
8. Pipet a 3-mL aliquot into a 10-mL volumetric flask and dilute to mark with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Transfer 15 mL 0.1 M HCl to a 50-mL volumetric flask.
   b. Pipet 1 to 10 mL of phenylhydrazine hydrochloride stock solution into the volumetric flask.
   c. Continue preparation as with samples (steps 7 and 8).
   d. Analyze together with samples and blanks (steps 11 and 12).
   e. Prepare calibration graph (absorbance vs. mg phenylhydrazine hydrochloride per sample).
10. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph is in control.

MEASUREMENT:

11. Set spectrophotometer according to manufacturer's recommendations and to conditions given on p. 3518-1. Fill 1-cm cuvette with sample from 10-mL volumetric flask.
12. Read sample absorbance at 730 nm against a reagent blank prepared in the same manner as the samples (steps 9.a, 7, and 8).

CALCULATIONS:

13. Calculate the mass, mg, of phenylhydrazine hydrochloride in each sample (W) and average field blank (B).
14. Calculate the concentration, C, of phenylhydrazine in the air volume sampled, V (L):

$$C = \frac{W - B}{V} \cdot \frac{108.1}{144.6} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 10.37 to 44.8 mg/m^3 at 22 °C and 761 mm Hg using 100-L samples [1,2]. The average recovery was 95%, while the recovery from samples after five days storage was 100% [1]. Sample stability during storage was evaluated at a level of 4.4 mg phenylhydrazine per sample [1].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S160, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S160, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Feinsilver, L. Perregrino, J.A., and Smith, C.J. Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," Am. Ind. Hyg. Assoc. J., 20, 26 (1959).
[4] Murty, N.K., Rao, V.J., and Rao, N.V.S., "Detection and Determination of Phenylhydrazine," Talanta, 31 (6), 466 (1984).
[5] Hasan, T., "Resin Bead Detection and Spectrophotometric Determination of Phenylhydrazine Using Inorganic Reagents," Anal. Lett., 21 (4), 633 (1988).
[6] NIOSH Criteria for a Recommended Standard: Occupational Exposure to Hydrazines, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-172 (1978).

[7] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Larry D. Olsen, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract CDC-99-74-45.

PHOSPHINE

PH_3 MW: 34.00 CAS: 7803-51-2 RTECS: SY7525000

METHOD: 6002, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 0.3 ppm
NIOSH: 0.3 ppm; 1 ppm STEL
ACGIH: 0.3 ppm; 1 ppm STEL
(1 ppm = 1.39 mg/m^3 @ NTP)

PROPERTIES: gas, BP −87.8 °C; vapor density 1.17 (air = 1); spontaneously flammable in air if P_2H_4 is present

SYNONYMS: hydrogen phosphide; phosphorous hydride; phosphorated hydrogen; phosphorous trihydride

SAMPLING

SAMPLER: SORBENT TUBE
($Hg(CN)_2$-coated silica gel, 300 mg/150 mg)

FLOW RATE: 0.01 - 0.2 L/min

VOL-MIN: 1 L @ 0.3 ppm
-MAX: 16 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.195 to 0.877 mg/m^3 [1] (16-L samples)
BIAS:	− 0.4%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.091 @ 2.64 to 17.41 µg per sample [2]
ACCURACY:	± 17.6%

MEASUREMENT

TECHNIQUE: UV-VIS SPECTROMETER

ANALYTE: phosphate

EXTRACTION: 10 mL hot (65-70 °C) acidic permanganate reagent solution

DETECTOR: UV @ 625 nm

CALIBRATION: standard solutions of potassium dihydrogen phosphate (KH_2PO_4) (1.00 mL = 49.94 µg PH_3)

RANGE: 0.3 to 10 µg per sample [2]

ESTIMATED LOD: 0.1 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.074 @ 2.6 to 17.4 µg per sample [2]

APPLICABILITY: The working range is 0.013 to 0.6 ppm (0.02 to 0.9 mg/m^3) for a 16-L air sample. The sampler is not commercially available.

INTERFERENCES: The colorimetric determination of phosphate is subject to interference by any species that also forms a molybdate complex under these condition; possible interfering species include PCl_3 and PCl_5 vapors and organic phosphorous compounds.

OTHER METHODS: This revises Method S332 [2]. OSHA Method ID-180, "Phosphine in Workplace Atmospheres", [3] employing potassium hydroxide-impregnated carbon media may be used as an alternative method.

REAGENTS:

1. Potassium dihydrogen phosphate, anhydrous, KH_2PO_4, ACS reagent grade
2. Sulfuric acid, concentrated, ACS reagent grade
3. Ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$
4. Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2$
5. Potassium permanganate, $KMnO_4$
6. Stannous chloride, $SnCl_2$
7. Glycerol
8. Toluene
9. Isobutanol
10. Methanol
11. Water, deionized or distilled.
12. Mercuric cyanide, $Hg(CN)_2$*
13. Standard phosphate solution. Dissolve 200 mg KH_2PO_4 in 1 L of distilled water. (1.00 mL = 49.94 μg PH_3)
14. Molybdate solution. Dissolve 49.4 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 112 mL concentrated H_2SO_4 in distilled water to a total volume of 1 L.
15. Alcoholic sulfuric acid solution. Add 50 mL of concentrated H_2SO_4 to 950 mL methanol.
16. Toluene-isobutanol solvent. Mix equal volumes of toluene and isobutanol.
17. Ferrous solution. Dissolve 7.9 g $Fe(NH_4)_2(SO_4)_2$ and 1 mL concentrated H_2SO_4 in water to a total volume of 100 mL.
18. Stannous chloride solution. Dissolve 0.4 g $SnCl_2$ in 50 mL glycerol (heat to dissolve).
19. Acidic permanganate solution. Dissolve 0.316 g $KMnO_4$ and 6 mL concentrated H_2SO_4 in 1 L water.
20. Mercuric cyanide solution.* Dissolve 2 g $Hg(CN)_2$ in 100 mL water.

* See Special Precautions

EQUIPMENT:

1. Sampler: Glass tube 12-cm long, 6-mm O.D., 4-mm I.D., flame-sealed ends with plastic caps, with two sections of mercuric cyanide-treated silica gel (45/60 mesh), (front = 300 mg, back = 150 mg), separated and retained by silylated glass wool plugs. (See Appendix)
2. Personal sampling pump, 0.01 to 0.2 mL/min, with flexible polyethylene or PTFE tubing.
3. Spectrometer capable of measuring absorbance or transmittance at 625 nm.
4. Two matched 5-cm absorbance cells, silica, with tight fitting caps.
5. Separatory funnel, 125-mL.
6. Beakers, 50-mL.
7. Pipets, 0.2-, 10-, and 25-mL, and other convenient sizes to make standard dilutions.
8. Volumetric flasks, 10-, 25-, 100-, and 1000-mL.
9. Water bath (maintained at 65-70°C).
10. Graduated cylinders, glass, 10-mL.
11. Syringes, 0.5- and 1.0-mL.
12. Balance.
13. Thermometer.
14. Stopwatch.
15. Barometer.

SPECIAL PRECAUTIONS: Caution should be exercised when preparing the sampling media because mercuric cyanide is toxic. Work only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the silica gel tubes to provide an opening of at least one half the internal diameter of the tube. Attach the silica gel tube to the sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 16 L.
4. Seal tubes with plastic (not rubber) caps.

SAMPLE PREPARATION:

5. Place front and back sorbent sections in separate 50-mL beakers.
6. Add 10 mL of acidic permanganate solution to each beaker. Place in a water bath maintained at 65-70 °C for 90 min.
7. Decant the acidic permanganate solution into a 10-mL volumetric flask, and dilute to volume with distilled water.
8. Wash the silica gel twice with 3 mL portions of distilled water and decant the contents into another 10-mL volumetric flask containing 1 mL of ferrous solution. Dilute to volume with distilled water.
9. Add the contents of both 10-mL volumetric flasks (extract and washings) to a 125-mL separatory funnel.
10. Add 7.5 mL of molybdate reagent and 25 mL of toluene-isobutanol solvent to the funnel. Shake funnel for 60 seconds. Let the separatory funnel stand for 60 seconds to allow the aqueous and nonaqueous layers to separate. Discard the lower (aqueous) layer.
11. Pipet 10 mL of the nonaqueous layer into a 25-mL volumetric flask containing 10 mL of the alcoholic sulfuric acid solution.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least six working standards.
    a. Add 10 mL of acidic permanganate solution and 1 mL of ferrous reagent to a 125-mL separatory funnel.
    b. Add 2 to 400 μL of the standard phosphate solution to cover the range 0.1 to 10 μg of PH_3. Add 8 to 9 mL of water to make the total volume of the solution (permanganate solution, ferrous solution, phosphate solution and water) equal to 20 mL. Prepare at least six calibration standards and a blank containing no phosphate.
    c. Analyze with samples and blanks (steps 15 through 18).
    d. Prepare a calibration graph (absorbance versus μg of PH_3 added).
13. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (20 to 400 μL) of standard phosphate solution directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze with working standards (steps 15 through 18).
    e. Prepare a graph of DE vs. μg recovered.
14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENTS

15. Turn on the spectrophotometer and allow sufficient time for warmup. Adjust the wavelength to 625 nm and set the zero and 100% transmittance scale using 5-cm cells filled with distilled water. Check these settings prior to making any measurement to check on instrument drift. **NOTE: Steps 16 through 18 must be performed within one minute.**
16. Add 0.5 mL (25 drops) of stannous chloride reagent and dilute to volume using alcoholic sulfuric acid solution. Mix thoroughly.
17. Transfer the sample into a 5-cm cell and stopper immediately.
18. Measure the absorbance or transmittance using water as a blank.

CALCULATIONS:

19. Determine mass, μg (corrected for DE), of phosphine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections. NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
20. Calculate concentration, C, of phosphine in the air volume sampled, V (L).

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 0.195 to 0.877 mg/m^3 at 19 °C and 765.3 mm Hg using 16-L samples [1]. Desorption efficiency must be determined over the range used. The upper range of the method depends on the adsorptive capacity of the mercuric cyanide treated gel. This capacity may vary with the concentration of phosphine and other substances in the air. When an atmosphere at 90% relative humidity containing 0.957 mg/m^3 of phosphine was sampled at a flow rate of 0.2 L/min, breakthrough was determined to occur at a sample volume of 20.75 liter (capacity = 19.86 μg PH_3).

REFERENCES:

[1] Backup Data Report for Phosphine, S332, prepared under NIOSH Contract No. 210-76-0123, March 17, 1978.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S332, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-80). Publ. No. (ISBN) 0-936712-66-X. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

APPENDIX: PREPARATION OF SAMPLING MEDIA

Coating of Silica Gel

1. Dry 100 g of silica gel (45/60 mesh) at 90 °C for 2 hours.
2. Prepare a 2% (w/v) mercuric cyanide solution in water (2 g $Hg(CN)_2$ in 100 mL water).
3. Add the dried silica gel to the mercuric cyanide solution and let set for 15 minutes with occasional stirring.
4. Drain the excess mercuric cyanide solution and dry the remaining silica gel at 90 °C for 3 hours.
5. Cool the silica gel to room temperature in a covered beaker.
6. Expose the silica gel to a humid atmosphere (>80% RH) for 24 hours.

Preparing the sampling tubes

7. Place a plug of silylated glass wool at the end of a glass tube (6-mm O.D. and 4-mm I.D.) about 12 cm long. Pour 300 mg of the treated silica gel into the tube. Place another plug of silylated glass wool behind this front section. Add another 150 mg of the treated silica gel into the tube. Place a final plug of silylated glass wool behind this backup section.
8. Check the pressure drop of a representative sampler. The pressure drop across the tube must be less than 2 inches of mercury at a flow rate of 0.2 L/min.
9. Flame seal both ends of the sampling tubes.

PHOSPHORIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure

PHOSPHORUS

P_4 MW: 123.90 CAS: 7723-14-0 RTECS: TH3500000

METHOD: 7905, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3
NIOSH: 0.1 mg/m^3; Group I Pesticide
ACGIH: 0.1 mg/m^3
(1 ppm = 5.07 mg/m^3 @ NTP)

PROPERTIES: solid; d 1.83 g/mL @ 20 °C; MP 44 °C; BP 280 °C; sublimes; VP 3.5 Pa (2.6 x 10^{-2} mm Hg; 172 mg/m^3) @ 20 °C; oxidizes spontaneously in air

SYNONYMS: white phosphorus; yellow phosphorus.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Tenax GC, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 5 L @ 0.1 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.056 to 0.24 mg/m^3 [1] (12-L samples)

BIAS: + 5.5%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.090 [1]

ACCURACY: ± 21.3%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD

ANALYTE: phosphorus

DESORPTION: 1 mL xylene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 200 °C
-COLUMN: 80 °C

CARRIER GAS: He, 30 mL/min

COLUMN: 1.8 m x 6-mm OD x 2-mm ID glass; 3% OV-101, 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of phosphorus in xylene

RANGE: 0.5 to 5 µg per sample

ESTIMATED LOD: 0.005 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.024 @ 0.6 to 2.4 µg per sample [1]

APPLICABILITY: The working range is 0.04 to 0.8 mg/m^3 (0.0008 to 0.16 ppm) for a 12-L air sample. The method is applicable to vapor-phase phosphorus only. If particulate P_4 is expected in the air sample, use a filter in the sampling train.

INTERFERENCES: None identified.

OTHER METHODS: This combines and replaces S334 [2] and P&CAM 257 [3]. P&CAM 242, utilizing impinger sampler (xylene), has not been revised [4].

REAGENTS:

1. Phosphorus (white), purified, stored under distilled water.*
2. Xylene (mixed), reagent grade.
3. Acetone, purified.
4. Calibration stock solution, 0.20 mg/mL. Prepare under nitrogen or other inert gas. Dissolve a known mass (ca. 2 mg) of acetone-washed, dried white phosphorus in 10 mL xylene. Stir until dissolved. Prepare in duplicate.
5. Helium, prepurified.
6. Hydrogen, prepurified.
7. Air, compressed, filtered.
8. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate glass tube, 7-cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 35/60 mesh Tenax GC (front = 100 mg; back = 50 mg) separated and retained by 2-mm silylated glass wool plugs. Pressure drop across the sampler at 0.2 L/min airflow must be less than 3.3 kPa (25 mm Hg).
   NOTE: If the air sample is expected to contain particulate elemental phosphorus, precede the Tenax tube with a 37-mm diameter, cellulose ester membrane filter.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector (phosphorus mode), integrator and column (page 7905-1).
4. Vials, 20-mL, PTFE-lined septum caps.
5. Syringes, 5-, 10- and 25-μL, for making standards and GC injections.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL with pipet bulb.
8. Balance, analytical, readable to 0.01 mg.

SPECIAL PRECAUTIONS: White phosphorus may be fatal if ingested, even in small quantities [5]. Phosphorus vapor is toxic; work in a contained atmosphere with adequate care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 5 to 100 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Pipet 1.0 mL xylene into each vial. Cap each vial.
   NOTE: Use 5.0 mL xylene for filters, if applicable.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution, or a serial dilution thereof, to xylene in 10-mL volumetric flasks and dilute to the mark to produce phosphorus concentrations in the

range 0.01 to 5 μg/mL.

b. Analyze with samples and blanks (steps 11 and 12)
c. Prepare calibration graph (peak area vs. μg phosphorus).

9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tub. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg phosphorus recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 7905-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with xylene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of phosphorus found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentrations, C, of phosphorus in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S334 was issued on November 25, 1977 [2], and validated with generated atmospheres using a solution (11 mg/mL) of phosphorus in tetralin in a calibrated syringe drive, verified by independent collection in xylene [1]. Average recovery was 106% with $\hat{S}_r$ = 7.4% (18 samples) in the range 0.056 to 0.24 mg/m^3 for 12-L samples. In an experiment in which 25-L samples of an atmosphere containing 0.35 mg/m^3 phosphorus vapor were analyzed, the same phosphorus concentration was found in xylene-filled impingers with or without cellulose ester membrane prefilters. Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.311 mg/m^3 at 85% RH. Desorption efficiency for 18 samples in the range 0.6 to 2.4 μg per sample average 95% with $\hat{S}_r$ = 2.6%. The overall precision, $\hat{S}_{rT}$, including pump error was 0.090.

REFERENCES:

[1] Backup Data Report, S334, (November 25, 1977), available as "Ten NIOSH Analytical Methods, Set 5," order No. PB 287-499, from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S334, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Ibid., Vol. 1, P&CAM 257, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977)
[4] Ibid., P&CAM 242.
[5] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

Gangadhar Choudhary, Ph.D., ATSDR, and Peter M. Eller, Ph.D., NIOSH/DPSE. S334 originally validated under NIOSH Contract CDC-210-75-0047.

PHOSPHORUS TRICHLORIDE 6402

PCl_3 MW: 137.33 CAS: 7719-12-2 RTECS: TH3675000

METHOD: 6402, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1985 **Issue 2:** 15 August 1994

OSHA : 0.5 ppm
NIOSH: 0.2 ppm; STEL 0.5 ppm
ACGIH: 0.2 ppm; STEL 0.5 ppm
(1 ppm = 5.61 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.574 g/mL @ 21 °C; BP 76 °C; MP −112 °C; VP 13 kPa (100 mm Hg; 13% v/v) @ 21 °C

SYNONYMS: phosporous chloride.

SAMPLING

SAMPLER: BUBBLER (15 mL H_2O)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 11 L @ 0.5 ppm
-MAX: 100 L

SHIPMENT: ship in sealed bubblers

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: ca. 3.1 mg/m³ [1]

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): unknown

ACCURACY: not determined

MEASUREMENT

METHOD: VISIBLE SPECTROPHOTOMETRY

ANALYTE: molybdenum blue

COLOR DEVELOPMENT: 3 mL Br_2 water + 5 mL Na_2 MoO4 + 2 mL hydrazine sulfate → molybdenum blue

WAVELENGTH: 830 nm

CALIBRATION: KH_2PO_4 solutions

RANGE: 0.03 to 0.5 mg PCl_3 per sample

ESTIMATED LOD: 3 µg PCl_3 per sample

PRECISION ($\bar{S}_r$): 0.06 @ 0.03 to 0.14 mg PCl_3 per sample [1]

APPLICABILITY: The working range is 0.2 to 14 ppm (1.2 to 80 mg/m³) for a 25-L air sample.

INTERFERENCES: Phosphorus (V) compounds do not interfere. The sample solutions are stable to oxidation by air during sampling [1].

OTHER METHODS: This revises P&CAM 305 [2].

REAGENTS:

1. Potassium dihydrogen phosphate stock solution, 100 μg H_3PO_4/mL. Dissolve 0.1389 g KH_2PO_4 in distilled H_2O and dilute to 1 L.
2. Calibration stock solution, 10 μg/mL H_3PO_4. Dilute 100 mL KH_2PO_4 stock solution to 1 L with distilled water.
3. Sulfuric acid, 10 N. Slowly add 279 mL conc. H_2SO_4 to 500 mL distilled water. Dilute to 1 L when cool.
4. Sodium molybdate solution. Dilute 25.0 g $Na_2MoO_4 \cdot 2H_4O$ to 1 L with 10 N surfuric acid.
5. Bromine water, saturated.* Add sufficient liquid Br_2 to saturate distilled water with stirring.
6. Hydrazine sulfate solution, 1.5 g/L. Dissolve 1.5 g $N_2H_6SO_4$ in distilled water to make 1 L solution.
7. Hydrazine sulfate, saturated. Add sufficient hydrazine sulfate to distilled water with stirring to saturate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget bubbler* with non-rubber (e.g., PTFE) stopper and fritted glass inlet (Corning EC or 170- to 220-μm max pore); 5-cm glass tube with glass wool plug for protection of pump from splashover.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Spectrophotometer, reading at 830 nm, with matched glass cuvettes, 1-cm path length.
4. Waterbath, boiling.
5. Pipets, 0.1-, 1-, 2-, 3-, 5- and 25-mL.*
6. Volumetric flasks, 50-mL and 1-L.*
7. Beakers, 50-mL.*
8. Cold water bath.

* Boil all glassware contaminated by phosphate detergent in 1:1 HCl. Rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Liquid bromine causes severe eye and skin burns. Bromine vapor is a severe irritant of the eyes and respiratory tract. Permanent breathing difficulty may result [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Add 15 mL distilled water to the bubbler. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 11 to 100 L.
   NOTE: The bubbler must be kept in a vertical position during sampling. If the bubbler solution spills into the trap, discard the sample.
3. Remove the bubbler stem and tap gently against the inside wall of the bubbler to recover as much of the sample solution as possible. Rinse the stem with several mL distilled water, collecting the rinse in the bubbler.
4. Seal the bubbler bottom with a stopper. Alternatively, connect the inlet of the bubbler top to the outlet with PTFE tubing and seal the top to the bottom with tape.

SAMPLE PREPARATION:

5. Transfer contents of the bubbler quantitatively to a 50-mL volumetric flask. Dilute to mark with distilled water and mix.
   NOTE: Start reagent blanks at this step.
6. Pipet 25 mL of the diluted sample into a 50-mL beaker.
7. Pipet 3 mL saturated bromine water into the beaker. Let stand 60 sec for oxidation to occur.
   NOTE: The purpose of the bromine water is to oxidize PCl_3, present in water as H_3PO_3, to H_3PO_4.

8. Add saturated hydrazine sulfate dropwise until the orange-yellow color of excess bromine is gone; add one drop in excess. Transfer the solution to a second 50-mL volumetric flask. Wash the beaker several times with a few mL of distilled water, adding the wash to the second volumetric flask.
9. Pipet 5 mL sodium molybdate solution and 2 mL of 1.5 g/L hydrazine sulfate solution into the second volumetric flask (containing the oxidized sample). Add identical amounts of reagents to the unoxidized 25-mL sample in the volumetric flask from step 5. Dilute both solutions to the mark with distilled water and shake well.
10. Immerse the volumetric flasks in a boiling water bath for 10 min. Remove and cool rapidly to room temperature in cold water bath. Proceed immediately with the measurement (steps 12 through 14).

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 3 to 500 μg PCl_3 (2 to 360 μg H_3PO_4) per sample.
    a. Pipet aliquots of calibration stock solution into 50-mL volumetric flasks.
    b. Prepare (steps 5 through 10) and measure (steps 12 through 14) together with the samples and blanks.
    c. Construct calibration graph (absorbance vs. μg phosphoric acid).

MEASUREMENT:

12. Set the spectrophotometer according to manufacturer's directions to read at 830 nm.
13. Transfer several mL of the sample or standard solution to a cuvette and place in the spectrophotometer.
14. Record the absorbance reading vs. reagent blank.

CALCULATIONS:

15. Determine from the calibration graph the mass (μg) of phosphoric acid present in each oxidized sample (M_o) and unoxidized sample (M_u) and the average media blank (M_b).
16. Calculate the concentration (C) of PCL_3 in the air volume sampled, V (L):

$$C = \frac{(2 \cdot M_o - 2 \cdot M_u - M_b) \cdot 1.4}{V}, \text{ mg/m}^3.$$

where: 1.4 = M.W. PCl_3/M.W. H_3PO_4 = 137.3/98.0.

EVALUATION OF METHOD:

This method is based on P&CAM 305 [1,2]. In that work, recoveries were determined for samples spiked at 0.5, 1, and 2 times the OSHA standard to be 0.992, 1.04, and 1.05. The overall precision and accuracy have not been completely determined. In one experiment, the efficiency of bubbler collection of PCl_3 was found to be 0.99 $\pm$0.06 based on six pairs of bubblers sampling from a 3.1 mg/m^3 atmosphere generated using a diffusion cell. At the concentrations studied, PCl_3 tended to react with water vapor in the air to produce fogs of H_3PO_3. Attempts to separate the H_3PO_3 aerosol from PCl_3 vapor by means of polyvinyl chloride membrane filters were unsuccessful because of reaction between the filters and PCl_3. The reactions for the molybdenum blue color development are:

(1) $PCl_3 + 3H_20 \rightarrow H_3PO_3 + 3HCl$
(2) $H_3PO_3 + Br_2 + H_2O \rightarrow H_3PO_4 + 2HBr$
(3) $H_3PO_4 + Na_2MoO_4 + N_2H_6SO_4 \rightarrow$ molybednum blue

REFERENCES:

[1] Arthur D. Little, Inc. Development of Methods for the Determination of Phosphoric Acid, PCl_3, PCl_5 and P_4S_{10} in Air, Final Report of NIOSH Contract 210-76-0038 (unpublished, May 10, 1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 305, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Martin Abell, NIOSH/DPSE; P&CAM 305 originally developed under NIOSH Contract 210-75-0038.

PLATINUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

POLYCHLOROBENZENES

(1) $C_6H_3Cl_3$	MW: (1) 181.45	CAS: (1) 120-82-1	RTECS:	(1) DC2100000
(2) $C_6H_2Cl_4$	(2) 215.89	(2) 95-94-3		(2) DB9450000
(3) C_6HCl_5	(3) 250.34	(3) 608-93-5		(3) DA6640000

METHOD: 5517, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : no PEL
NIOSH: (1) C 5 ppm, Group III Pesticides; (2) & (3) no REL
ACGIH: (1) C 5 ppm; (2) & (3) no TLV

PROPERTIES: Table 1

SYNONYMS: (1) 1,2,4-trichlorobenzene
(2) 1,2,4,5-tetrachlorobenzene
(3) pentachlorobenzene

SAMPLING

SAMPLER: FILTER + SOLID SORBENT TUBE (PTFE filter + XAD-2, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 12 L

SHIPMENT: separate filter and sorbent tube

SAMPLE STABILITY: at least 13 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 2

BIAS: Table 2

OVERALL PRECISION ($\hat{S}_{rT}$): Table 2

ACCURACY: Table 2

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: compounds above

DESORPTION: 2 mL hexane; 30 min ultrasonic agitation

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 220 °C
-DETECTOR: 300 °C
-COLUMN: 160 °C

GASES-CARRIER: nitrogen, 30 mL/min
-PURGE: nitrogen, 90 mL/min

COLUMN: 2.0 m x 2-mm ID nickel, 10% Carbowax 20M-TPA on 80/100-mesh Chromosorb WAW

CALIBRATION: standard solutions of analytes in hexane

RANGE: 0.02 to 500 µg per sample [1]

ESTIMATED LOD: 0.001 µg/mL in hexane [1]

APPLICABILITY: The working range is 0.002 to greater than 30 mg/m^3 for each analyte for a 10-L air sample. Linear range of the detector is limited but samples are diluted prior to measurement.

INTERFERENCES: Using chromatographic conditions given above, 1,2,3,5-tetrachlorobenzene coelutes with 1,2,4,5-tetrachlorobenzene.

OTHER METHODS: This revises P&CAM 343 [2].

REAGENTS:

1. Hexane, distilled in glass.*
2. Pentachlorobenzene, 98%.*
3. 1,2,4,5-Tetrachlorobenzene, 98%.*
4. 1,2,4-Trichlorobenzene, 99%.*
5. Calibration stock solution, 100 mg/mL. Dilute accurately weighed 500-mg portions of each analyte to 5 mL with hexane. Store in airtight container. Stock solution is stable indefinitely.
6. Amberlite, XAD-2, 20/50 mesh. Cleanse by Soxhlet extraction for 4 h with 4:1 (v/v) acetone/methanol, 4 h with hexane, and drying overnight at 70 to 100 °C under vacuum.

   NOTE: During method evaluation, the capacity of cleansed bulk Amberlite XAD-2 was much higher than that of Amberlite XAD-2 obtained from some commercially available sorbent tubes.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Two-stage sampler:
   a. Filter: PTFE filter, 13-mm, 5-μm pore size, unlaminated (Millipore, SKC, Inc., or equivalent) in stainless steel holder, Swinny-type (Millipore, SKC, or equivalent).
   b. Sorbent tube: glass, 7 cm long, 6.4-mm OD, 4-mm ID, flame sealed with plastic caps, containing two sections of cleansed Amberlite XAD-2 (front = 100 mg; back = 50 mg), separated and held in place by 4-mm silanized glass wool plugs. Tubes are commercially available (SKC, Inc. or equivalent).
   c. Assembly: To outlet (male luer tip) of filter holder, attach a short (ca. 1.5") piece of PTFE tubing, 6-mm OD, 4-mm ID. Attach sorbent tube to PTFE tube on filter holder with a short piece of flexible tubing. Seal inlet of filter holder and outlet of sorbent tube with PTFE tape and plastic caps.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron capture detector, integrator, and column (see page 5517-1).
4. Vials, 5-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 5-mL, and convenient sizes for making dilutions.
7. Pipets, 2-mL, and convenient sizes for making dilutions.
8. Ultrasonic bath.
9. Balance, readable to 1 mg.
10. PTFE tape.

SPECIAL PRECAUTIONS: Hexane (flash point = −22 °C) is highly flammable. Prepare samples and standards in well-ventilated hood.

Chlorinated benzenes may irritate skin, eyes, and mucous membranes. Avoid inhalation and contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.

   NOTE: The filter stage permits measurement of exposures to polychlorobenzene aerosols. If it is known that such exposure is not likely, the filter may be omitted.

2 Remove caps from sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.

3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for total sample size of 3 to 12 L.
4. Separate filter from sorbent tube and seal both with PTFE tape and caps. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place filter in one vial, front glass wool plug and sorbent section in another vial, and rear sorbent section and enclosing glass wool plugs in third vial.
6. Add 2.0 mL hexane to each vial. Cap each vial.
7. Allow to stand 30 min with ultrasonic agitation.
8. Wash inside surfaces of filter holder with 2 to 3 mL hexane. Transfer washings to 5-mL volumetric flask and dilute to mark with hexane.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the linear range of the detector.
   a. Prepare working standards by serial dilution of the calibration stock solution.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph for each analyte (peak height or area vs. μg/mL analyte).
10. Determine desorption efficiency (DE) over range of interest at least once for each lot of filters and sorbent used. Prepare three samplers at each of five levels plus three media blanks.
    a. Prepare known concentrations of the analytes in hexane.
    b. Inject a 5-μL aliquot directly onto the filter of an assembled sampler with a microliter syringe while drawing 12 L of analyte-free air through the sampler at 0.2 L/min.
    c. Separate filter holder and sorbent tube, seal, and allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 12 and 13).
       NOTE: Significant amounts should be found on the filters and holders only at the higher loadings. See EVALUATION OF METHOD.
    e. Prepare graph of DE vs. μg of each analyte recovered. DE is the sum of amounts recovered from filter, holder, and sorbent sections divided by the amount taken.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5517-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, approximate t_Rs are: 1,2,4-trichlorobenzene, 2.0 min; 1,2,4,5-tetrachlorobenzene, 3.3 min; pentachlorobenzene, 7.5 min.
    NOTE 2: If peak area is above range of working standards, dilute with hexane, reanalyze and apply appropriate dilution factor in calculations.
13. Measure peak height or area.

CALCULATIONS:

14. Determine the concentration, μg/mL, for each analyte, and multiply by the desorption volume, mL, and the dilution factor, if any, to calculate the mass, μg, recovered.
15. Add the amounts recovered from filter, filter holder, sorbent front (W_f), and sorbent back (W_b) sections to determine the mass found in a field sample (W) or the average sampler blank (B), and correct for DE.

NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

16. Calculate concentration, C, of each analyte in air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 343 was issued on August 31, 1981 [2]. A two-stage sampler was tested using 10- to 12-L samples at 28 to 30 °C and >80% RH over the ranges 0.002 to 100 mg/m^3 for 1,2,4-trichlorobenzene, 0.003 to 31 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 0.008 to 22 mg/m^3 for pentachlorobenzene for this issue of Method 5517 [1,2]. The average recoveries were 0.957 for 1,2,4-trichlorobenzene, 1.014 for 1,2,4,5-tetrachlorobenzene, and 0.968 for pentachlorobenzene, with concentrations independently verified by collection in impingers. These biases were insignificant at a 0.05 significance level. For levels of 0.02, 0.1, 0.4, 0.5, 25, and 500 μg per sample, the average desorption efficiencies were 0.908 for 1,2,4-trichlorobenzene, 0.901 for 1,2,4,5-tetrachlorobenzene, and 0.917 for pentachlorobenzene. At 25 μg, only pentachlorobenzene was observed in significant amounts on the filter and holder (4.7% of the total amount recovered). However, at 500 μg, the average contribution from the filter and holder to the totals were 7.2% for 1,2,4-trichlorobenzene, 55.2% for 1,2,4,5-tetrachlorobenzene, and 67.9% for pentachlorobenzene. The use of polypropylene filter holders was rejected because even at the 500-ng level, polypropylene filter holders retained 14% of the 1,2,4-trichlorobenzene, 34% of the 1,2,4,5-tetrachlorobenzene, and 45% of the pentachlorobenzene. After storage for several days, this might not be recoverable. Polystyrene holders did not appear to retain chlorobenzenes, but were not available in the 13-mm size.

The capacity of the 100-mg sorbent section for 1,2,4-trichlorobenzene, the most volatile of the analytes, was 24 L for a concentration of 45 mg/m^3 at 40 °C and >80% RH. The test atmosphere also contained 1,2,4,5-tetrachlorobenzene at 22 mg/m^3 and pentachlorobenzene at 15 mg/m^3. Capacities for the latter two analytes were not specifically determined, but were greater than 24 L. A storage stability study found no significant losses after 13-day storage in the dark at room temperature for 2.5-L samples containing 35 ng 1,2,4-trichlorobenzene, 63 ng 1,2,4,5-tetrachlorobenzene, and 43 ng pentachlorobenzene.

The configuration of the two-stage sampler has been simplified.

REFERENCES:

[1] Dillon, H. K., and M. L. Bryant. Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene; and Polychlorinated Terphenyls: Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene, NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL (1981).

[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 343, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0102.

TABLE 1. PROPERTIES.

Name	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)	mg/m^3 per ppm @ NTP
1,2,4-Trichlorobenzene	16.95	213.5	0.291	0.039	1.454	7.42
1,2,4,5-Tetrachlorobenzene	139.5-140.5	243-246	<0.1	<0.0133	1.858[a]	8.83
Pentachlorobenzene	86	277			1.834[b]	10.23

[a] Solid @ 22 °C.
[b] Solid @ 6.5 °C.

TABLE 2. ACCURACY

Name	Range Studied[a] (mg/m^3)	Analytical Precision $\hat{S}_r$	Bias (%)	Overall Precision $\hat{S}_{rT}$	Accuracy (± %)
(1) 1,2,4-Trichlorobenzene	0.002 to 100	0.044	−4.3	0.093	19.3
(2) 1,2,4,5-Tetrachlorobenzene	0.003 to 31	0.042	1.4	0.097	19.5
(3) Pentachlorobenzene	0.008 to 22	0.057	−3.2	0.098	19.6

[a] 10-L samples.

POLYCHLOROBIPHENYLS

mixture: $C_{12}H_{10-x}Cl_x$ [where x = 1 to 10] MW: ca. 258 (42% Cl ; $C_{12}H_7Cl_3$); ca. 326 (54% Cl ; $C_{12}H_5Cl_5$) CAS: Table 1 RTECS: Table 1

METHOD: 5503, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Revision #1: 15 August 1987
Issue 2: 15 August 1994

OSHA : 1 mg/m^3 (42% Cl); 0.5 mg/m^3 (54% Cl)
NIOSH: 0.001 mg/m^3/10 h (carcinogen)
ACGIH: 1 mg/m^3 (42% Cl) (skin); 0.5 mg/m^3 (54% Cl) (skin)

PROPERTIES: 42% Cl: BP 325 to 366 °C; MP – 19 °C; d 1.38 g/mL @ 25 °C; VP 0.01 Pa (8 x 10^{-5} mm Hg; 1 mg/m^3) @ 20 °C
54% Cl: BP 365 to 390 °C; MP 10 °C; d 1.54 g/mL @ 25 °C; VP 0.0004 Pa (3 x 10^{-6} mm Hg; 0.05 mg/m^3) @ 20 °C

SYNONYMS: PCB; 1,1'-biphenyl chloro; chlorodiphenyl, 42% Cl (Aroclor 1242); and 54% Cl (Aroclor 1254)

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (13-mm glass fiber + Florisil, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min or less

VOL-MIN: 1 L @ 0.5 mg/m^3
-MAX: 50 L

SHIPMENT: transfer filters to glass vials after sampling

SAMPLE STABILITY: unknown for filters; 2 months for Florisil tubes [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied
BIAS: none identified
OVERALL PRECISION ($\hat{S}_{rT}$): not evaluated
ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD (^{63}Ni)

ANALYTE: polychlorobiphenyls

DESORPTION: filter + front section, 5 mL hexane; back section, 2 mL hexane

INJECTION VOLUME: 4-μL with 1-μL backflush

TEMPERATURE-INJECTION: 250 to 300 °C
-DETECTOR: 300 to 325 °C
-COLUMN: 180 °C

CARRIER GAS: N_2, 40 mL/min

COLUMN: glass, 1.8 m x 2-mm ID, 1.5% OV-17/1.95% QF-1 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard PCB mixture in hexane

RANGE: 0.4 to 4 μg per sample [2]

ESTIMATED LOD: 0.03 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.044 [1]

APPLICABILITY: The working range is 0.01 to 10 mg/m^3 for a 40-L air sample [1]. With modifications, surface wipe samples may be analyzed [3,4].

INTERFERENCES: Chlorinated pesticides, such as DDT and DDE, may interfere with quantification of PCB. Sulfur-containing compounds in petroleum products also interfere [5].

OTHER METHODS: This method revises methods S120 [6] and P&CAM 244 [1]. Methods S121 [7] and P&CAM 253 [8] for PCB have not been revised.

REAGENTS:

1. Hexane, pesticide quality.
2. Florisil, 30/48 mesh sieved from 30/60 mesh. After sieving, dry at 105 °C for 45 min. Mix the cooled Florisil with 3% (w/w) distilled water.
3. Nitrogen, purified.
4. Stock standard solution of the PCB in methanol or isooctane (commercially available).*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter without binders in a Swinnex cassette (Cat. No. SX 0001300, Millipore Corp.) followed by a glass tube, 7 cm long, 6-mm OD, 4-mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. (SKC 226-39, Supelco ORBO-60, or equivalent) Join the cassette and Florisil tube with PVC tubing, 3/8" L x 9/32" OD x 5/32" ID, on the outlet of the cassette and with another piece of PVC tubing, 3/4" L x 5/16" OD x 3/16" ID, complete the union.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Tweezers.
4. Vials, glass, 4- and 7-mL, with aluminum or PTFE-lined caps
5. Gas chromatograph, electron capture detection (^{63}Ni), integrator and column (page 5503-1).
6. Volumetric flasks, 10-mL and other convenient sizes for preparing standards.
7. Syringe, 10-μL.

SPECIAL PRECAUTIONS: Avoid prolonged or repeated contact of skin with PCB and prolonged or repeated breathing of the vapor [9-11].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the Florisil tube immediately before sampling. Connect Florisil tube to Swinnex cassette and attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 50 L.
   NOTE: At low PCB concentrations, the sampler was found to be efficient when operated at flow rates up to 1 L/min, for 24 hours [4]. Under these conditions, the limit of detection was 0.02 $\mu g/m^3$.
4. Transfer the glass fiber filters to 7-mL vials. Cap the Florisil tubes with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and 100-mg Florisil bed in the same 7-mL vial in which the filter was stored. Add 5.0 mL hexane.
6. In a 4-mL vial, place the 50-mg Florisil bed including the two urethane plugs. Add 2.0 mL hexane.
7. Allow to stand 20 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 10 to 500 ng/mL PCB.
   a. Add known amounts of stock standard solution to hexane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (sum of areas of selected peaks vs. ng PCB per sample).
9. Determine desorption efficiency (DE) at least once for each lot of glass fiber filters and Florisil used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank Florisil tube.
   b. Inject known amounts of stock standard solution directly onto front sorbent section and onto a media blank filter with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg PCB recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5503-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Where individual identification of PCB is needed, a procedure using a capillary column may be used [12].
    NOTE 2: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze and apply the appropriate dilution factor in calculations.
12. Sum the areas for five or more selected peaks.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of PCB found on the glass fiber filter (W) and in the Florisil front (W_f) and back (W_b) sorbent sections, and in the average media blank filter (B) and front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of PCB in the air volume sampled, V (L):

$$C = \frac{(W + W_f + W_b - B - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method uses 13-mm glass fiber filters which have not been evaluated for collecting PCB. In Method S120, however, Aroclor 1242 was completely recovered from 37-mm glass fiber filters using 15 mL isooctane [8,13,14]. With 5 mL of hexane, Aroclor 1016 was also completely recovered from 100-mg Florisil beds after one-day storage [1]. Thus, with no adsorption effect likely on glass fiber filters for PCB, 5 mL hexane should be adequate to completely extract PCB from combined filters and front sorbent sections. Sample stability on glass fiber filters has not been investigated. Breakthrough volume was >48 L for the Florisil tube at 75% RH in an atmosphere containing 10 mg/m^3 Aroclor 1016 [1].

REFERENCES:

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[13] Backup Data Report for S120, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. Pb 271-464 from NTIS, Springfield, VA 22161.
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METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S120 originally validated under NIOSH Contract 210-76-0123.

Table 1. General Information.

Compound	CAS	RTECS
Polychlorinated Biphenyls	1336-36-3	TQ1350000
Chlorobiphenyl	27323-18-8	DV2063000
Aroclor 1016 (41% Cl)	12674-11-2	TQ1351000
Aroclor 1242 (42% Cl)	53469-21-9	TQ1356000
Aroclor 1254 (54% Cl)	11097-69-1	TQ1360000

Table 2. Composition of some Aroclors [15].

Major Components	Aroclor 1016	Aroclor 1242	Aroclor 1254
Biphenyl	0.1%	<0.1%	<0.1%
Monochlorobiphenyls	1	1	<0.1
Dichlorobiphenyls	20	16	0.5
Trichlorobiphenyls	57	49	1
Tetrachlorobiphenyls	21	25	21
Pentachlorobiphenyls	1	8	48
Hexachlorobiphenyls	<0.1	1	23
Heptachlorobiphenyls	none detected	<0.1	6
Octachlorobiphenyls	none detected	none detected	none detected

POLYCHLOROBIPHENYLS in serum

$C_{12}H_{10-x}Cl_x$ (x = 1 to 10) MW: 188 to 498 CAS: Varies RTECS: Varies

METHOD: 8004, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to PCB.

SYNONYMS: Aroclor; PCB; chlorodiphenyl

BIOLOGICAL SAMPLING		MEASUREMENT	
SPECIMEN:	serum	**TECHNIQUE:**	GAS CHROMATOGRAPHY, ECD
VOLUME:	10 mL	**INJECTION VOLUME:**	3 µL, Grob type splitless
PRESERVATIVE:	none	**COLUMN:**	capillary, 15 m x 0.2-mm ID, WCOT SE-54
SHIPMENT:	polyethylene shippers @ 10 °C	**CARRIER GAS:**	5% methane in argon, 1 mL/min
STABILITY:	indefinite if serum is kept frozen	**TEMPERATURE-INJECTOR:**	260 °C
CONTROLS:	collect 3 specimens from unexposed populations per study or 1 per 10 unknowns for studies exceeding 30 specimens	**-COLUMN:**	100 °C for 2 min; 20 °C/min to 260 °C for 4 min
BULK:	submit a bulk sample of material to which workers were exposed	**-DETECTOR:**	350 °C
		CALIBRATION:	hexane solutions of Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260
		QUALITY CONTROL:	pooled or spiked serum
		RANGE:	0.005 to 1.0 µg/mL
		ESTIMATED LOD:	0.001 µg/mL
		RECOVERY:	greater than 80%
		PRECISION ($\bar{S}_r$):	0.16
		ACCURACY:	> ± 30%

APPLICABILITY: Since PCBs are rapidly absorbed from the lung, GI tract, and skin, this procedure is useful for estimating acute and chronic exposures to PCB, assuming (a) no metabolism of PCB, (b) all isomers of PCB are extracted with equal efficiency, and (c) similar ECD response for all PCBs. PCBs have high biological and chemical stability. They accumulate in adipose tissue and may present a serious latent health threat. Metabolism involves hydroxylation and conjugation with glucose and sulfates.

INTERFERENCES: Chlorinated hydrocarbons, phthalate based plasticizers, dibenzofurans, and chlorinated naphthalenes interfere.

OTHER METHODS: This replaces P&CAM 329 [1]. Other methods include a screening method for Aroclor 1254 in whole blood [2].

REAGENTS:

1. Methanol, hexane, ethyl ether, and acetone (pesticide grade).
2. Potassium hydroxide, KOH.
3. Calibration stock solutions, 0.1 mg/mL.* Dissolve 10 mg of the bulk sample or other suitable standard, e.g., Aroclor 1016, 1221, 1232, 1242, 1248, 1254, and 1260 in 100 mL n-hexane (standards available from EPA).
4. Silica gel, activity grade I.
   a. Heat to 130 °C for 24 h.
   b. Cool and add 3 g water per 100 g silica gel. Mix for 2 h in a sealed container.
5. Sodium sulfate (anhydrous).
6. 1,1-Dichloro-2,2-bis (p-chlorophenyl)ethylene (DDE) solution, 50 ng/mL, in hexane.
7. Methanol KOH, 2% (w/v). Dissolve 2 g KOH in methanol to make 100 mL solution.
8. Methanol-water, 1:1 (v/v).
9. Hexane-ethyl ether, 1:1 (v/v).
10. Nitrogen, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Gas-liquid chromatograph equipped with an electron capture detector.
2. Syringes, glass, 30-mL.**
3. Culture tubes, 16- x 150-mm, organic-free, with PTFE-lined screw caps.**
4. Rotary mixer, variable speed.
5. Centrifuge.
6. Kuderna-Danish concentrator tubes, 25-mL.**
7. Micro-Synder Columns.**
8. Tube heater.
9. Chromatography column, 7-mm ID x 200 mm, with 50-mL reservoir and PTFE stopcock.**
   a. Put a small plug of glass wool in the bottom of the column.
   b. Pour a suspension of 3 g silica gel in 50 mL hexane into the column.
   c. Let the suspension settle and add 5 to 7 g sodium sulfate.
10. Syringes, 10-µL, glass.
11. Graduated cylinder, 25-mL.**
12. Pipet, Pasteur.

** Clean all glassware, including that used in sampling as follows: Wash in detergent. Rinse with tap water. Soak in chromic acid. Rinse with, in order, tap water, distilled water, acetone and hexane.

SPECIAL PRECAUTIONS: Samples of blood collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

PCBs have potential carcinogenicity in humans. They are microsomal enzyme inducers and liver toxins; therefore, use extreme caution when handling these substances [3].

SAMPLING:

1. Collect 20 to 25 mL whole blood samples by venipuncture via 30-mL glass syringe.
2. After the blood has clotted, centrifuge for 10 min at 2000 rpm. Transfer the serum to a 16 x 150-mm culture tube with a PTFE-lined screw cap.
3. Ship the serum in an insulated container with bagged refrigerant to keep the samples at 4 °C.
4. Freeze the samples upon arrival at the laboratory.

SAMPLE PREPARATION:

5. Pipet 5 mL serum into a clean culture tube containing 4 mL methanol.
6. Cap the tube and mix 4 min on a rotary mixer.
7. Add 5 mL hexane-ethyl ether (1:1, v/v).
8. Mix on a rotary mixer for 15 min.
9. Centrifuge at 2000 rpm for 5 min.
10. Transfer the upper solvent layer by pipet into a 25-mL Kuderna-Danish concentrator tube.
11. Repeat steps 7 through 10 twice, combining the extracts in the concentrator tube.
12. Concentrate the extract to 0.5 mL under a gentle stream of dry organic-free nitrogen.
13. Add 2 mL methanolic KOH to the concentrator tube. Add a piece of hollow glass (end of a Pasteur pipet) to prevent bumping.
14. Attach a micro-Synder column and bring the contents to a gentle boil with of a tube heater and reduce the volume to 0.3 mL.
    NOTE: If a precipitate forms, add a few drops of methanolic KOH solution and warm gently with a tube heater until it dissolves.
15. Cool the solution slightly and add 2 mL 1:1 methanol:water.
16. Add 2 mL n-hexane when the solution reaches room temperature.
17. Stopper and shake the tube vigorously.
18. Rinse the prepared chromatography column (EQUIPMENT, 9.) with 20 mL hexane. As the hexane settles into the sodium sulfate bed, add the sample.
19. Place a 25-mL graduated cylinder below the chromatographic column.
20. Rinse the concentrator tube and the micro-Synder column with 1 mL hexane.
21. As the saponified extract enters the sodium sulfate layer, add the concentrator tube and micro-Synder column rinses to the chromatographic column.
22. As the rinses settle in the sodium sulfate layer, add 25 mL hexane.
23. Collect 25 mL eluate from the column in the graduated cylinder.
24. Rinse the walls of the graduated cylinder with 2 mL hexane.
25. Concentrate to 1 mL under a gentle stream of nitrogen. Add 10 mL DDE solution and analyze (steps 29 and 30).

CALIBRATION AND QUALITY CONTROL:

26. Analyze the bulk sample for PCB content [4].
27. Calibrate daily with at least five working standards over the range 0.005 to 1 mg/mL PCB.
    a. Add known amounts of calibration stock solution to n-hexane in 10-mL volumetric flasks and dilute to the mark with n-hexane.
    b. Analyze the working standards together with samples and blanks (steps 29 and 30).
    c. Prepare calibration graph (concentration of each PCB standard vs. the sum of PCB peak areas).
28. Analyze at least three pooled or spiked serum samples.

MEASUREMENT:

29. Set gas chromatograph according to manufacturer's instructions and conditions on page 8004-1. Inject 2-μL sample together with 1 mL DDE solution.
30. Measure the PCB peak areas. Calculate the retention time of the analyte peaks relative to that of DDE.

CALCULATIONS:

31. Compare sample retention times (relative to DDE) with those of the working standards and bulk sample to ascertain the valid PCB peaks.
32. Read the concentration of PCB in the hexane solution (μg/mL) from the calibration graph.

33. Calculate the serum PCB concentration, C (μg/mL), by dividing the PCB concentration found in the extract, C_e, by 5 (5 mL serum yields 1 mL extract):

$$C = \frac{C_e}{5}, \ \mu g/mL.$$

GUIDES FOR INTERPRETATION:

PCBs are present in the biosphere. Baselt [5] indicates a level 2 to 4 μg/L of plasma is indicative of significant exposure. Finklea [6] reported 57% of individuals tested had levels below 5 μg/L. Most control populations have PCB levels below 20 μg/L serum. What levels present a health hazard is not documented; however, a 200 μg/L as an upper limit has been suggested [7]. If a serious exposure is suspected, then the serum PCB levels should be augmented by liver battery and triglyceride tests plus a complete medical evaluation to ascertain the employee health risk.

EVALUATION OF METHOD:

Eighty-nine analyses of four spiked human serum for the Aroclors 1242 and 1254 with a concentration range of 0.025 to 0.400 μg/L indicated recoveries greater than 80% with precision, $\bar{S}_r$, of 0.16 [8].

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METHOD WRITTEN BY:

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POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC 5506

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 5506, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

NIOSH : Table 3
OSHA:
ACGIH:

PROPERTIES: Table 1

COMPOUNDS:

acenaphthene	benzo[ghi]perylene	fluorene
acenaphthylene	benzo[a]pyrene	indeno[1,2,3-cd]pyrene
anthracene	benzo[e]pyrene	naphthalene
benz[a]anthracene	chrysene	phenanthrene
benzo[b]fluoranthene	dibenz[a,h]anthracene	pyrene
benzo[k]fluoranthene	fluoranthene	

SYNONYMS: PAH; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (2-μm, 37-mm PTFE + washed XAD-2, 100 mg/50 mg)

FLOW RATE: 2 L/min

VOL-MIN: 200 L
-MAX: 1000 L

SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C

SAMPLE STABILITY: unknown; protect from heat and UV radiation

FIELD BLANKS: 3 to 10 field blanks per set
MEDIA BLANKS: 6 to 10

AREA SAMPLES: 8 replicates on preweighed filters for solvent selection

ACCURACY

RANGE STUDIED, BIAS, AND OVERALL PRECISION ($\hat{S}_{rT}$): not measured

MEASUREMENT

METHOD: HPLC, FLUORESCENCE/UV DETECTION

ANALYTE: compounds above

EXTRACTION: 5 mL organic solvent appropriate to sample matrix (step 7)

COLUMN: 15 cm x 4.6-mm, reverse phase, 5-μm C_{18}

INJECTION VOLUME: 10 to 50 μL

MOBILE PHASE: H_2O/CH_3CN gradient @ ambient temperature, 1 mL/min

DETECTORS: UV @ 254 nm; fluorescence @ 340 nm (excitation), 425 nm (emission)

CALIBRATION: external standards in CH_3CN

RANGE, LOD, and PRECISION ($\hat{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: The working range for B[a]P is 1 to 50 $\mu g/m^3$ for a 400-L air sample. Specific sample sets may require modification in extraction solvent used, choice of measurement method, and measurement conditions (see EVALUATION).

INTERFERENCES: Any compound which elutes at the same HPLC or GC retention time may interfere. Heat, ozone, NO_2, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 206 and 251 [1]. The spectrophotometric methods, P&CAM 183, 184, and 186 [1], have not been revised. Method 5515 uses the same sampling technique, with gas chromatographic measurement.

REAGENTS:

1. Filter extraction solvent: benzene,* cyclohexane, methylene chloride or other appropriate solvents, pesticide grade (see step 7).
2. Water, distilled, deionized, degassed.
3. Acetonitrile, HPLC grade, degassed.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with acetonitrile. Stable six months if refrigerated and protected from light.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter. PTFE-laminated membrane filter, 2-μm pore size, 37-mm diameter (Zefluor, Membrana, Pleasanton, CA, or equivalent), backed by a gasket (37-mm OD, 32-mm ID) cut from a cellulose support pad, or SKC # 225-23, in cassette filter holder.
      NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
      NOTE 2: Take filters to be preweighed (see step 2, NOTE) from the filter package and allow to equilibrate 24 h with laboratory atmosphere before taring.
   b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H_2O).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Syringe filters, 0.45-μm, PTFE (Millex-LCR, Millipore Corp., Bedford, MA or Acrodisc-CR PTFE, Gelman Sciences, Ann Arbor, MI).
9. Pipet, 5-mL.
10. Syringe or micropipets, 1- to 100-μL.
11. Ultrasonic bath.
12. HPLC, with gradient capability, fluorescence (excitation @ 240 nm, emission @ 425 nm) and UV (254 nm) detectors in series, electronic integrator, and column [HC-ODS-SILX] (Perkin-Elmer Corp.), or Vydac 201TP (The Separations Group) or equivalent; see page 5506-1].

EQUIPMENT:

13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.
15. Kunderna-Danish extractor.

SPECIAL PRECAUTIONS: Treat benzene and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed out in a glove box. Spent samples and unused standards should be considered toxic waste and disposed of in an appropriate manner. Counter tops and equipment should be checked regularly with a "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L. Take a concurrent set of four replicate area samples at 2 to 4 L/min on preweighed 2-μm PTFE filters in an area of highest expected PAH concentration.
   NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a culture tube. Hold filter at edge to avoid disturbing the collected sample. Cap the tube and wrap it in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes due to sublimation.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAHs. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
   a. Allow the preweighed area filter samples to equilibrate 24 h with the laboratory atmosphere.
   b. Weigh the area filters. Determine total weight collected on each.
   c. Extract the first pair of area filters with acetonitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
      NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and absorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [2,3] and benzene:ethanol (4:1 v/v) [4] have been recommended for extraction of PAH from diesel exhaust particulate.
   d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
   e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
   a. Add 5.0 mL of the solvent selected in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
   b. Cap and let stand 15 to 20 min in an ultrasonic bath.

NOTE 1: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.

NOTE 2: The sample must be dissolved in acetonitrile for chromatography. If needed, perform solvent exchange as follows:

CAUTION: To avoid loss of volatile components, do not allow the sample to go to dryness at any time.

(1) After filtration (step 10), take the sample to near dryness in a Kuderna-Danish extractor.

(2) Add ca. 1 mL acetonitrile, take to near dryness, and adjust final volume to 1.0 mL with acetonitrile and filter again.

9. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the front (larger) sorbent section. Break tube at score line.
   b. Transfer front glass wool plug and front sorbent section to a culture tube. Transfer back sorbent section, and the middle glass wool plug to a second culture tube.
   c. Add 5.0 mL acetonitrile to each culture tube. Cap the culture tubes.
   d. Allow samples to stand for 30 min. Swirl occasionally.
10. Filter all sample extracts through an 0.45-μm syringe filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards.
   a. Dilute aliquots of calibration stock solution with acetonitrile in 10-mL volumetric flasks (e.g., to 2.5, 0.5, 0.1, 0.02, and 0.002 μg/mL).
   b. Intersperse working standards and samples in the measurements.
   c. Prepare calibration graphs (peak area vs. μg of each PAH per sample).
12. Recovery and desorption efficiency.
   a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
      (1) Filters. Using a microliter syringe or a micropipette, spike four filters at each of five concentration levels with a mixture of the analytes. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.
         NOTE: This step may not be appropriate for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.
      (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. Prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blank in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight. Analyze (steps 9, 10, and 14 through 16). Prepare graphs of DE vs. amounts found.
   b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R and DE graphs if checks do not agree to within $\pm$5% of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set HPLC according to conditions on page 5506-1 and in step 15. Equilibrate column at 60% CH_3CN/40% H_2O at 1.0 mL/min for 15 min before injecting first sample.
15. Inject sample aliquot. Start mobile phase gradient:
   a. Linear gradient 60% CH_3CN to 100% CH_3CN, 20 min.
   b. Hold at 100% CH_3CN for 20 min.
      NOTE: Hold longer if necessary to prevent carryover of background, e.g., from coal dust.
   c. Linear gradient to initial condition, 5 min.

16. Measure peak areas.
    NOTE 1: Approximate retention times appear in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [5,6] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. Read the mass, μg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
18. Calculate concentration, C (mg/m^3), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

$$C = \frac{(W - B + W_f + W_b - B_f - B_b)}{V}, \ mg/m^3.$$

NOTE: W_f and W_b include analyte originally collected on the filter as particulate, then volatilized during sampling. This can be a significant fraction for many PAHs (e.g., fluoranthane, naphthalene, fluorene, anthracene, phenanthrene).

EVALUATION OF METHOD:

The fluorescence detector used in this method is both sensitive and selective. The detector can see as little as 50 pg of many PAH injected on the column. LODs for the 17 analytes range from 50 to 350 ng per sample. It does not respond to non-fluorescent molecules such as aliphatics. The method is, therefore, most amenable to determination of trace amounts of PAH in mixtures of aliphatic compounds. Successful applications include: aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

This method has been evaluated by analyzing spiked filters, spiked sorbent tubes, and complete spiked sampling trains through which were drawn 500 L of air [7]. Each of the three groups was spiked with each analyte at two concentration levels in sextuplicate. Particular note should be made that the effect of particulate matter has not been evaluated, and every sampling matrix is unique. The data below were obtained on spiked samplers stored refrigerated in the dark for three months followed by measurement with HPLC.

COMPOUND	CALIBRATION RANGE (μg per sample)	LOD (μg per sample)	MEASUREMENT PRECISION SPIKED[a]	SPIKED + AIR[b]
1. ACENAPHTHENE	2.0 - 13	0.8	.058 S	.093 (50)
2. ACENAPHTHYLENE	1.0 - 100	0.35	.032 S	.075 (100)
3. ANTHRACENE	0.4 - 13	0.05	.039 S	.037 (5)
4. BENZ[a]ANTHRACENE	0.4 - 13	0.15	.032 F	.084 (5)
5. BENZO[b]FLUORANTHENE	0.4 - 12	0.1	.027 F	.028 (10)
6. BENZO[k]FLUORANTHENE	0.4 - 13	0.15	.025 F	.027 (1)
7. BENZO[ghi]PERYLENE	0.5 - 25	0.2	.031 F	.029 (10)
8. BENZO[a]PYRENE	0.4 - 14	0.2	.027 F	.029 (5)
9. BENZO[e]PYRENE	0.5 - 13	0.2	(c)	(c)
10. CHRYSENE	0.4 - 12	0.15	.039 F	.024 (5)
11. DIBENZ[a,h]ANTHRACENE	0.5 - 25	0.2	.026 F	.029 (10)
12. FLUORANTHENE	0.4 - 13	0.15	.026 S	.050 (10)
13. FLUORENE	0.7 - 13	0.25	.031 S	.090 (10)
14. INDENO[1,2,3-cd]PYRENE	0.5 - 12	0.2	.044 F	.032 (10)
15. NAPHTHALENE	0.6 - 13	0.25	.041 S	.125 (50)
16. PHENANTHRENE	0.4 - 13	0.1	.036 S	.070 (2)
17. PYRENE	0.5 - 13	0.2	(c)	(c)

[a]RSD for filter (F) where volatilization is nil; for sorbent (S) where substantial volatilization may occur during sampling.
[b]RSD determined at the μg level shown in parenthesis for a filter/sorbent tube sampling train (spiked filter) through which laboratory air was drawn at 2 L/min for 4 h.
[c]Not determined.

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METHOD REVISED BY:

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Table 1. Formulae and physical properties.

COMPOUND (by M.W.)	EMPIRICAL FORMULA	MOLECULAR WEIGHT	DETECTOR	MELTING POINT (°C)	BOILING POINT (°C)*	REF.
1. NAPHTHALENE	$C_{10}H_8$	128.17	UV	80.2	218	[9]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	UV	92-93	265-275	[10]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	UV	96.2	279	[10]
4. FLUORENE	$C_{13}H_{10}$	166.22	UV	116	293-295	[9]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	UV	218	340	[9]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	UV	100	340	[9]
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	FL	110	384	[9], [11]
8. PYRENE	$C_{16}H_{10}$	202.26	FL	156	393	[9]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	FL	162-167	435	[9]
10. CHRYSENE	$C_{18}H_{12}$	228.29	UV	255-256	448	[9]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	168	--	[9]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	217	480	[10]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	FL	179	495	[9]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	FL	178-179	--	[9]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	FL	273	--	[9]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	FL	161.5-163	530	[8]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	FL	267	524	[9]

*Many of these compounds will sublime.

Table 2. Synonyms.

COMPOUND (alphabetically)	SYNONYMS
1. ACENAPHTHENE	CAS# 83-32-9; RTECS # AB1000000
2. ACENAPHTHYLENE	CAS# 208-96-8; RTECS # AB1254000
3. ANTHRACENE	CAS# 120-12-7; RTECS # CA9350000
4. BENZ[a]ANTHRACENE	1,2-benzanthracene; benzo[b]phenanthrene; 2,3-benzophenanthrene; tetraphene; CAS# 56-55-3; RTECS # CV9275000
5. BENZO[b]FLUORANTHENE	3,4-benzofluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene; B[b]F; CAS# 205-99-2; RTECS # CU1400000
6. BENZO[k]FLUORANTHENE	11,12-benzofluoranthene; CAS# 207-08-9; RTECS # DF6350000
7. BENZO[ghi]PERYLENE	1,12-benzoperylene; CAS# 191-24-2; RTECS # DI6200500
8. BENZO[a]PYRENE	3,4-benzopyrene; 6,7-benzopyrene; B[a]P; BP; CAS# 50-32-8; RTECS # DJ3675000
9. BENZO[e]PYRENE	1,2-benzopyrene; 4,5-benzopyrene; B[e]P; CAS# 192-97-2; RTECS # DJ4200000
10. CHRYSENE	1,2-benzophenanthrene; benzo[a]phenanthrene; CAS# 218-01-9; RTECS # GC0700000
11. DIBENZ[a,h]ANTHRACENE	1,2,5,6-dibenzanthracene; CAS# 53-70-3; RTECS # HN2625000
12. FLUORANTHENE	benzo[jk]fluorene; CAS# 206-44-0; RTECS # LL4025000
13. FLUORENE	CAS# 86-73-7; RTECS # LL5670000
14. INDENO[1,2,3-cd]PYRENE	2,3-phenylenepyrene; CAS# 193-39-5; RTECS # NK9300000
15. NAPHTHALENE	naphthene; CAS# 91-20-3; RTECS # QJ0525000
16. PHENANTHRENE	CAS# 85-01-8; RTECS # SF7175000
17. PYRENE	benzo[def]phenanthrene; CAS#129-00-0; RTECS #UR2450000

Table 3. Exposure Limits.

COMPOUND (alphabetically)	OSHA	NIOSH	ACGIH	
1. ACENAPHTHENE	--		--	--
2. ACENAPHTHYLENE	--		--	--
3. ANTHRACENE	--		--	--
4. BENZ[A]ANTHRACENE	--		--	--
5. BENZO[B]FLUORANTHENE	--		--	suspect carcinogen
6. BENZO[K]FLUORANTHENE	--		--	--
7. BENZO[GHI]PERYLENE	--		--	--
8. BENZO[A]PYRENE	0.2 mg/m^3 (benzene sol.)		0.1 mg/m3 (cyclohexane sol.)	suspect carcinogen
9. BENZO[E]PYRENE	--		--	--
10. CHRYSENE	0.2 mg/m^3 (benzene sol.)		lowest feasible, carcinogen	suspect carcinogen
11. DIBENZ[A,H]ANTHRACENE	--		--	--
12. FLUORANTHENE	--		--	--
13. FLUORENE	--		--	--
14. INDENO[1,2,3-CD]PYRENE	--		--	--
15. NAPHTHALENE	10 ppm		10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
16. PHENANTHRENE	0.2 mg/m^3		--	--
17. PYRENE	--		--	--

Table 4. Approximate PAH retention times.

COMPOUND	RETENTION TIME (min)*
1. NAPHTHALENE	2.4
2. ACENAPHTHALENE	2.8
3. ACENAPHTHENE	3.6
4. FLUORENE	3.9
5. PHENANTHRENE	4.7
6. ANTHRACENE	5.8
7. FLUORANTHENE	6.8
8. PYRENE	7.7
9. BENZ[a]ANTHRACENE	11.2
10. CHRYSENE	12.1
11. BENZO[e]PYRENE	14.0
12. BENZO[b]FLUORANTHENE	14.8
13. BENZO[k]FLUORANTHENE	16.5
14. BENZO[a]PYRENE	17.3
15. DIBENZ[a,h]ANTHRACENE	20.0
16. BENZO[ghi]PERYLENE	20.0
17. INDENO[1,2,3-cd]PYRENE	21.2

* NOTE: Determined with a Perkin-Elmer HC-ODS-SILX column. Actual retention times will vary with individual columns and column age.

Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 5515, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

NIOSH: Table 3
OSHA :

PROPERTIES: Table 1

COMPOUNDS:

- acenaphthene
- acenaphthylene
- anthracene
- benz[a]anthracene
- benzo[b]fluoranthene
- benzo[k]fluoranthene
- benzo[ghi]perylene
- benzo[a]pyrene
- benzo[e]pyrene
- chrysene
- dibenz[a,h]anthracene
- fluoranthene
- fluorene
- indeno[1,2,3-cd]pyrene
- naphthalene
- phenanthrene
- pyrene

SYNONYMS: PAH; PNA; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT (2-μm, 37-mm PTFE + washed XAD-2, 100 mg/50 mg)

FLOW RATE: 2 L/min

VOL-MIN: 200 L
-MAX: 1000 L

SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C

SAMPLE STABILITY: unknown; protect from heat and UV radiation

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 to 10

AREA SAMPLES: 8 replicates on preweighed filters for solvent selection

ACCURACY

RANGE STUDIED, ACCURACY, BIAS, and OVERALL PRECISION ($\hat{S}_{rT}$): not measured

MEASUREMENT

METHOD: GAS CHROMATOGRAPHY, CAPILLARY COLUMN, FID

ANALYTE: compounds above

EXTRACTION: 5 mL organic solvent appropriate to sample matrix (step 7)

INJECTION VOLUME: 4 μL; 10:1 split

COLUMN: 30 m x 0.32-mm ID, fused silica capillary, 1-μm DB-5

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 250 °C
-PROGRAM: 130 to 290 °C @ 4 °C/min

GASES-CARRIER: He @ 1 mL/min
-MAKEUP: He @ 20 mL/min

LOD: ca. 0.3 to 0.5 μg per sample [1]

CALIBRATION: external standards in toluene

RANGE, LOD, and PRECISION ($\bar{S}_r$): EVALUATION OF METHOD

APPLICABILITY: The working range for B[a]P is 3 to 150 $\mu g/m^3$ for a 400-L air sample. Specific sample sets may require modification in filter extraction solvent, choice of measurement method, and measurement conditions.

INTERFERENCES: Any compound which elutes at the same GC retention time may interfere. Heat, ozone, NO_2, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 183 [2]. The spectrophotometric methods, P&CAM 184 and 186 [2], have not been revised. Method 5506 (HPLC) uses the same sampling technique and is more sensitive.

REAGENTS:

1. Filter extraction solvent: acetonitrile, benzene,* cyclohexane, methylene chloride,* or other appropriate solvents, pesticide grade (step 7).
2. Toluene, pesticide grade.
3. Water, distilled, deionized.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with toluene. Stable six months if refrigerated and protected from light.
6. Helium, prepurified.
7. Hydrogen, dry.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter. PTFE-laminated membrane filter, 2-μm pore size, 37-mm diameter (Gelman Zefluor, Membrana, Pleasantown, CA, or equivalent), backed by a spacer (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.
      NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
      NOTE 2: Take filters to be preweighed from the filter package and allow to equilibrate 24 h with laboratory atmosphere before taring.
   b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H_2O).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Filters, 0.45-μm, PTFE (for filtering sample solutions).
9. Pipet, 5-mL.
10. Syringes or micropipets, 1- to 100-μL.
11. Ultrasonic bath.
12. Gas chromatograph with FID, electronic integrator, and capillary column (page 5515-1).
13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat benzene, methylene chloride, and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L. Take a concurrent set of eight replicate area samples at 2 to 4 L/min on preweighed, 2-μm PTFE filters in an area of highest expected PAH concentration.
   NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a scintillation vial. Hold filter at edge to avoid disturbing the deposit. Cap the scintillation vial and wrap it in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes due to sublimation and degradation by light.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAH. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
   a. Allow the preweighed area filter samples to equilibrate 24 h with the laboratory atmosphere.
   b. Weigh the area filters. Determine total weight collected on each.
   c. Extract the first pair of area filters with acetronitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
      NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and adsorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [3,4] and benzene:ethanol (4:1 v/v) [5] have been recommended for extraction of PAH from diesel exhaust particulate.
   d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
   e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
   a. Add 5.0 mL of the solvent chosen in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
   b. Cap and let stand 15 to 20 min in an ultrasonic bath.
      NOTE: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.
9. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the primary (larger) sorbent section. Break tube at score line.
   b. Transfer front glass wool plug and front sorbent section to a culture tube. Transfer back sorbent section and the middle glass wool plug to a second culture tube.
   c. Add 5.0 mL toluene to each culture tube. Cap the culture tubes.
   d. Allow samples to stand for 30 min. Swirl occasionally.
10. Filter all sample extracts through an 0.45-μm membrane filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards.
    a. Dilute aliquots of calibration stock solution with toluene in 10-mL volumetric flasks (e.g., to 5, 1, 0.2, 0.05, and 0.005 μg/mL).

b. Intersperse working standards and samples in the measurements.
c. Prepare calibration graphs (peak area vs. μg of each PAH per sample).

12. Recovery and desorption efficiency.
    a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
        (1) Filters. Using a microliter syringe or micropipette, spike four filters at each of five concentration levels with calibration stock solution. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.
            NOTE: This step may not be used for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.
        (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blanks in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight in the dark. Analyze (steps 9, 10, and 14 through 16). Prepare graphs of DE vs. amounts found.
    b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R and DE graphs if checks do not agree to within $\pm 5\%$ of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set GC according to manufacturer's recommendations and to the conditions on page 5515-1.
15. Inject sample aliquot. Start temperature program.
16. Measure peak areas.
    NOTE 1: Approximate retention times appear in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [6,7] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. Read the mass, μg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
18. Calculate concentration, C (mg/m^3), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

$$C = \frac{(W - B + W_f + W_b - B_f - B_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Owing to large interferences that occured while utilizing NIOSH Method P&CAM 206 for samples collected during asphalt roofing operations, the gas chromatographic capillary column method was developed. The GC method has been evaluated using several hundred field filter and sorbent tube sampling trains. To date, no statistical studies have been initiated. Overall, standard spiked filters and sorbent tubes have yielded reproducible measurement calibration graphs. The method has been applied to the following sources with semi-quantitative results using three separate particulate extraction solvents (benzene, cyclohexane, acetonitrile): aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

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METHOD REVISED BY:

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Table 1. Formulae and physical properties.

COMPOUND (by M.W.)	EMPIRICAL FORMULA	MOLECULAR WEIGHT	MELTING POINT (°C)*	BOILING POINT (°C)*	REF.
1. NAPHTHALENE	$C_{10}H_8$	128.17	80.2	218	[10]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	92-93	265-275	[11]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	96.2	279	[11]
4. FLUORENE	$C_{13}H_{10}$	166.22	116	293-295	[10]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	218	340	[10]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	100	340	[10]
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	110	384*	[10], [12]
8. PYRENE	$C_{16}H_{10}$	202.26	156	393	[10]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	162-167	435	[10]
10. CHRYSENE	$C_{18}H_{12}$	228.29	255-256	448	[10]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	168	--	[10]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	217	480	[11]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	179	495	[10]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	178-179	--	[10]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	273	--	[10]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	161.5-163	530	[9]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	267	524	[10]

*Many of these compounds will sublime.

Table 2. Synonyms.

COMPOUND (alphabetically)	SYNONYMS
1. ACENAPHTHENE	CAS# 83-32-9; RTECS# AB1000000
2. ACENAPHTHYLENE	CAS# 208-96-8; RTECS# AB1254000
3. ANTHRACENE	CAS# 120-12-7; RTECS# CA9350000
4. BENZ[a]ANTHRACENE	1,2-benzanthracene; benzo[b]phenanthrene; 2,3-benzophenanthrene; tetraphene; CAS# 56-55-3; RTECS# CV9275000
5. BENZO[b]FLUORANTHENE	3,4-benzofluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene; B[b]F; CAS # 205-99-2; RTECS# CU1400000
6. BENZO[k]FLUORANTHENE	11,12-benzofluoranthene; CAS# 207-08-9; RTECS# DF6350000
7. BENZO[ghi]PERYLENE	1,12-benzoperylene; CAS# 191-24-2; RTECS# DI6200500
8. BENZO[a]PYRENE	3,4-benzopyrene; 6,7-benzopyrene; B[a]P; BP; CAS# 50-32-8; RTECS# DJ3675000
9. BENZO[e]PYRENE	1,2-benzopyrene; 4,5-benzopyrene; B[e]P; CAS# 192-97-2; RTECS# DJ4200000
10. CHRYSENE	1,2-benzophenanthrene; benzo[a]phenanthrene; CAS# 218-01-9; RTECS# GC0700000
11. DIBENZ[a,h]ANTHRACENE	1,2,5,6-dibenzanthracene; CAS# 53-70-3; RTECS# HN2625000
12. FLUORANTHENE	benzo[jk]fluorene; Idryl; CAS# 206-44-0; RTECS# LL4025000
13. FLUORENE	o-biphenylenemethane; CAS# 86-73-7; RTECS# LL5670000
14. INDENO[1,2,3-cd]PYRENE	2,3-phenylenepyrene; CAS# 193-39-5; RTECS# NK9300000
15. NAPHTHALENE	naphthene; CAS# 91-20-3; RTECS# QJ0525000
16. PHENANTHRENE	CAS# 85-01-8; RTECS# SF7175000
17. PYRENE	benzo[def]phenanthrene; CAS# 129-00-0; RTECS# UR2450000

Table 3. Exposure Limits.

COMPOUND (alphabetically)	OSHA	NIOSH	ACGIH
1. ACENAPHTHENE	--	--	--
2. ACENAPHTHYLENE	--	--	--
3. ANTHRACENE	0.2 mg/m^3	--	--
4. BENZ[A]ANTHRACENE	--	--	--
5. BENZO[B]FLUORANTHENE	--	--	suspect carcinogen
6. BENZO[K]FLUORANTHENE	--	--	--
7. BENZO[GHI]PERYLENE	--	--	--
8. BENZO[A]PYRENE	0.2 mg/m^3 (benzene sol.)	0.1 mg/m^3 (cyclohexane sol.)	suspect carcinogen
9. BENZO[E]PYRENE	--	--	--
10. CHRYSENE	0.2 mg/m^3 (benzene sol.)	lowest feasible, carcinogen	suspect carcinogen
11. DIBENZ[A,H]ANTHRACENE	--	--	--
12. FLUORANTHENE	--	--	--
13. FLUORENE	--	--	--
14. INDENO[1,2,3-CD]PYRENE	--	--	--
15. NAPHTHALENE	10 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
16. PHENANTHRENE	0.2 mg/m^3	--	--
17. PYRENE	--	--	--

Table 4. Approximate PAH retention times.

COMPOUND	RETENTION TIME (min)*
1. NAPHTHALENE	not available
2. ACENAPHTHALENE	7.66
3. ACENAPHTHENE	8.37
4. FLUORENE	10.5
5. PHENANTHRENE	15.0
6. ANTHRACENE	15.3
7. FLUORANTHENE	21.4
8. PYRENE	22.6
9. BENZ[a]ANTHRACENE	29.4
10. CHRYSENE	29.6
11. BENZO[e]PYRENE	36.4
12. BENZO[b]FLUORANTHENE	35.1
13. BENZO[k]FLUORANTHENE	35.2
14. BENZO[a]PYRENE	36.2
15. DIBENZ[a,h]ANTHRACENE	43.9
16. BENZO[ghi]PERYLENE	45.6
17. INDENO[1,2,3-cd]PYRENE	43.6

*NOTE: Actual retention times will vary with individual columns and column age.

n-PROPYL ACETATE

See ESTERS I (Method 1450) for procedure

n-PROPYL ALCOHOL

See ALCOHOLS II (Method 1401) for procedure

PROPYLENE DICHLORIDE

$CH_3CHClCH_2Cl$ MW: 112.99 CAS: 78-87-5 RTECS: TX9625000

METHOD: 1013, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 75 ppm
NIOSH: lowest feasible; carcinogen; Group I Pesticide
ACGIH: 75 ppm; STEL 110 ppm; carcinogen
(1 ppm = 4.62 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.159 g/mL @ 25 °C; BP 95 °C; MP −70 °C; VP 5.3 kPa (40 mm Hg; 5.2% v/v) @ 20 °C; explosive range 3.4 to 14.5% v/v in air

SYNONYMS: 1,2-dichloropropane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.1 L @ 75 ppm
-MAX: 3.5 L

SAMPLE STABILITY: at least 26 days @ 25 °C in the dark [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 128 mg/m^3 [1] (3-L samples)

BIAS: 3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.064 [1]

ACCURACY: ± 15.5%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY WITH ELECTROLYTIC CONDUCTIVITY DETECTOR (HALL)

ANALYTE: propylene dichloride

DESORPTION: 1 mL 15% (v/v) acetone/cyclohexane; ultrasonic bath, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-COLUMN: 50 °C

HALL DETECTOR FURNANCE: 840 °C
-ELECTROLYTE: 0.9 mL/min
-HYDROGEN: 50 mL/min

CARRIER GAS: N_2, 25 mL/min

COLUMN: nickel, 3 m x 2-mm ID, 3% Carbowax 1500 on 60/80 mesh Chromosorb WHP

CALIBRATION: solutions in acetone/cyclohexane

RANGE: 0.5 to 400 µg per sample [2]

ESTIMATED LOD: 0.1 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.031 @ 0.5 to 520 µg per sample [1]

APPLICABILITY: The working range is 0.05 to 130 ppm (0.25 to 600 mg/m^3) for a 2-L air sample at about 90% RH.

INTERFERENCES: Propylene dichloride cannot be resolved from 1,2-dichloroethane with a Carbowax packed column. They were resolved with a Carbowax capillary column.

OTHER METHODS: This revises P&CAM 321 [2].

REAGENTS:

1. Acetone, distilled in glass.*
2. Cyclohexane, distilled in glass.*
3. Eluent: 15% (v/v) acetone in cyclohexane.
4. Propylene dichloride, reagent grade.*
5. Nitrogen, high purity, for GC carrier gas.
6. Hydrogen, prepurified, for Hall detector.
7. Electrolyte solution for Hall detector: 2-propanol and distilled, deionized water, 50% (v/v).
8. Calibration stock solution, 34.7 mg/mL. Dilute 3.00 mL (3.47 g) 1,2-dichloropropane to 100 mL with eluent. Stable indefinitely at room temperature in airtight container.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated petroleum-based charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 0.2 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (SKC No. 226-65 or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tape.
4. Gas chromatograph with Hall electrolytic conductivity detector and column (page 1013-1).
5. Vials, 1-mL, with PTFE-lined silicone rubber septa and serum caps.*
6. Syringes, 10-mL and other convenient sizes for making dilutions.
7. Pipets, 1-mL and other convenient sizes for making dilutions.*
8. Volumetric flasks, 10- and 100-mL.*
9. Ultrasonic bath.

* Clean thoroughly and rinse with, in order, 50% (v/v) HNO_3, distilled water, acetone and cyclohexane.

SPECIAL PRECAUTIONS: Propylene dichloride vapor is a narcotic and an eye irritant [3]. Acetone and cyclohexane are extremely flammable. Work with these in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 3.5 L.
4. Cap the samplers with PTFE tape. Pack securely for shipment. Store samplers in the dark.
5. Refrigerate the samplers in an airtight container upon receipt.

SAMPLE PREPARATION:

6. Bring the samplers to room temperature before uncapping to prevent moisture condensation on the sorbent.
7. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool plug with the front sorbent section and the foam plugs with the back sorbent section.

8. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
9. Allow to stand 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.1 to 400 μg propylene dichloride per sample.
    a. Add known amounts of calibration stock solution, or a serial dilution thereof, to eluent in 10-mL volumetric flasks and dilute to the mark.
    b. Analyze together with samples and blanks (steps 13 and 14).
    c. Prepare calibration graph (peak height vs. μg propylene dichloride).
11. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 10). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 6 through 9) and analyze together with working standards (steps 13 and 14).
    e. Prepare a graph of DE vs. μg propylene dichloride recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1013-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak height is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
14. Measure peak height.

CALCULATIONS:

15. Determine the mass, μg (corrected for DE) of propylene dichloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration, C, of propylene dichloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 321 was issued on June 15, 1980 [2] and was validated over the range 0.37 to 384 μg propylene dichloride per charcoal tube [1]. The $\hat{S}_{rT}$ for replicate measurements from generated atmospheres was 0.064 for 17 samples. Recoveries ranged from 97% to 103%. The pooled relative standard deviation for the analysis of spiked samplers was 0.031. The breakthrough volume was found to be about 20 L with sampling rates of 0.07 to 0.17 L/min at 1,2-dichloropropane concentrations of 62 to 85 mg/m^3 at RH >90% and ca. 6 L at concentrations of 738 to 865 mg/m^3. Desorption efficiency averaged 0.95 in the range 0.5 to 520 μg 1,2-dichloropropane per sampler.

REFERENCES:

[1] Research Report for 1,2-Dichloropropane, NIOSH Contract No. 210-78-0012, Southern Research Institute, Birmingham, AL (NIOSH, unpublished, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 321, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Propylene dichloride, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

PROPYLENE OXIDE 1612

C_3H_6O MW: 58.08 CAS: 75-56-9 RTECS: TZ2975000

METHOD: 1612, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: lowest feasible (carcinogen); Group I Pesticide
ACGIH: 20 ppm
(1 ppm = 2.37 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8287 g/mL @ 20 °C; BP 34 °C; MP −104 °C; VP 59 kPa (442 mm Hg; 58% v/v) @ 20 °C; explosive range 2.1 to 37% (v/v) in air

SYNONYMS: 1,2-epoxypropane; methyloxirane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 100 ppm
-MAX: 5 L

SHIPMENT: refrigerated

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 121 to 482 mg/m^3 [1] (5-L samples)

BIAS: − 1.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.085 [1]

ACCURACY: ± 11.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: propylene oxide

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 190 °C
-DETECTOR: 255 °C
-COLUMN: 40 °C, 6 min; 50 °C/min to 250 °C

CARRIER GAS: N_2, 1 mL/min; makeup 29 mL/min

COLUMN: 30 m x 0.32-mm fused silica capillary column, 1.0-µm DB-5 [2]

CALIBRATION: propylene oxide in CS_2

RANGE: 0.03 to 3 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\bar{S}_r$): 0.029 @ 0.6 to 2.4 mg per sample [1]

APPLICABILITY: The working range is 8 to 295 ppm (20 to 700 mg/m^3) for a 5-L air sample [1].

INTERFERENCES: None found.

OTHER METHODS: This revises method S75 [3].

REAGENTS:

1. Propylene oxide (PrO), reagent grade.*
2. Carbon disulfide (CS_2), chromatographic quality.*
3. Hexane, reagent grade.*
4. Calibration stock solution, 10 mg/mL, in carbon disulfide.
5. Desorption efficiency (DE) stock solution, 150 mg/mL, in hexane.
6. Nitrogen, purified.
7. Hydrogen, purified.
8. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Shipping container, with bagged refrigerant.
4. Gas chromatograph, FID, integrator, and column (page 1612-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL, readable to 0.1 μL, and other convenient sizes for preparing standards.
7. Volumetric flasks, 10-mL.
8. Pipet, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a dangerous fire and explosion hazard (flash point = −30 °C). Propylene oxide is a suspect carcinogen and is extremely flammable (flash point = −37 °C) [4]. Hexane is extremely flammable. Work with these only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 5 L.
4. Cap the samplers and pack securely for shipment in an insulated container with bagged refrigerant. Refrigerate upon receipt.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 3 mg propylene oxide (PrO) per sample.
   a. Add known amounts of PrO or calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg PrO).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg PrO recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1612-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of PrO found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of PrO in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - W_f - W_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S75 was issued on February 14, 1975 [3], and validated over the range 121 to 482 mg/m^3 at 24 °C and 766 mm Hg using a 5-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.085, with an average recovery of 94.4% at the OSHA standard level. Desorption efficiencies averaged 0.88, 0.95, and 0.96 at 0.6, 1.2, and 2.4 mg propylene oxide per sample, respectively. Breakthrough (5% on back section) occurred at 45 min when sampling an atmosphere of propylene oxide containing 484 mg/m^3 in dry air at 0.185 L/min. At this time, the front section contained 4 mg propylene oxide. Breakthrough in humid air and storage stability were not determined.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S75, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] DataChem, Inc. NIOSH Sequences #6599, 6722, 6723 (unpublished, 1989).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S75, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

George Williamson, NIOSH/DPSE.

$C_{20}H_{28}O_3$ to $C_{22}H_{30}O_5$ (Table 1) MW: 316.4 to 372.4 (active constituents) CAS: 8003-34-7 RTECS: UR4200000

METHOD: 5008, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group II pesticide
ACGIH: 5 mg/m^3

PROPERTIES: viscous brown resin or solid; VP not significant

SYNONYMS: Active constituents include pyrethrin I and II, jasmolin I and II, and cinerin I and II.

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (glass fiber)	**TECHNIQUE:**	HPLC, UV DETECTION
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	six active constituents of pyrethrum
VOL-MIN:	20 L	**EXTRACTION:**	10 mL acetonitrile; stand 30 min
-MAX:	400 L		
SHIPMENT:	routine; ship bulk sample separately	**INJECTION VOLUME:**	25 µL
SAMPLE STABILITY:	at least 1 week @ 25 °C [1]	**COLUMN:**	C_{18} reverse phase, 10-µm packing, 25 to 30 cm
FIELD BLANKS:	2 to 10 field blanks per set	**MOBILE PHASE:**	85% acetonitrile/15% water, isocratic, 1.0 mL/min, room temperature, 2800 kPa (400 psi)
ACCURACY		**DETECTOR:**	UV absorption @ 225 nm
RANGE STUDIED:	1.4 to 8.5 mg/m^3 [1] (132-L samples)	**CALIBRATION:**	solutions of pyrethrum in acetonitrile
BIAS:	− 4.5%	**RANGE:**	0.1 to 1.8 mg per sample
OVERALL PRECISION ($\hat{S}_{rT}$):	0.070 [1]	**ESTIMATED LOD:**	0.01 mg per sample
ACCURACY:	± 13.8%	**PRECISION ($\bar{S}_r$):**	0.040 [1]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample.

INTERFERENCES: Specific interferences have not been studied. Mass spectrometry or gas-liquid chromatography with electron-capture detection may be needed for confirmation [1].

OTHER METHODS: This method is S298 [2] in a revised format. For bulk samples, gas-liquid chromatography with electron-capture detection has been recommended [3]. A modified HPLC method (C_8 column, programmed methanol/water or acetonitrile, isocratic) has been used [4].

REAGENTS:

1. Pyrethrum*, analytical standard solution(McLaughlin Gormley King Co., Minneapolis, MN; Chem Service, Inc., West Chester, PA; or other supplier).
   NOTE: Store away from direct light. Active constituents of pyrethrum oxidize in air and photo-decompose.
2. Acetonitrile, HPLC grade.*
3. Water, HPLC grade.
4. Isopropanol.
5. Calibration stock solution,* 60 mg/mL, in isopropanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm glass fiber filter and cellulose backup pad in filter holder held together with tape or shrinkable band.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with UV absorption detector at 225 nm, integrator and column (page 5008-1).
4. Ointment jars, 2-oz, squat form, with PTFE-lined screw caps.
5. Tweezers.
6. Pipet, TD, 10-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-mL, with syringe filter.
9. Syringes or pipets, 5- to 100-μL.

SPECIAL PRECAUTIONS: Acetonitrile and pyrethrum solutions are toxic and flammable. Use gloves, goggles and other appropriate equipment to prevent eye contact or repeated and prolonged skin contact [5]. Wash skin and change clothes if contact occurs. Use in fume hoods and away from ignition sources.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 20 to 400 L.

SAMPLE PREPARATION:

3. Transfer the filter carefully to an ointment jar using tweezers.
4. Add 10.0 mL acetonitrile. Seal and gently swirl the jar to wet the filter. Let stand 30 min with occasional swirling.
5. Filter the sample solution through a syringe filter.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.01 to 1.8 mg pyrethrum per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 9, 10 and 11).
   c. Prepare calibration graph (peak area vs. mg pyrethrum/10 mL).
7. Determine recovery (R) at least once for each batch of filters used for sampling in the range of the samples. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of calibration stock solution, or a dilution thereof, onto the filters. Allow filters to air-dry.
   b. Store samples overnight in ointment jars.

c. Prepare (steps 4 and 5) and analyze together with working standards (steps 9 through 11).
d. Prepare a graph of R vs. mg pyrethrum recovered.

8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set HPLC system according to manufacturer's recommendations and to conditions on page 5008-1.
10. Inject sample aliquot using syringe, fixed volume sample loop, or autosampler.
11. Measure peak area.
    NOTE: Pyrethrum is a mixture of at least six components which elute in two major peaks (t_r = 5 to 7 min under these conditions). The minor peaks have been shown by mass spectrometry not to be pyrethrums. The components may be separated by gas chromatography [1,4].

CALCULATIONS:

12. Determine the mass, mg (corrected for R) of pyrethrum found in the sample (W) and in the average media blank (B) from the calibration graph.
13. Calculate concentration, C, of pyrethrum in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S298 [2] was issued on August 3, 1979, and validated over the range 1.4 to 8.5 mg/m^3 using atmospheres generated from Premium Pyrocide 175 (McLaughlin Gormley King Co.) [1]. Standards and collected filter samples were analyzed by GC/MS. Lab testing was done with spiked filters and atmospheres dynamically generated by atomization of a hydrocarbon solution; verified by PTFE filter/isooctane bubbler analyzed by gas chromatography with electron capture detector (absence of pyrethrum in the bubbler was established by mass spectrometry). Samples containing 0.7 mg pyrethrum collected from a test atmosphere were stable for seven days at ambient conditions (average recovery = 98.2%). Collection efficiency = 99.7% for 120-L samples collected at 1 L/min at 9 mg/m^3. Precision and accuracy are given on page 5008-1.

REFERENCES:

[1] Backup Data Report, S298 (NIOSH, unpublished, August 3, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S298, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] Changes in Official Methods of Analysis, J. Assoc. Off. Anal. Chem., 65, 455-456 (1982).
[4] UBTL, Inc., NIOSH Sequence Reports 3481-J (unpublished, August 30, 1982) and 4151-J (unpublished, November 3, 1983).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE.

Table 1. Active constituents of Pyrethrum.

Compound	Formula	M.W.	CAS #
Cinerin I	$C_{20}H_{28}O_3$	316.44	25402-06-6
Cinerin II	$C_{21}H_{28}O_5$	260.45	
Jasmolin I	$C_{21}H_{30}O_3$	330.47	
Jasmolin II	$C_{22}H_{30}O_5$	374.48	
Pyrethrin I	$C_{21}H_{28}O_3$	328.45	121-21-1
Pyrethrin II	$C_{22}H_{28}O_5$	372.46	121-29-9

PYRIDINE

C_5H_5N MW: 79.10 CAS: 110-86-1 RTECS: UR8400000

METHOD: 1613, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 5 ppm
NIOSH: 5 ppm; Group III Pesticide
ACGIH: 5 ppm
(1 ppm = 3.23 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.982 g/mL @ 20 °C; BP 115 °C; MP −42 °C; VP 2.4 kPa (18 mm Hg; 2.4% v/v) @ 20 °C; explosive limits 1.8 to 12.4% v/v in air

SYNONYMS: azine; azabenzene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 18 L
-MAX: 150 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7.6 to 30 mg/m^3 [1] (100-L samples)

BIAS: 9.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.059 [1]

ACCURACY: ± 19.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: pyridine

DESORPTION: 1 mL methylene chloride; stand 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 260 °C
-DETECTOR: 285 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh acid-washed DMCS Chromosorb W

CALIBRATION: standard solutions of pyridine in methylene chloride

RANGE: 0.3 to 4.5 mg per sample

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.014 @ 0.8 to 3.1 mg per sample [1]

APPLICABILITY: The working range is 1 to 14 ppm (3 to 45 mg/m^3) for a 100-L air sample.

INTERFERENCES: None detected. The chromatographic column or separation may be changed to circumvent interference problems (e.g., 30 m x 0.32-mm capillary column with 1 μm DB-5 at 50 °C [2]).

OTHER METHODS: This revises Method S161 [3].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality.
2. Pyridine, reagent grade.*
3. Hexane, chromatographic quality.
4. DE stock solution, 300 mg/mL. Weigh 3 g pyridine (ca. 3.1 mL) into a 10-mL volumetric flask. Dilute to volume with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1613-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.
8. Balance, analytical.

SPECIAL PRECAUTIONS: Pyridine can cause liver and kidney damage, and CNS depression if it is inhaled or contacts the eyes or skin [4,5]. Methylene chloride is a suspect carcinogen [6].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 18 to 150 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Pipet 1.0 mL CH_2Cl_2 into each vial. Cap each vial.
   NOTE: A suitable internal standard, such as toluene, may be added at this step [2].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of pyridine to CH_2Cl_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain pyridine concentrations in the range 0.02 to 4.5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg pyridine).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg pyridine recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1613-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CH_2Cl_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of pyridine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of pyridine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_r - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S161 was issued on August 1, 1975 [3], and validated with atmospheres generated by calibrated syringe pump and confirmed using a total hydrocarbon analyzer [2]. Average recovery was 109% ±3.6% (18 samples) in the range 7.6 to 30.4 mg/m^3 for 100-L samples. Breakthrough (effluent concentration = 5% of test concentration) was not observed after sampling for 240 min at 0.93 L/min from an atmosphere containing 30.4 mg/m^3 pyridine in dry air. Carbon disulfide and methanol were tested and rejected as possible desorbing solvents. Carbon disulfide gave an average DE of 0.734; methanol, 0.201. Desorption efficiency using methylene chloride for 18 spiked samples in the range 0.8 to 3.1 mg pyridine per sample averaged 0.81 with S_r = 0.013.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S161, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] UBTL, Inc. Report, NIOSH Sequences 4949-K (unpublished, May 24, 1985) and 3030-K (unpublished, July 20, 1981).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S161, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[5] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
[6] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

$C_8H_{12}N_4O_5$ MW: 244.21 CAS: 36791-04-5 RTECS: XZ4250000

METHOD: 5027, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solid; MP 170 °C; VP negligible; sol. (water): 142 mg/mL @ 25 °C

SYNONYMS: 1-ß-D-ribofuranosyl-1,2,4-triazole-3-carboxamide; Virazole; ICN 1229

SAMPLING

SAMPLER: FILTER (1-μm, 37-mm glass fiber)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 5 L @ 0.4 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable in dark at room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: unknown

OVERALL PRECISION ($\hat{S}_{rT}$): unknown

ACCURACY: unknown

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Ribavirin

EXTRACTION: 3 mL H_2SO_4 (pH = 2.5), agitate 30 min

INJECTION VOLUME: 30 μL

MOBILE PHASE: H_2SO_4, (pH = 2.5), isocratic

TEMPERATURE: 65 °C

FLOW RATE: 0.6 mL/min

COLUMN: 30 cm x 7.8 mm, cation exchange resin

DETECTOR: UV, 210 nm

CALIBRATION: standard solutions of Ribavirin in H_2SO_4 (pH = 2.5)

RANGE: 2 μg to 2000 μg per sample [1, 2]

ESTIMATED LOD: 0.7 μg per sample [1, 2]

PRECISION ($\hat{S}_r$): 0.057 @ 19 to 112 μg per sample [1, 2]

APPLICABILITY: The working range is 0.04 to 40 mg/m^3 for a 50-L air sample.

INTERFERENCES: None known.

OTHER METHODS: This method is a modification of a bulk assay procedure developed by Eastman Kodak Company [3].

REAGENTS:

1. Ribavirin,* reagent grade.
2. H_2SO_4,* conc.
3. Mobile phase: Add conc. H_2SO_4,* to deionized, distilled water until pH is 2.5 $\pm$0.1 as measured by a pH meter.
4. Calibration stock solution: Dilute 5 mg Ribavirin to 10 mL in a volumetric flask using mobile phase as solvent. Prepare fresh daily.
5. Standard buffer solutions (pH 7.00 and 3.00) for calibrating pH meter. Available as a reference standard from USP (Cat. No. 60270-6).

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 1-μm, 37-mm glass fiber filter (Type A/E; Cat. No. 61652, Gelman Sciences, Inc., Ann Arbor, MI 48106, or equivalent) with a cellulose backup pad in a 2-piece cassette.
2. Personal sampling pump capable of operating for 8 hours at 1 to 4 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph, isocratic, with water jacket (or equivalent) to maintain column temperature at 65 °C; UV detector (210 nm); peak integrator; and cation exchange resin column (Cat. No. HPX-87H, Bio-Rad Laboratories, Richmond, CA 94804 or equivalent).
4. Vials, 10-mL, glass with PTFE-lined caps.
5. Culture tubes, PTFE-lined screw caps, 13-mm x 100-mm.
6. Syringe filters, disposable, 0.45-μm pore size, for filtering samples.
7. Pipets, 1- to 10-mL.
8. Volumetric flasks, 10-mL.
9. Forceps.
10. Shaker, mechanical, wrist-action
11. pH meter.

SPECIAL PRECAUTIONS: Ribavirin has been found to be teratogenic in animals. [4, 5] Use protective gloves when handling. Work only in a fume hood. Women of childbearing age should exercise extreme caution. Avoid skin contact with concentrated sulfuric acid.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line. Attach sampler to personal sampling pump with flexible tubing.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 5 to 1000 L. Avoid overloading the filter (ca. 2 mg total dust maximum loading).
3. Seal the samplers and pack securely for shipment.
4. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

5. Carefully remove the filter from the cassette. Use forceps to fold the filter in half, and insert into a culture tube. Discard the backup pad.
6. Add 3 mL mobile phase. Seal tightly with screw cap and agitate samples with a shaker for 30 minutes.
   NOTE: Although Ribavirin is stable as a solid, it degrades after 12 h in the mobile phase necessitating daily preparation of standards and prompt analysis of extracted samples [3].
7. Filter the sample solution through a syringe filter.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.2 to 700 μg/mL.
   a. Add known amounts of calibration stock solution to mobile phase in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 through 13).
   c. Prepare calibration graph (peak area vs. μg Ribavirin).
9. Determine recovery (R) at least once for each lot of filters used for sampling in the range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of Ribavirin onto the filter. Allow filters to air dry.
   b. Store samples overnight in the dark.
   c. Prepare (steps 5 through 7) and analyze with working standards.
   d. Prepare a graph of R vs. μg Ribavirin spiked.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

11. Set liquid chromatograph system according to manufacturer's recommendations and to the conditions given on page 5027-1.
12. Inject sample aliquot using syringe, fixed volume sample loop or autosampler.
    NOTE: If peak area is above linear range of calibration graph, dilute, reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for R) of Ribavirin found in the sample (W), and in the average media blank (B), from the calibration graph.
15. Calculate concentration, C, of Ribavirin in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method is a modification of a bulk assay procedure developed by Eastman Kodak Company [3]. Measurement precision, $\bar{S}_r$, was 0.057 with average recovery of 100% representing no bias, based on 16 samples ranging from 19.2 to 112 μg per filter. Sampling precision was not determined. The calibration curve was shown to be linear between 0.63 and 666 μg of Ribavirin/mL of extraction solution. A least-squares fit of the calibration curve yielded a limit of detection of 0.7 μg per filter and a limit of quantitation of 2 μg per filter [1,2].

REFERENCES:

[1] Belinky, Barry, "NIOSH/DPSE/MRSB Analytical Report for Ribavirin, Sequence #6138-B," (unpublished, 7/6/88).

[2] Belinky, Barry, "NIOSH/DPSE/MRSB Analytical Report for Ribavirin, Sequence #6138-A," (unpublished, 7/25/88).

[3] "Liquid Chromatographic Analysis of Ribavirin in Bulk Active Form," Eastman Kodak Company Internal Test Method, #KPAT-A-SS52956-LC-16-1, Rochester, New York (1985).

[4] "Assessing Exposures of Health-Care Personnel to Aerosols of Ribavirin," Morbidity and Mortality Weekly Report (MMWR), Centers for Disease Control, Atlanta, Georgia, September 16, 37 560 (1988).

[5] Physician's Desk Reference, 41st. ed., E. R. Barnhart Publisher, pp 1025-1026 (1987).

METHOD WRITTEN BY:

Barry R. Belinky and G. David Foley, NIOSH/DPSE.

ROTENONE

$C_{23}H_{22}O_6$ MW: 394.43 CAS: 83-79-4 RTECS: DJ2800000

METHOD: 5007, Issue 2 **EVALUATION:** FULL **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m³
NIOSH: 5 mg/m³; Group II Pesticide
ACGIH: 5 mg/m³

PROPERTIES: solid, MP 163 °C or 181 °C; BP 220 °C @ 0.5 mm Hg; d ca. 1 g/cm³; VP not significant

SYNONYMS: tubatoxin; cube

SAMPLING

SAMPLER:	FILTER (1-mm PTFE membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	8 L
-MAX:	400 L
SHIPMENT:	routine
SAMPLE STABILITY:	at least 7 days @ 25 °C in dark
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	desirable; 1 g

ACCURACY

RANGE STUDIED:	1 to 11 mg/m³ [1] (100-L sample)
BIAS:	− 0.6%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.079
ACCURACY:	± 13.5%

MEASUREMENT

TECHNIQUE:	HPLC; UV DETECTION
ANALYTE:	Rotenone
EXTRACTION:	4 mL acetonitrile; 30 min
INJECTION VOLUME:	10 µL
MOBILE PHASE:	60% methanol/40% water, 2 mL/min
DETECTOR:	UV @ 290 nm; 0.1A full-scale; 1-cm cell
COLUMN:	µ-Bondapak C_{18} (30 cm x 3.9-mm ID stainless steel); ambient temperature
CALIBRATION:	solutions of Rotenone in acetonitrile
RANGE:	0.04 to 1 mg per sample
ESTIMATED LOD:	4 µg per sample [1,2]
PRECISION ($\hat{S}_r$):	0.024 [1]

APPLICABILITY: The working range is 0.4 to 10 mg/m³ for a 100-L air sample and the method is applicable to commercial formulations.

INTERFERENCES: None known. Rotenone, a naturally occurring insecticide, is adequately separated by HPLC from other compounds (e.g., sumatrol, α-toxicarol, deguelin, elliptone, malaccol, and tephrosin [3]) present in commercial cube root extracts [4]. Rotenone is sensitive to photodecomposition.

OTHER METHODS: This is Method S300 [2] in a revised format.

REAGENTS:

1. Acetonitrile, HPLC grade.*
2. Methanol, HPLC grade.
3. Rotenone, 97% purity.
4. Water, distilled, HPLC grade.
5. Calibration stock solution, 3 mg/mL. Dissolve 0.075 g Rotenone in 25 mL acetonitrile. Prepare fresh daily in duplicate.
6. Recovery stock solution, 50 mg/mL. Dissolve 0.500 g Rotenone in acetone. Dilute to 10 mL. Prepare fresh daily.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, two-piece cassette containing 1-μm PTFE membrane filter with backup pad.
   NOTE: Use an opaque cassette or otherwise shield the filter from light to minimize photodecomposition of Rotenone during and after sampling.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. HPLC, UV detector, integrator and column (page 5007-1).
4. Jars, ointment, 60-mL, with PTFE-lined caps.
5. Vials, 4-mL, with PTFE-lined caps.
6. Syringes, 5-mL.
7. Filtration device, Swinney 13-mm with 1-μm PTFE filters, or PTFE syringe filters.
8. Volumetrics, 10- and 25-mL.
9. Syringes, microliter, for sample injection and standard preparation.
10. Pipet, 4-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Avoid breathing acetonitrile vapors; may cause skin irritation.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 8 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Collect a bulk sample (1 g) in a glass vial with PTFE-lined cap; ship separately from filters.

SAMPLE PREPARATION:

4. Open filter cassette; transfer filter to ointment jar.
5. Add 4.0 mL acetonitrile; gently swirl for 30 min.
6. Filter each sample using a 5-mL syringe with PTFE syringe filter or Swinney filtration device. Deliver filtrate to a 4-mL vial.

CALIBRATION AND QUALITY CONTROL:

7. Prepare at least six working standards daily in the range 0.01 to 1 mg Rotenone per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg Rotenone).
8. Check recovery (R) with at least three spiked media blanks per sample set in the calibration range (step 7).
   a. Add aliquots of recovery stock solution to blank filters with a microliter syringe. Air dry.
   b. Analyze together with working standards (steps 4 through 6, 9 and 10).
   c. Calculate recovery [(mg recovered - mg blank)/mg added].
   d. Prepare recovery graph (R vs. mg Rotenone).

MEASUREMENT:

9. Set HPLC system according to manufacturer's recommendations and to conditions given on page 5007-1. Inject 10-μL sample.
   NOTE: If peak area is above linear range of calibration graph, dilute, reanalyze, and apply appropriate dilution factor in calculations.
10. Measure peak area.

CALCULATIONS:

11. Read the mass, mg (corrected for recovery) of Rotenone found on the filter (W) and average media blank (B) from the calibration graph.
12. Calculate the concentration, C (mg/m^3), of Rotenone in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S300 [2] was issued on May 11, 1979, and validated over the range 1.16 to 11.1 mg/m^3 at 25°C and 760 mm, using 100-L samples [1, 5]. Overall precision, $\hat{S}_{rT}$, was 0.079 with average recovery 100.4%, representing a non-significant bias. The concentration of Rotenone (generated by Wright dust feeder using Ortho Rotenone Dust [1%; Chevron Chemical Co.] enriched to 10% Rotenone with analytical grade Rotenone [Aldrich Chemical Co.]) was independently verified by collection in dioxane and HPLC analysis. Recovery was 0.98 in the range 250 to 1000 μg Rotenone per sample. Collection efficiency of the PTFE filter was found to be greater than 99% and no detectable Rotenone (LOD = 4 μg) was found on Chromosorb 102 tubes placed behind the PTFE filters at 11.8 mg/m^3. No loss was seen from spiked filters stored in the dark at room temperature for seven days.

REFERENCES:

[1] Backup Data Report prepared under NIOSH Contract 210-76-0123, available as Order No. PB 82-114729 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S300, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Gunther, F. A., and R. G. Blinn. Analysis of Insecticides and Acaricides, 419-420, Interscience, NY (1955).
[4] Bushway, R. J., B. S. Engdahl, B. M. Colvin, and A. R. Hanks. J. Assoc. Official Anal. Chemists, 58, 965 (1975).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Jerome Smith, Ph.D., NIOSH/DPSE; S300 originally validated under NIOSH Contract 210-76-0123.

SELENIUM

See ELEMENTS (Method 7300) for procedure

SILICA, AMORPHOUS

SiO_2 MW: 60.08 CAS: Table 1 RTECS: Table 1

METHOD: 7501, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: solid; d 2.2 g/mL; MP >1600 °C

SYNONYMS: fumed amorphous silica (Aerosil, silica aerogel, silicic anhydride); fused amorphous silica (Cab-o-sil, colloidal silica, diatomaceous earth); hydrated amorphous silica (Hi-sil)

SAMPLING

SAMPLER:	FILTER (Total) or CYCLONE + FILTER (Respirable) (10-mm cyclone, nylon, Higgins-Dewell (HD) + 5-μm PVC)
FLOW RATE:	1 to 3 L/min (total) or
NYLON CYCLONE:	1.7 L/min (respirable)
HD CYCLONE:	2.2 L/min (respirable)
VOL-MIN:	50 L
-MAX:	400 L @ 5 mg/m^3 (limit to ≤ 2 mg dust on filter).
SHIPMENT:	routine
SAMPLE STABILITY:	stable indefinitely
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	high volume area air sample required

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	X-RAY POWDER DIFFRACTION
ANALYTE:	cristobalite
ASH:	low temperature plasma; acid wash; deposit on PVC filter
XRD ANALYSIS:	XRD for quartz, cristobalite and tridymite before and after heating
HEAT:	1500 °C, 2 h (fumed amorphous silica) or 1100 °C, 6 h (other amorphous silica); redeposit on Ag filter
CALIBRATION:	standard suspensions of amorphous silica in 2-propanol, converted to cristobalite as for samples
RANGE:	0.2 to 2 mg per sample
ESTIMATED LOD:	0.005 mg per sample
PRECISION ($\bar{S}_r$):	0.10 @ 0.4 to 5 mg; 0.33 @ 0.2 mg [1]

APPLICABILITY: The method is specific for amorphous silica in crystalline (e.g., quartz) matrices in the range 1 to 10 mg/m^3 for a 200-L air sample. Amorphous silica usually contains some crystalline silica [2].

INTERFERENCES: Albite, ammonium phosphate, and tridymite interfere with the largest peak of cristobalite. Quartz and cristobalite are quantitated prior to heat treatment and subtracted from the final quantity of cristobalite. Alkali and alkaline earth oxides prevent 100% conversion; these are removed by acid-wash prior to heat treatment. XRD signal intensity is proportional to particle size; similar particle size of samples and standards is desirable.

OTHER METHODS: This method makes improvements in sample handling and quality assurance to P&CAM 316, which it replaces [3,4]. The XRD analysis steps are similar to those in Method 7500 (Silica, crystalline).

REAGENTS:

1. Amorphous silica standard appropriate to the air sample, i.e., one of the following:
   a. fumed amorphous silica, grade M-5 or M-7 (Cabot Corp.);
   b. gelled amorphous silica, grade CD806 (The PQ Corp.);
   c. diatomaceous earth amorphous silica, grade 680 Multicel;
   d. precipitated amorphous silica, grade EP22 or DENT1 (The PQ Corp.) or grade Zeothix 177 (J.M. Huber Corp.).

   NOTE 1: Some gelled or precipitated amorphous silicas contain up to 7% moisture. Dry all amorphous samples overnight at 115 °C [5].

   NOTE 2: XRD signal intensity is proportional to particle size. Sieve the standards (10-μm sieve), if necessary, to match the particle size expected in the samples.
2. 2-Propanol, reagent grade.
3. Water, deionized.
4. Sodium chloride, reagent grade.
5. Hydrochloric acid, 2% (v/v). Dilute 20 mL conc. HCl to 1 L with deionized water.
6. Desiccant.

EQUIPMENT:

1. Sampler:
   a. Total dust: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter (MSA, Gelman GLA-5000, or equivalent) supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.

      NOTE: Gelman VM-1 and Millipore BS filters are unacceptable because of high ash or amorphous silica content.
   b. Respirable dust: PVC filter (1.a. above) plus cyclone, 10-mm nylon, Higgins-Dewell (HD), or equivalent with sampling head holder. Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
   c. Area sample: PVC filter (1.a. above) at 3 L/min.
2. Personal sampling pumps: 1 to 3 L/min (total or area); 1.7 L/min (nylon cyclone) or 2.2 L/min (HD cyclone).
3. Filters, PVC, 25-mm diameter, 0.45-μm pore size.

   NOTE: These may be cut from acceptable 37-mm PVC filters (not Gelman VM-1 or Millipore BS) by cutting up to five filters, interleaved with separator papers, with a sharp, 25-mm cork borer.
4. Filters, silver membrane, 25-mm diameter, 0.45-μm pore size (Poretics, Costar/Nuclepore, or equivalent).
5. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
6. Glue or tape for securing Ag filters to XRD holders.
7. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
8. Low temperature plasma asher (LTA) or muffle furnace.
9. Filtration apparatus with side-arm vacuum flask and 25- and 37-mm filter holders.
10. Sieve, 10-μm pore size, for wet sieving.
11. Furnace capable of maintaining 1100 °C for 6 h or 1500 °C for 2 h and of temperature programming to 500 °C at 50 °C/min.
12. Crucibles, platinum, with covers.
13. Analytical balance (0.01 mg).
14. Stirrer, magnetic, with thermally-insulated top.
15. Ultrasonic bath or probe.
16. Pipets, 2- to 25-mL.

EQUIPMENT - cont.:

17. Volumetric flasks, 1-L.
18. Desiccator.
19. Bottle, 1-L, with ground glass stopper.
20. Drying oven.
21. Wash bottle, polyethylene.
22. Mortar and pestle, agate.
23. Rubber policeman.
24. Beakers, 100-mL, with watchglass covers.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 3 L/min (total and area), 1.7 L/min (nylon cyclone) or 2.2 L/min (HD) for a total sample size of 50 to 400 L.
   NOTE: Do not allow the cyclone to be inverted at any time. Turning the cyclone more than 90 °C from vertical may deposit over-sized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

3. Ash the sample filter in a 100-mL beaker in the LTA according to manufacturer's instructions. After ashing, carefully (so as to avoid loss of sample) add 50 mL 2% HCl to each beaker.
4. Cover the beaker with a watchglass. Agitate in an ultrasonic batch for at least 3 min (until the agglomerated particles are broken up). Wash the underside of the watchglass with distilled water, collecting the washings in the same beaker.
5. Place a 25-mm PVC filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL deionized water onto the filter. Pour the sample suspension from the beaker into the funnel, and apply vacuum. Rinse the beaker with deionized water and add rinsings to funnel. When filtration is complete, keep vacuum on until filter is dry. Remove the filter with forceps and attach it to the sample holder for XRD analysis.
   NOTE: Control filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add deionized water to the funnel when the liquid level is lower than 4 cm above the filter.

CALIBRATION AND QUALITY CONTROL:

6. Weigh ca. 100 mg dried amorphous silica to the nearest 0.01 mg. Quantitatively transfer to a 1-L bottle using 1.00 L 2-propanol. The resulting concentration is 100 μg/mL.
7. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the 1-L bottle to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
8. Prepare a series of standard filters, in triplicate, over the range 0.005 to 2 mg per sample.
   a. Mount a 37-mm PVC filter on the filtration apparatus. Add ca. 3 mL 2-propanol to wet the filter.
   b. Shake the bottle vigorously by hand. Immediately remove the stopper and withdraw an aliquot (e.g., 2 to 25 mL) by pipet from the center of the suspension.
      NOTE: Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot.
   c. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension. Rinse the pipet with ca. 5 mL 2-propanol, draining the

rise into the funnel. Repeat the rinse three more times.

d. Apply vacuum and rapidly filter the suspension. Keep vacuum on until the filter is dry. Do not wash down the sides of the funnel after the deposit is in place.

9. Prepare and analyze standard filters exactly like samples.
   a. Ash in LTA; redeposit on 25-mm PVC filters (steps 3 through 5).
   b. Analyze by XRD (step 13).
   c. Heat to convert amorphous silica to cristobalite; redeposit on Ag filters (steps 13 through 15).
   d. Analyze by XRD (step 17).
10. Prepare calibration graph ($\hat{I}_x^o$ vs. mg of standard).
    NOTE: Poor repeatability (i.e., $S_r > 0.1$) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/S^2$ weighing) is preferable. Curvature can be eliminated with absorption corrections (step 20) [6].
11. Select six silver membrane filters to be analyzed as media blanks. make the selection randomly from the same box of filters used for depositing samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine net normalized intensity for the silver peak for each media blank.

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (broad 2-Θ range) of the bulk (high-volume respirable) sample to determine the presence of free silica polymorphs and any matrix interference. The diffraction peaks are:

	Peak (2-Θ Degrees)	
Substance	Primary	Secondary
Quartz	26.66	20.85
Cristobalite	21.93	36.11
Tridymite	21.62	20.50
Silver	38.12	44.28

NOTE: For quantitative determination of amorphous silica in bulk samples, wet-sieve a portion of the bulk sample through a 10-μm sieve with 2-propanol in an ultrasonic bath. Evaporate the alcohol and dry in an oven 2 h. Weigh out, in triplicate, 2-mg portions of the sieved dust and transfer to beakers. Add 10 mL 2-propanol, deposit on a PVC filter (step 5) and continue with steps 13 through 17.

13. Mount the filter (sample, standard, or blank) in the XRD instrument and perform the following:
    a. Determine net intensity, I_r^o, of the reference specimen before filter is scanned. Select a convenient scale factor, N, which is approximately equivalent to the net count for the reference specimen peak; use this for all analyses.
    b. Step-scan the most intense diffraction peak of each compound to be determined, integrating the counts.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning and add the counts from each side for a total (average) background.
    d. Calculate net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank, and standard:

$$\hat{I}_x = \frac{N}{I_r^o} \cdot I_x$$

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and net intensities should be normalized to the most recently measured reference intensity.

14. Remove the PVC filter from the XRD holder, fold the filter carefully and place it in a platinum crucible in the furnace. Raise the temperature of the furnace slowly (ca. 50 °C/min) to 500 °C to ash the filter. When ashing is completed (ca. 0.5 h), raise the temperature to 1500 °C and maintain at 1500 °C for 2 h (for fumed amorphous silica) or to 1100 °C and maintain at 1100 °C for 6 h (for other amorphous silicas). Turn the furnace off and let the crucibles cool overnight in the furnace.
15. Place ca. 10 mg NaCl in the crucible and mix with the ash in the crucible. Transfer contents of the crucible to an agate mortar and grind to a fine powder using an agate pestle. Add distilled water from a polyethylene squeeze bottle to the mortar. Use a rubber policeman to stir. When the NaCl is dissolved, transfer the solution to a 100-mL beaker (hold the rubber policeman at the edge of the mortar to guide the flow into the beaker). Rinse mortar, pestle, crucible, and rubber policeman, collecting rinsings in the beaker. Cover the beaker with a watchglass and place in an ultrasonic bath for 2 to 3 min.
    NOTE 1: Use extreme care to avoid air currents when working with the dry sample, as it is easily lost in the form of an aerosol.
    NOTE 2: Use uniform grinding techniques to produce similar particle size in standards and samples.
16. Wash the underside of the watchglass and collect rinsings in the beaker. Place a silver membrane filter in the filtration apparatus and filter the contents of the beaker (step 5).
17. Mount the silver membrane filters in the XRD instrument and:
    a. Analyze for the three silica polymorphs (step 13); and
    b. Determine the net intensity, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure.
        NOTE: Scan times should be shorter for the silver peak (e.g., about 5% of scan times for analyte peaks) and consistent throughout the method.

CALCULATIONS:

18. Calculate normalized intensities for the cristobalite peak on the PVC filter before heating, $\hat{I}_x$ (step 13); the cristobalite peak on the Ag filter, $\hat{I}'_x$ (step 17.a.); the silver peak on the Ag filter, $\hat{I}_{Ag}$ (step 17.b.); and the average silver peak on six media blank Ag filters, $\hat{I}_{\bar{A}g}$ (step 11).
19. Calculate the transmittance of each sample: $T = \hat{I}_{Ag}/\hat{I}_{\bar{A}g}$.
20. Calculate the matrix absorption correction factor for each sample, $f(T) = -R\ln T/(1-T^R)$, where $R = \sin(\Theta_{Ag})/\sin(\Theta_x)$ (or use Table 1).
21. Calculate the concentration of amorphous silica, C (mg/m^3), in the air sample as the difference in cristobalite concentrations measured before and after heat treatment using the slope, m, and intercept, b, of the calibration graph and the air volume sampled, V (L):

$$C = \frac{[(\hat{I}_x - b)/m]\, f(T) - [(\hat{I}_x - b)/m] \cdot 10^3}{V}, \ mg/m^3.$$

NOTE: Compute the applicable OSHA standard using the formulae on page 7501-1 and the % crystalline silica found in the air sample before heat treatment.

EVALUATION OF METHOD:

This method is based on NIOSH P&CAM 316 [3,4] which was further evaluated with field samples in July, 1982 [1]. The relative standard deviation was determined to be related to the type of amorphous silica; gelled, fumed, and precipitated amorphous silica yielded 4.4%, 8.2%, and 4.7%, respectively, over

the range of 0.5 to 5 mg. The method was further evaluated using 11 different types of gelled, precipitated, and fumed amorphous silicas and diatomaceous earth [5], with the following conclusions:

1. Not all fumed silicas converted to cristobalite at 1100 °C. A higher temperature (1500 °C) was needed to convert all the fumed silicas to cristobalite.
2. The moisture content of the gelled and precipitated silicas was ca. 7%; of diatomaceous earth, ca. 4%; and of fumed, from 0.5 to 3%.
3. The calibration curves from the four different types of amorphous silicas indicated very similar slopes (S_r = ± 6.6%).
4. Comparing the four slopes to a slope of a pure respirable cristobalite material, they were running approximately 30% lower in slope value. Therefore, field samples of amorphous silicas must be compared only to standards prepared from amorphous silicas.
5. Precision studies at 0.2-, 1-, and 2.5-mg levels (six samples per level) of gelled, precipitated, diatomaceous earth, and fumed silicas indicated a pooled precision, $\bar{S}_r$, of 8.8, 10.5, 5.6, and 21.5%, respectively, for the above silicas.
6. Recovery studies of the same silicas and concentration levels indicated average recoveries of 82, 115, 95, and 111%, respectively, with pooled $\bar{S}_r$ equal to 18.2, 13.1, 12.9, and 15.3%, respectively, for the gelled, precipitated, and fumed silicas, and diatomaceous earth.

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METHOD REVISED BY:

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TABLE 1. CAS Numbers, RTECS Numbers, and Exposure Limits for Amorphorous Silica Forms

Amorphous Forms	CAS#	RTECS	OSHA PEL (mg/m^3)	NIOSH REL (mg/m^3)	ACGIH TLV (mg/m^3)
diatomaceous earth, <1% crystalline SiO_2	61790-53-2	HL8600000	80/% SiO_2	6	10 (total)
precipitated, and gel	7699-41-4, 112926-00-8	VV8850000	80/% SiO_2	6	10 (total)
fumed	112945-52-5	VV7310000	80/% SiO_2	--	2 (respir)

Table 2. Matrix Absorption Correction Factors for Cristobalite (Heat-Converted Amorphous Silica) and Silver Peaks.

	Degrees 2-Θ					
Cristobalite		21.93	21.93		21.93	21.93
Silver		38.12	44.28		38.12	44.28
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2806	1.3278
	0.99	1.0087	1.0100	0.73	1.2944	1.3440
	0.98	1.0174	1.0201	0.72	1.3084	1.3605
	0.97	1.0264	1.0305	0.71	1.3226	1.3774
	0.96	1.0355	1.0410	0.70	1.3372	1.3946
	0.95	1.0447	1.0517	0.69	1.3521	1.4122
	0.94	1.0541	1.0625	0.68	1.3673	1.4303
	0.93	1.0636	1.0736	0.67	1.3829	1.4487
	0.92	1.0733	1.0849	0.66	1.3987	1.4675
	0.91	1.0831	1.0963	0.65	1.4150	1.4868
	0.90	1.0932	1.1080	0.64	1.4316	1.5064
	0.89	1.1034	1.1199	0.63	1.4485	1.5266
	0.88	1.1137	1.1320	0.62	1.4659	1.5472
	0.87	1.1243	1.1443	0.61	1.4836	1.5684
	0.86	1.1350	1.1568	0.60	1.5018	1.5900
	0.85	1.1460	1.1696	0.59	1.5204	1.6122
	0.84	1.1571	1.1827	0.58	1.5394	1.6349
	0.83	1.1685	1.1959	0.57	1.5590	1.6582
	0.82	1.1800	1.2095	0.56	1.5790	1.6820
	0.81	1.1918	1.2232	0.55	1.5995	1.7065
	0.80	1.2038	1.2373	0.54	1.6205	1.7317
	0.79	1.2160	1.2516	0.53	1.6421	1.7575
	0.78	1.2284	1.2663	0.52	1.6642	1.7840
	0.77	1.2411	1.2812	0.51	1.6870	1.8112
	0.76	1.2540	1.2964	0.50	1.7103	1.8391
	0.75	1.2672	1.3199			

SILICA, CRYSTALLINE in coal mine dust, by IR 7603

SiO_2 MW: 60.08 CAS: 14808-60-7 RTECS: VV7330000

METHOD: 7603, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

quartz (respirable):
OSHA : 10 mg/m^3/(%SiO_2 + 2)
NIOSH: 0.05 mg/m^3 (suspect carcinogen)
ACGIH: 0.1 mg/m^3

PROPERTIES: solid; crystalline transformations: quartz to tridymite @ 867 °C: tridymite to crystobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + PREWEIGHED FILTER (10-mm cyclone, nylon, or Higgins-Dewell (HD), and PVC filter, 37-mm, 5-μm)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 300 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required for OSHA standard calculations; area respirable or settled dust

ACCURACY

RANGE STUDIED: 25 to 160 μg/sample [1]
(2 mg quartz/m^3 atmosphere)

BIAS: unknown

OVERALL PRECISION ($\hat{S}_{rT}$): 0.13 to 0.22 (varies with sample loading and matrix)

ACCURACY: ±25.6 to 43.4%

MEASUREMENT

TECHNIQUE: INFRARED SPECTROPHOTOMETRY (IR)

ANALYTE: quartz

WEIGH: dust cassette

ASH: muffle furnace or RF plasma asher

REDEPOSIT: 0.45-μm acrylic copolymer membrane filter

IR: scan, 1000 to 650 cm^{-1}, absorbance mode with blank filter in reference beam

CALIBRATION: standard suspension of quartz in 2-propanol

RANGE: 30 to 250 μg quartz per sample [1]

ESTIMATED LOD: 10 μg quartz per sample [1]

PRECISION ($\bar{S}_r$): 0.05 to 0.10 (varies with sample matrix) @ 100 to 500 μg per sample [1,2]

APPLICABILITY: The working range is 0.03 to 2 mg/m^3 for a 1000-L sample. The method was specifically developed for respirable coal mine dust samples [2].

INTERFERENCES: Calcite is used as a dusting agent in coal mines and interferences by reacting with quartz during muffle furnace treatment resulting in low quartz assay. Kaolinite is sometimes present in coal dust and interferes by absorbing radiation at the quartz analytical wavelength of 800 cm^{-1}. These interferences are corrected by procedures given in this method. Muscovite does not interfere. Cristobalite and tridymite have absorbance peaks at 800 cm^{-1}. Cristobalite and tridymite have not been detected in coal mine dust.

OTHER METHODS: This method was based on an unpublished Bureau of Mines method that was collaboratively tested [1]. Quartz can also be determined by NIOSH Methods 7500 (XRD), 7602 (IR), and 7601 (UV-VIS) and MSHA Method P7 [3].

REAGENTS:

1. Quartz (SRM 1878, available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards Technology, Gaithersburg, MD 20899).
2. 2-Propanol, reagent grade.
3. Calibration stock solution, 15 μg/mL. Suspend 7.5 mg of quartz in 2-propanol in a 500-mL volumetric flask and dilute the suspension to the mark with 2-propanol (See CALIBRATION AND QUALITY CONTROL).
4. Kaolinite (Hydrite UF from Georgia Kaolin), for standard samples, 100 μg/mL. Suspend 50 mg of dried kaolinite in a 500-mL volumetric flask with 2-propanol and dilute the suspension to the mark with 2-propanol.
   NOTE: This is not required if muffle furnace is used to ash samples (see step 5).
5. Hydrochloric acid solution. 25% v/v conc. HCl in distilled water. Required if calcite is present and samples are ashed with a muffle furnace.
6. Dessicant (Drierite).
7. Oxygen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area air sampler: PVC membrane filter, 37-mm, 5-μm pore size in two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps for: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Filters for standards and redeposition, 47-mm diameter, 0.45-μm pore size, vinyl chloride-acrylonitrile copolymer membrane (DM-450 Gelman Sciences, or equivalent).
5. Glass fiber filters, 25-mm diameter, for backup during filtration.
6. Filtration apparatus for redepositing sample after ashing, consisting of fritted support (Millipore XX1002502), side-arm vacuum flask and special funnel similar to Millipore XX1002514 but with an internal diameter of 1.0 cm. The funnel is glass with a bakelite base and should seal to the fritted support to make the fit liquid-tight.**
7. Funnel for treating filters to remove calcite (required only if using a muffle furnace): Millipore XX1002514 with apparatus in item 5 above except with funnel internal diameter ca. 1.6 cm; 0.5-μm pore size PVC filters, 37-mm diameter to recollect residue.**
8. Double-beam infrared spectrophotometer, with sample holders for infrared instrument: metal (preferably steel) plates with a center hole to match the diameter of the sample deposit (1 cm), and small ring magnets to hold the filter in position on the plate.
9. Low-temperature radio frequency asher (LTA) or muffle furnace (600 °C).
10. Ultrasonic bath.
11. Porcelain crucibles with covers, 10-mL.**
12. Beakers, 50-mL.**
13. Analytical balance, 0.01-mg; dessicator cabinet.
14. Magnetic stirrer with thermally insulated top, and stirring bars.

EQUIPMENT: - cont.

15. Reagent bottles with ground glass stoppers, 500-mL, and volumetric flasks, 500-mL.**
16. Tweezers.
17. Petri dishes, plastic, for 47-mm diameter filters.
18. Polyethylene wash bottles; metal spatulas.
19. Serological pipets, various sizes as required.
20. Lighted viewing box (optional).

** Glassware should be detergent-washed, rinsed thoroughly with distilled or deionized water, and then with 2-propanol, and dried in a dust-free area.

SPECIAL PRECAUTIONS: Avoid inhaling quartz dust [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Preweigh each filter to the nearest 0.01 mg.
3. Sample at 1.7 ± 5% L/min with nylon cyclone or 2.2 ± 5% L/min with HD cyclone for a total sample volume of 300 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

4. Reweigh the filters under conditions identical to those before preweighing. The difference is the sample weight, W_s (μg).
5. Ash sample and blank filters by one of the following methods:
   a. **Low-temperature ashing.**
      Using forceps, transfer filter to a 50-mL beaker. Ash 2 h at 300 watts RF power and oxygen flow rate of 75 mL/min following techniques recommended in the instrument manual. After ashing, add 15 mL 2-propanol to each beaker.
   b. **Muffle furnace ashing.**
      (1) If the samples contain calcite in concentrations greater than 20% of the total dust loading, wash the filters with acid using the filtration apparatus with the 1.6-cm ID glass funnel. Place a 25-mm glass fiber filter over the frit area, then place a 0.5-μm, 37-mm PVC filter over the glass fiber filter. Clamp down the filter funnel. Add 5 mL 2-propanol and check for leakage. Remove the sample filter from the cassette. Fold it in half with the collection surface inside, then in quarters. Place the folded filter into the funnel. If necessary, push the filter to the bottom half of the funnel with a glass rod. Add 10 mL HCl solution, then 5 mL 2-propanol. Apply suction and continue until all of the liquid has been removed. Press the folded sample filter onto the surface of the collecting filter if necessary to remove all the liquid. Remove both filters and place in a porcelain crucible. Allow filters to air-dry.
      (2) If acid wash was not required, transfer filter samples and blanks to porcelain crucibles.
      (3) Loosely cover the crucibles and place in a muffle furnace. Hold for 2 h at 600 °C. After ashing, add several mL 2-propanol to the ash, scrape the crucible to loosen all particles and transfer to a 50-mL beaker. Wash the crucible several times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to ca. 15 mL.

6. Redeposit the sample residue as follows using the filtration apparatus with the 1.0-cm funnel. With a slight vacuum applied, place a 25-mm glass fiber filter on the fritted base. Cut a 47-mm DM-450 filter in half. Superimpose one half over the other, glossy sides down, and place on the glass fiber filter. (The lower half of the DM-450 filter serves as a blank and is used in the reference beam of the infrared spectrometer). Position filter funnel, apply clamp and turn off vacuum. Add several mL 2-propanol to the funnel. Check that the funnel is securely and uniformly clamped. Place sample beakers into ultrasonic bath for at least 30 sec to ensure homogeneous dispersion. Remove a beaker, wipe excess water from the outside, transfer slurry to the filtration funnel and reapply vacuum. During filtration, rinse the beaker twice with 2-propanol to remove all dust and add rinsings to funnel. Control the filtration rate to keep the liquid near the funnel top during rinsing to avoid disturbing the deposit. When the depth of liquid in the funnel reaches ca. 4 cm above the filter, gently rinse the inside of funnel with 2-propanol and complete filtration. Remove the clamp and lift off the funnel, taking care not to disturb and deposit. Release the vacuum. Define the deposit area by marking around the circumference using a pencil or scriber. This is especially important for standards or light-colored samples. Place the DM-450 filter halves in petri dishes and allow to air-dry.

CALIBRATION AND QUALITY CONTROL:

7. Prepare and analyze standard quartz filters.
   a. Place the flask containing the calibration stock solution in an ultrasonic bath for 30 to 45 min.
   b. Move the flask to a magnetic stirrer and stir slowly while the flask cools to room temperature. Continue to stir slowly while preparing standards.
   c. Mount a DM-450 filter in the filtration apparatus in the same manner used to redeposit the samples. Add 5 mL 2-propanol to the funnel. Withdraw an aliquot of the quartz suspension from the center of the flask. Draw liquid to the mark but do not attempt to adjust volume by draining pipet. Carefully wipe the outside of the pipet, then drain the suspension into the filter funnel. Rinse down the inside wall of the pipet with a few mL of 2-propanol, draining the washings into the filter funnel. Apply vacuum to complete the filtration. Prepare quartz standards to cover the range 10 to 250 μg per filter.
   d. Carry an additional set of these standards and media blanks through steps 5 and 6 to monitor for contamination and losses.

   NOTE: Accuracy depends on obtaining uniform deposition of samples and standards across the filter surface and obtaining reproducible aliquots from the quartz suspension. This requires some skill. The quartz calibration curve should be prepared before analyzing samples as a check on the analyst's ability to prepare uniform deposits. Repeatability should be <10% on replicate standards with more than 40 μg quartz.
8. Perform an IR scan for each standard filter using the other half of the filter in the reference beam (steps 10 through 12). Construct a calibration graph (absorbance at 800 cm^{-1} vs. μg quartz per filter). This graph should be linear and pass through the origin.
9. (Only for samples ashed in LTA). Prepare suspensions of at least 5 kaolinite standards in the range 100 to 600 μg per filter. Perform an IR scan of the kaolinite standards from 1000 to 650 cm^{-1}. Draw baselines as described in step 12 and measure the height of the absorbance bands at both 915 and 800 cm^{-1}. Prepare a graph with absorbance at 915 cm^{-1} as ordinate vs. absorbance at 800 cm^{-1} as abscissa. Plot a point for each standard. If possible, generate the correction curve data on the same day that coal mine dust samples are analyzed since curve parameters may vary somewhat from day to day. A curve through the points should be linear but will not pass through the origin since the peak at 915 cm^{-1} is more intense than the peak at 800 cm^{-1} and small amounts of kaolinite do not interfere with the quartz analysis.

   NOTE: Kaolinite correction calibration curve is required when samples are ashed in an LTA since kaolinite is not destroyed under these circumstances and has as interfering peak at 800 cm^{-1} for which a correction must be performed.

MEASUREMENT:

10. Set appropriate instrument conditions for quantitative analysis.
11. Place the dry DM-450 filter-half containing the dust deposit on a holder. Center the deposit over the hole in the holder and secure the filter with a magnet. (A lighted viewing box facilitates this procedure). Insert the sample into the beam of the spectrophotometer. Place the other half of the DM-450 filter on another holder, secure with a magnet and insert it into the reference beam.
    NOTE: For the best precision, the reference filter should be half of the same DM-450 filter which contains the redeposit. However, for routine analysis, the same 2-propanol-treated blank can be used for all filters with the same lot number.
12. Run an infrared scan, in linear absorbance mode from 1000 to 650 cm^{-1}. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from ca. 820 to 670 cm^{-1}. Measure and record the absorbance at 800 cm^{-1}, baseline to maximum. If the sample was ashed in an LTA, the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw a baseline under this band from ca. 960^{-1} to 860 cm^{-1}. Measure and record the absorbance at 915 cm^{-1}, baseline to maximum.
13. Analyze blanks. Check results for contamination.

CALCULATIONS:

14. Correct for kaolinite, if required. Using the sample absorbance at 915 cm^{-1}, refer to the kaolinite curve to find the absorbance at 800 cm^{-1} due to kaolinite. Subtract this amount from the sample absorbance at 800 cm^{-1}. Use this corrected value to calculate μg quartz in the sample.
15. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} determined in step 12. Determine the weight of quartz, W_q (μg), from the quartz standard curve. Since the deposition area for samples and standards is the same, it is not necessary to correct for area.
16. Calculate the percent quartz by dividing the weight of quartz, W_q (μg), by the total sample weight, W_s (μg).

$$\% \text{ quartz} = \frac{W_q}{W_s} \cdot 100.$$

EVALUATION OF METHOD:

This method is based on a previously unpublished Bureau of Mines method which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher, amount of calcite or kaolinite on the sample, ashing time, pH of solvent to remove calcite, shipment of samples and others. None of these factors was found to have an effect. Results obtained by this method are equivalent to those obtained by Method 7500. A collaborative study of the ruggedized method was performed with 15 laboratories participating [2]. The total errors and interlaboratory and intralaboratory errors were found to be dependent on the types of samples. For samples collected from laboratory-generated aerosols, using a set of matched-flow orifices, the lower and upper limits of the relative standard deviation over the range 60 to 150 μg quartz were:

	Lower	Upper
Total error (RSD)	0.13	0.22
Intralaboratory error	0.07	0.10
Interlaboratory error	0.08	0.14

The lower limit applies to samples containing up to 1 mg coal mine dust with less than 2% kaolinite; the upper limit was found for samples with 2 mg coal mine dust or a lower amount of coal mine dust with more than a few percent kaolinite. The total error increased to 0.36 to 0.40 (lower and upper range) when personal sampling pumps were used to collect the samples. The pump error increased the

interlaboratory error. Precision for pure quartz samples is ca. 0.05 in the 100 to 500 μg range [3]. Precision for actual samples is not as good and depends on sample size and ashing technique.

This method is particle size dependent. The particle sizes of the standards and samples should be matched as closely as possible to prevent a bias in the results, which is not correctable with this method. A thorough study of the range of biases has not been done for IR methods.

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[1] Anderson, C. C. Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-124 (1983).

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[3] Infrared Determination of Quartz in Respirable Coal Mine Dust. Mine Safety and Health Administration, Method No. P7, Pittsburgh, PA (1984).

[4] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).

METHOD REVISED BY:

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SILICA, CRYSTALLINE, by XRD 7500

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
14464-46-1 (cristobalite) VV7325000 (cristobalite)
15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7500 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : quartz (respirable) 10 mg/m³/(%SiO_2+2); cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m³; carcinogen
ACGIH: quartz (respirable) 0.1 mg/m³
cristobalite (respirable) 0.05 mg/m³
tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING		MEASUREMENT	
SAMPLER:	CYCLONE + FILTER (10-mm nylon cyclone, or Higgins-Dewell (HD) cyclone + 5-μm PVC membrane	**TECHNIQUE:**	X-RAY POWDER DIFFRACTION
FLOW RATE:	nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min	**ANALYTE:**	crystalline SiO_2
VOL-MIN:	400 L	**ASH:**	muffle furnace or RF plasma asher or dissolve in tetrahydrofuran
-MAX:	1000 L	**REDEPOSIT:**	on 0.45-μm Ag membrane filter
SHIPMENT:	routine	**XRD:**	Cu target X-ray tube, graphite monochromator Optimize for intensity; 1° slit Slow step scan, 0.02°/10 sec Integrated intensity with background subtraction
SAMPLE STABILITY:	stable		
BLANKS:	10% of samples	**CALIBRATION:**	suspensions of silica in 2-propanol
		RANGE:	0.02 to 2 mg SiO_2 per sample [2]
ACCURACY		**ESTIMATED LOD:**	0.005 mg SiO_2 per sample [2]
RANGE STUDIED:	25 to 2500 μg/m³ [1] (800-L sample)	**PRECISION ($\hat{S}_r$):**	0.08 @ 0.05 to 0.2 mg per sample [1]
BIAS:	none known		
OVERALL PRECISION ($\hat{S}_{rT}$):	0.09 (50 to 200 μg) [1]		
ACCURACY:	± 18%		

APPLICABILITY: The working range is 0.025 to 2.5 mg/m³ for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is similar to the method in the Criteria Document [3] and P&CAM 259 [4] which has been collaboratively tested [2]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. Colorimetry [10] is an alternate measurement procedure (used in Method 7601), as is IR spectrometry (Methods 7602 and 7603).

REAGENTS:

1. Silica Standards.
   a. Quartz* (SRMs 1878 and 2679) and Cristobalite* (SRM 1879), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.
   b. Tridymite*, available from NIOSH, DPSE, MRB, 4676 Columbia Pkwy., Cincinnati, OH 45226.
2. 2-Propanol, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. Optional (if calcite present): 25% v/v concentrated hydrochloric acid (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 μm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-μm pore size supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
      NOTE: Gelman VM-1 filters are unacceptable because of high ash and background. If THF is used, check for complete dissolution by dissolving a blank PVC filter and following through steps 5c-8.
   b. Cyclone: 10-mm nylon cyclone, or Higgins-Dewell (HD) cyclone, or equivalent.
2. Sampling pumps: nylon cyclone, 1.7 L/min; cyclone, 2.2 L/min; and bulk sampler, 3 L/min.; with flexible connecting tubing.
3. Area air sampler: PVC membrane filter, 37-mm diameter, 5-μm pore size; three-piece filter cassette; with high-volume pump, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-μm pore size.
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone, or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher or muffle furnace, or ultrasonic bath ($\geq$150 W), for filter preparation.
8. Vacuum filtration assembly and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-μm. for wet sieving.
10. Analytical balance (0.001 mg); magnetic stirrer with thermally insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); 40-mL wide-mouth or 50-mL centrifuge tubes (THF method); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3]. THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with nylon cyclone or 2.2 ± 5% L/min with HR cyclone for a total sample size of 400 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
3. Take an area air sample or collect a settled dust sample.

SAMPLE PREPARATION:

4. Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust exposure. Wet sieve with a 10-μm sieve, 2-propanol, and an ultrasonic bath [11], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a desiccator. Deposit the end product on a filter (steps 7-8) or pack in a conventional XRD powder holder.
   NOTE 1: For quantitative determination of % SiO_2, weigh out, in triplicate, 2 mg sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.
   NOTE 2: In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be carefully treated in hot phosphoric acid [12] to dissolve the interfering compound(s) and avoid the loss of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD.
5. Use one of the following methods to prepare filter samples and blanks:
   a. **Low Temperature Ashing:** Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or
   b. **Muffle Furnace Ashing:**
      1. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of $CaSiO_3$. Remove the calcite by the following procedure: Place a 0.5-μm, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold, and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and 5 mL 2-propanol to the filter funnel and allow to sit for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
      2. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or
   c. **Filter Dissolution:** Using forceps and a spatula, remove the filter from the cassette, fold the filter three times, and place in the bottom of a 40- or 50-mL centrifuge tube. Add 10 mL THF and allow to stand for at least 5 min. Cap the centrifuge tube with aluminum foil to prevent contamination. Gently agitate the centrifuge tube by hand or with a vortex mixer making sure the THF does not go near the top of the tube. Place the tube in an ultrasonic bath (water level 2.5 cm from top) for at least 10 min. (The filter should be totally dissolved.) Just prior to filtering, agitate the sample for 10 to 20 sec on a vortex mixer. Continue with step 6, substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.

7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
8. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze standard filters.
   a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.
   b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally insulated top and add a stirring bar. Cool to room temperature before withdrawing aliquots.
   c. Mount a silver filter on the filtration apparatus. Place several mL 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several times.
   e. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Transfer the silver filter to the diffractometer sample mount. Prepare working standard filters, in triplicate, at e.g., 20, 30, 50, 100, 200, and 500 μg.
   f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x° and are then normalized (step 12.e) to obtain $\hat{I}_x^\circ$. Correct the intensities of working standards >200 μg for matrix absorption (steps 12.f and 13).
   g. Prepare a calibration graph ($\hat{I}_x^\circ$, vs μg of each standard).
      NOTE: Poor repeatability (>10% above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.
   h. Determine the slope, m, of the calibration graph in counts/μg. The intercept, b, on the abscissa should be within $\pm$ 5 μg of zero.
      NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.
10. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry, and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2θ) of the area air sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The expected diffraction peaks are:

	Peak (2-Theta Degrees)		
Mineral	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

12. Perform the following for each sample, working standard, and blank filter:
    a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (S_r <0.01) measured.
    b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N.$$

    NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.
    f. Determine the normalized count, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Scan each field blank over the same 2-Θ range used for the analyte and silver peaks to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

13. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(t) - b}{m \cdot V}, \text{ mg/m}^3$$

$\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration graph ($\hat{I}_x^\circ$ vs. W)
m = slope of calibration graph, counts/μg

$f(t) = -R \ln T/(1 - T^R)$ = absorption correction factor (Table 1)
$R = \sin(\Theta_{Ag})/\sin(\Theta_x)$
$T = \hat{I}_{Ag}/(\text{average } \hat{I}^{\circ}_{Ag})$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}^{\circ}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and sonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [10] and when all standards and samples were Min-U-Sil 5. The relative standard deviations for intralaboratory, total measurement and overall (including sampling) variability are:

Measurement Precision, S_r:

Intralaboratory:	50 to 200 μg -- 0.08 [1]
	20 μg -- 0.20 [5]
	10 μg -- 0.28 [9]
Total (intra-and interlaboratory):	50 to 200 μg -- 0.17 [1]
Overall (Sampling & Measurement) Precision, S_r:	
Total (intra- and interlaboratory):	50 to 200 μg -- 0.29 [1]

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METHOD REVISED BY:

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APPENDIX: INTERFERENCES

Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide.

The patterns for three forms of aluminum phosphate [JCPDS 10-423, 11-500, 20-44] are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-William [17] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations [13-18].

		f(T) (at indicated degrees 2-θ)							
Transmittance	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
1.00		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99		1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98		1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97		1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96		1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95		1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94		1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0635
0.93		1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92		1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91		1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90		1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89		1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88		1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87		1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86		1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85		1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84		1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83		1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82		1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81		1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80		1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79		1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78		1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77		1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76		1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75		1.2175	1.2535	1.2822	1.3297	1.2672	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3456	1.2806	1.3278	1.2849	1.3328
0.73		1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72		1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71		1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70		1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69		1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68		1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67		1.3103	1.3682	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66		1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65		1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64		1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63		1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62		1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61		1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60		1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995
0.59		1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58		1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57		1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56		1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55		1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54		1.4991	1.6858	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53		1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52		1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51		1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50		1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531

SILICA, CRYSTALLINE by VIS

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
14464-46-1 (cristobalite) VV7325000 (cristobalite)
15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7601, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : quartz (respirable) 10 mg/m^3/(%SiO_2+2); cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m^3; carcinogens
ACGIH: quartz (respirable) 0.1 mg/m^3
cristobalite (respirable) 0.05 mg/m^3
tridymite (respirable) 0.05 mg/m^3

PROPERTIES: solid; Crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm cyclone, nylon or Higgins-Dewell (HD) + 0.8-μm MCE or 5-μm PVC)

FLOW RATE: HD cyclone: 2.2 L/min; nylon cyclone: 1.7 L/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none known

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: silicon complexes-silicomolybdate (420 nm) and molybdenum blue (820 nm)

DIGESTION: phosphoric acid, to remove interfering silicon compounds

FILTRATION: to collect undigested material

DISSOLUTION: crystalline silica in HF

CALIBRATION: quartz dissolved in HF

RANGE: silicomolybdate: 0.1 to 2.5 mg SiO_2; molybdenum blue: 0.02 to 0.15 mg SiO_2

ESTIMATED LOD: 10 μg SiO_2

PRECISION ($\bar{S}_r$): 0.09 [1]

APPLICABILITY: Determination of crystalline silica in respirable or total dust, settled dust and in biological samples [1,2]. The three crystalline polymorphs cannot be distinguished by this method. The working range is 0.04 to 5 mg/m^3 for a 500-L air sample.

INTERFERENCES: Any silicon-containing compound which is soluble in HF will give a positive interference. See APPENDIX A.

OTHER METHODS: This is P&CAM 106 in a revised format [1]. X-ray diffraction (XRD; Method 7500) can distinguish the three polymorphs and does not detect amorphous silica. Silicates interfere with XRD but are removed by phosphoric acid cleanup. Infrared spectrometry (IR; Method 7602) can determine the three polymorphs, although if two or more are present, a less sensitive peak must be used; however, amorphous silica and silicates, in large amounts, interfere with IR.

REAGENTS:

1. Quartz* (NIST SRMs # 1878, 2679, or Min-U-Sil 5 (quartz), Pennsylvania Glass Sand Co., Berkley Springs, WV).
2. Hydrofluoric acid, 48% (HF).*
3. Orthophosphoric acid, 85% H_3PO_4.*
4. Silica-free water. All water used must be deionized and stored in polyethylene containers.
5. Hydrochloric acid (HCl),* 1:10 v/v conc. HCl in deionized water.
6. Sulfuric acid, 10 N.* Cautiously add 555 mL conc. H_2SO_4 to about 1.3 L of deionized water. Cool. Dilute to 2 L.
7. Nitric acid, conc.*
8. Perchloric acid, conc. Use only if samples have been collected on PVC filters.
9. Boric acid solution, 5%. 200 g boric acid crystals in 4 L warm deionized water. Cool. Filter with vacuum through a 0.45-μm membrane filter. Store in a polyethylene container.
10. Molybdate reagent. Dissolve 50 g ammonium molybdate tetrahydrate in about 400 mL deionized water. Add 50 mL conc. sulfuric acid. Cool. Dilute to 500 mL. Store in dark.
11. Reducing solution. Dissolve 9 g sodium bisulfite in 80 mL deionized water. In 10 mL deionized water, dissolve 0.7 g anhydrous sodium sulfite and 0.15 g 1-amino-2-naphthol-4-sulfonic acid, in that order. Combine these solutions and dilute to 100 mL with deionized water. Stable about one month if stored in refrigerator.
12. Silica stock standard, 0.5 mg/mL. Dissolve 250 mg quartz in 10 mL 48% HF. Dilute to 500 mL with silica-free water. Store in a polyethylene container. Stable indefinitely.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-μm pore size, or mixed cellulose ester (MCE) filter, 37-mm, 0.8-μm, supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
      NOTE: If PVC filters are used, a perchloric acid fume hood, low-temperature radio-frequency plasma asher or muffle furnace will be needed to ash them (Appendix B).
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area Air Sampler: PVC membrane filter, 37-mm, 5-μm pore size in a two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Precision heater, 550-watt, 115-V, Type RH; 750-watt variable transformer with built-in voltmeter; variable speed rotator, about 30 to 80 rpm range (can be achieved with a variable transformer).
5. Stopwatch or laboratory timer.
6. Phillips beakers, borosilicate glass, 250-mL; short-stemmed glass funnels with bent stems (must be done by laboratory); crucible tongs with tygon or rubber-padded tips; polyethylene stirring rods; polyethylene 50-mm discs.
7. Vacuum filtration assembly: MCE membrane filters, 0.45-μm pore size, 47-mm diameter; filter funnel, including membrane mount and flask assembly, 47-mm.
8. Buret, polypropylene, 10-mL; polyethylene reagent bottles for water, boric acid, and standard solutions.
9. Constant temperature bath, 40 °C.
10. Spectrophotometer, at 420 to 820 nm and 1-cm cuvettes.
11. Hotplate, 150 °C surface temperature.
12. Graduated cylinder or graduated pipet, 10- and 25-mL.
13. Polyethylene graduated cylinder or pipets, 25- and 5-mL.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3].

Use personal protective equipment to prevent contact of acids with the skin. HF dissolves glass. Use plastic labware for all solutions containing HF. Concentrated acids are corrosive.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 2.2 ± 5% L/min with HD cyclone and 1.7 ± 5% L/min with nylon cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

NOTE: Successful use of this method depends on close attention to details and uniformity in sample handling procedures.

3. Place a weighed sample containing no more than 2.5 mg SiO_2, or a membrane filter sample, in a 250-mL Phillips beaker. Add 3 to 4 mL conc. HNO_3 to ash membrane filters. Heat on a hotplate to absence of brown fumes.
4. Add an additional 2 mL conc. HNO_3 and heat to dryness. Repeat this step until any remaining residue is white.
   NOTE: Ash PVC filters using 2 mL conc. $HClO_4$. Heat slowly until the filter shrinks, turns brown and is dissolved. Add additional portions of $HClO_4$ if necessary. If a perchloric acid hood is not available, see APPENDIX B for alternate ashing procedures for PVC filters. Pretreatment procedures to remove various contaminants from bulk samples are outlined in reference [4].
5. Add 25 mL 85% H_3PO_4 to the beaker. Cover the beaker with a bent-stem funnel. Make sure that the tip of the funnel stem touches the wall of the flask. Start reagent blanks at this time.
   NOTE: The bent-stem funnel is used to prevent too rapid dehydration of the sample and to prevent spattering.
6. Place the 550-watt heater on the rotator in a fume hood. Preheat the heater and adjust to maintain a temperature of 240 °C. Heat each sample and blank for exactly 8 min, swirling it by the action of the variable speed rotator.
   NOTE: The solution in the flask should reach 240 °C during this procedure.
7. Remove the beaker from the heater with padded tongs and swirl it for 1 min. Allow the beaker to cool. Add about 125 mL warm (60 to 70 °C) deionized water and swirl to mix completely.
8. Filter the sample with suction through a 47-mm filter. Wash thoroughly with 1:10 HCl.
9. Place the 47-mm filter in the bottom of a 150-mL polyethylene beaker. Add 0.5 mL 48% HF to the filter surface. Float a thin polyethylene disc of about 50-mm diameter over the 47-mm filter and cover the beaker. Allow to stand for 30 min.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a calibration graph for the silico-molybdate range.
    a. Dilute 1-, 2-, 3-, 4-, 5- and 6-mL aliquots of the silica stock standard to 25 mL with silica-free water in polyethylene beakers.
    b. Analyze together with samples and blanks (steps 14 through 16).
    c. Plot absorbance vs. mg SiO_2.

11. Prepare a calibration graph in the molybdenum blue range.
    a. Dilute the working standards in step 10 1:25.
    b. Analyze the resulting standard solutions (steps 14 through 16).
    c. Plot absorbance vs. mg SiO_2.
12. Prepare control samples containing a silicate compound (about 50 mg $MgSiO_4$ sample) in addition to the quartz. Recovery of quartz is low and precision is much worse if quartz only is present during the phosphoric acid treatment.

MEASUREMENT:

13. Add 25 mL silica-free water to samples in polyethylene beakers.
14. Add 50 mL boric acid solution. Stir well. Cover. Heat the solution in a 40 °C waterbath for 10 min.
15. Add 4 mL molybdate reagent while stirring, staggering the addition at 2-min intervals between samples. Exactly 20 min after the addition of the molybdate reagent, add 20 mL 10 N H_2SO_4 and stir thoroughly.
16. Note the color of the solution.
    a. If any yellow persists, read within 2 min after acidification in a spectrophotometer at 420 nm against deionized water.
    b. If a colorless solution results, allow it to stand for 2 to 5 min and add 1 mL 1-amino-2-naphthol-4-sulfonic acid reagent. Mix and read after 20 min at 820 nm against deionized water. This color is stable for several hours.
    c. Record the absorbances of the sample, A, and reagent blank, B.

CALCULATIONS:

17. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L), using the slope, m (μg^{-1}) of the appropriate calibration graph:

$$C = \frac{(A - B)}{m \cdot V}.$$

EVALUATION OF METHOD:

This method is based on the well-characterized Talvitie method [1,5,6].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 106, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Sweet, D. V., F. R. Wolowicz, and J. V. Crable. Spectrophotometric Determination of Free Silica, Am. Ind. Hyg. Assoc. J., 34, 500-506 (1973).
[3] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).
[4] Talvitie, N. A. and Frances Hyslop. Colorimetric Determination of Siliceous Atmospheric Contaminants, Am. Ind. Hyg. Assoc. J., 19(1), 54-58 (1958).
[5] Talvitie, N. A. Determination of Free Silica: Gravimetric and Spectrophotometric Procedures Applicable to Airborne and Settled Dust, Am. Ind. Hyg. Assoc. J., 25, 169-178 (1964).
[6] Talvitie, N. A. Determination of Quartz in Presence of Silicates Using Phosphoric Acid, Anal. Chem., 23(4), 623-626 (1951).

METHOD WRITTEN BY:

Jensen Groff, NIOSH/DPSE, and Doris Sweet, NIOSH/DSDTT.

APPENDIX A:

INTERFERENCES

Some silicates may be resistant to phosphoric acid digestion [6]. Any silicates not removed by the phosphoric acid treatment will give a positive interference. Amorphous silica, if not completely removed by phosphoric acid treatment, will give a positive interference. Phosphate ion complexes molybdic acid to produce a yellow phosphomolybdate color which is dissipated by lowering the pH of the solution with 10 N sulfuric acid. Excess ferric ion (more than 1 mg) will consume the reducing agent and inhibit the reduction of silicomolybdate to molybdenum blue. If more than 1 mg ferric ion is present, it should be removed by pretreatment with 10:1 HCl:HNO_3.

APPENDIX B:

ALTERNATE ASHING PROCEDURES FOR PVC FILTERS

If a perchloric acid fume hood is unavailable, ash PVC filters with one of the following methods.

1. **Muffle furnace ashing:** Wash the filters with 25% v/v HCl if the samples contain a significant amount of calcite (20% of the total dust loading); otherwise, proceed to next paragraph. Place a 0.5-μm, 37-mm PVC filter in the filtration apparatus. Center the sample filter on top of the first filter. Clamp the filter funnel over the frit so that the dust deposit is completely exposed. Add 10 mL HCl solution and 5 mL 2-propanol to the filter funnel; allow to stand for 5 min. Apply vacuum to aspirate the acid/alcohol solution from the filter. Wash with three 10-mL portions of deionized water. Release the vacuum.

   Place the filter samples in porcelain crucibles, cover loosely and ash in a muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL of 2-propanol to the ash, scrape the crucible to loosen all particles and transfer the residue to a 250-mL borosilicate glass Phillips beaker. Wash crucible several times and add wash to the beaker. Heat on a sparkless hotplate to evaporate the 2-propanol. When beaker is dry, proceed with step 4 of sample preparation.

2. **Low temperature ashing:** Place the filters in 50-mL glass beakers within the LTA so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, add 2-propanol to the beaker to transfer the residue to a 250-mL borosilicate Phillips beaker. Wash the beaker with 2-propanol several times, adding the washings to the Phillips beaker. Heat on a sparkless hotplate to remove the 2-propanol. When the beaker is dry, proceed to step 4 of sample preparation.

SILICA, CRYSTALLINE by IR

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
14464-46-1 (cristobalite) VV7325000 (cristobalite)
15468-32-3 (tridymite) VV335000 (tridymite)

METHOD: 7602, Issue 2 **EVALUATION:** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : quartz (respirable): 10 mg/m^3/(% SiO_2 + 2); cristobalite and tridymite (respirable): 1/2 the above
NIOSH: 0.05 mg/m^3; carcinogens
ACGIH: quartz (respirable) 0.1 mg/m^3
cristobalite (respirable) 0.05 mg/m^3

PROPERTIES: solid; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon, or Higgins-Dewell (HD) + 0.8-μm or 5-μm PVC or MCE membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 l/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; area respirable or settled dust

ACCURACY

RANGE STUDIED: not studied

BIAS: unknown

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: INFRARED ABSORPTION SPECTROPHOTOMETRY

ANALYTE: quartz

ASH: muffle furnace or RF plasma asher

PELLET: mix residue with KBr; press 13 mm pellet

IR: scan absorbance from 1000 to 600 cm^{-1}

CALIBRATION: quartz diluted in KBr

RANGE: 10 to 160 μg quartz

ESTIMATED LOD: 5 μg quartz

PRECISION ($\bar{S}_r$): < 0.15 @ 30 μg quartz per sample, in coal dust [1]

APPLICABILITY: The working range is 0.025 to 0.4 mg/m^3 for a 400-L air sample. Cristobalite and tridymite also have major absorbance peaks at 800 cm^{-2} which can be used for their determination [1-6].

INTERFERENCES: Amorphous silica, calcite, cristobalite, kaolinite and tridymite interfere; see APPENDIX.

OTHER METHODS: This is P&CAM 110 [1]. It is similar to Method 7603, except for sample preparation (KBr pellet vs. redeposition). Crystalline silica can also be determined by X-ray diffraction (Method 7500) and spectrophotometry (Method 7601). XRD can distinguish the three polymorphs and does not detect amorphous silica. Silicates, which interfere with XRD, are removed by phosphoric acid cleanup.

REAGENTS:

1. Quartz* (NIST SRMs # 1878 and 2679, Standard Reference Materials Program, Rm 204, Bldg. 202, National Institute of Standards and Technology, Gaithersburg, MD 20899).
2. Potassium bromide (KBr), infrared quality.
3. Ethanol, 95% for cleaning sample handling equipment.*
4. Hydrochloric acid, 9% w/w. Dilute 25 mL conc. HCl (37% w/w) to 100 mL with deionized water.
5. Calibration stock standard, 0.5% w/w. Accurately weigh and thoroughly mix 5 g KBr (dried overnight at 110 °C) with 25 mg quartz. Store in a bottle in a desiccator.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area air sampler: PVC membrane filter, 37-mm, 5-μm pore size in two piece filter cassette. Sample closed-face at 3 L/min.
3. Sampling pumps for HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Infrared spectrophotometer; laboratory press for preparing KBr pellets; 13-mm KBr pellet die (evacuable).
5. Low-temperature (RF Plasma) asher and aluminum weighing pans or muffle furnace and porcelain crucibles.
6. Mortar and pestle, 50 mm agate or mullite metal microspatula; non-serrate, non-magnetic forceps; desiccator, camel's hair brush, glassine paper.
7. Analytical balance (0.01 mg) for preparing standards.
8. Membrane filtration apparatus, 37-mm.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1].

Ethanol is flammable. Keep away from flames.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with nylon cyclone or 2.2 ± 5% with HD cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg total dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

3. Use one of the following methods to ash samples and blanks:
   a. **Low temperature (RF Plasma) asher**: Place the filters in labelled aluminum dishes (previously rinsed with distilled water, followed by ethanol, and air dried). Place the dishes

in the low temperature asher so that sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. Carefully bring asher to atmospheric pressure and remove the dishes.

b. **Muffle furnace**: For samples containing a significant amount of calcite (> 20% of the total dust loading), wash filters with 9% w/w hydrochloric aicd. Other samples proceed to step 3.b.ii.
   i. Place a 0.5-μm, 47-mm PVC filter in the filtration apparatus. Remove sample filter from cassette and center on top of first filter. Clamp funnel over the frit so that dust deposit is completely exposed. Add 10 mL 9% w/w HCl and 5 mL 2-propanol; allow to stand 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Wash with three successive 10-mL portions of distilled water. Release vacuum.
   ii. Place filter samples and blanks in porcelain crucibles, loosely cover, and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present).

4. Add approximately 300 mg KBr, weighed to 0.1 mg and dried overnight at 110 °C, directly to each sample. Mix the sample ash and KBr thoroughly with a pestle. Transfer to mortar to complete mixing if necessary. Transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Press a pellet using standard technique. Weight the finished pellet to 0.1 mg. Calculate the ratio (weight of finished pellet/weight KBr initially added); it is usually about 0.98. Clean sample handling equipment with ethanol between samples.
NOTE: A low relative humidity environment will facilitate sample handling when using KBr.

CALIBRATION AND QUALITY CONTROL:

5. Prepare working standard pellets:
   a. Weigh, to 0.001 mg, portions of calibration stock standard containing 10 to 200 μg quartz.
   b. Add an accurately-weighed 300 mg KBr. Proceed as in step 4.
   c. Calculate the ratio (weight of finished pellet/weight of solids added); usually about 0.98.
   d. Determine the absorbance at 800 cm^{-1} for each standard pellet following the analytical procedure (step 8). Plot absorbances vs. μg SiO_2.
6. If samples were low temperature ashed (step 3.a.) and kaolinite is present, prepare pellets containing 100 to 600 μg kaolinite. Determine the absorbance at 800 cm^{-1} and at 915 cm^{-1} as abscissa. Prepare at least five different kaolinite concentrations. Use this curve to correct the absorbance value at 800 cm^{-1} for any sample containing kaolinite.
7. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures (steps 3 and 4) to monitor for contamination and losses.

MEASUREMENT:

8. Set the infrared spectrophotometer to absorbance mode and to the appropriate settings for quantitative analysis. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1}. Rotate the pellet 45° and scan this diameter. Repeat twice more until 4 scans have been obtained. If the peak at 800 cm^{-1} is small, use 5X ordinate expansion to enhance the peak height. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1}. Measure the absorbance at 800 cm^{-1} from maximum to baseline in absorbance units. Average the four values for each sample.
9. If the sample was ashed at low temperature (step 3.a), the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw an appropriate baseline under this band from approximately 960 to 860 cm^{-1} and measure the absorbance at 915 cm^{-1} from this baseline to the maximum.

CALCULATIONS:

10. Correction for kaolinite. Determine the sample absorbance at 915 cm^{-1} (step 9), refer to the kaolinite curve (step 6) to find the absorbance at 800 cm^{-1}. Use this corrected value in step 11.
11. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} to find the weight of quartz, W_q (μg), from the calibration graph.
12. Calculate the concentration of silica, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{W_q}{V}, \ mg/m^3.$$

13. If percent quartz, % Q, is required, divide the weight of quartz, W_q (μg), by the total sample weight, W_s (μg):

$$\% \ Q = \frac{W_q}{W_s} \cdot 100.$$

EVALUATION OF METHOD:

This method is based on the well-characterized infrared method [1]. This method is particle size dependent. A mismatch of standards and sample particle sizes will result in an uncorrectable bias. A thorough study of the range of biases in IR methods has not been done.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 110, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Talvitie, N.A. Determination of Quartz in the Presence of Silicates Using Phosphoric Acid, Anal. Chem., 23, 623-626 (1951).
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[6] Taylor, D.G., C.M. Nenadic and J.V. Crable. Infrared Spectra for Mineral Identification, Am. Ind. Hyg. Assoc. J., 31, 100-108 (1970).
[7] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

APPENDIX:

INTERFERENCES

Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm^{-1} (quartz) and 625 cm^{-1} (cristobalite). Tridymite can only be determined in the absence of the other two polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [2].

Cristobalite and tridymite interfere positively at the 800 cm^{-1} peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.

SILVER

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

METALS IN URINE (Method 8310)

SODIUM

See ELEMENTS (Method 7300) for procedure

STIBINE

SbH_3 MW: 124.77 CAS: 7803-52-3 RTECS: WJ0700000

METHOD: 6008, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm/10 h
ACGIH: 0.1 ppm
(1 ppm = 5.10 mg/m^3 @ NTP)

PROPERTIES: gas; BP −17 °C; MP −88 °C; VP >1 atm

SYNONYMS: antimony trihydride

SAMPLING

SAMPLER: SOLID SORBENT TUBE ($HgCl_2$-coated silica gel, 1 g/0.5 g)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 4 L
-MAX: 50 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.12 to 1 mg/m^3 [1] (20-L samples)

BIAS: −1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 [1]

ACCURACY: ± 17.0%

MEASUREMENT

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: antimony

EXTRACTION: 15 mL conc. HCl; 30 min

WAVELENGTH: 552 NM

CALIBRATION: standard solutions of Sb(III) in conc. HCl

RANGE: 2 to 20 μg Sb per sample [1]

ESTIMATED LOD: 0.4 μg SbH_3 per sample [1]

PRECISION ($\bar{S}_r$): not defined

APPLICABILITY: The working range is 0.1 to 3.5 mg/m^3 (0.02 to 0.7 ppm) for a 20-L air sample.

INTERFERENCES: Colorimetric determination of Sb is subject to interference by elements which form a Rhodamine B complex extractable into isopropyl ether. Am(III) (>250 μg); Au (>1000 μg); Fe(III) (>30,000 μg); Tl(I) (>1000 μg); and Sn(II) (>1000 μg) interfere [2]. If the possibility of an interference exists, an alternate measurement procedure should be used (e.g., ICP or AAS).

OTHER METHODS: This revises Method S243 [3].

REAGENTS:

1. Water, distilled or deionized.
2. Hydrochloric acid (HCl), conc.*
3. Antimony stock solution, 1000 μg/mL Sb(III).
4. Ceric sulfate, $Ce(SO_4)_2$, solid.
5. Isopropyl ether.
6. Rhodamine B stock solution, 0.2% in water. Dissolve 0.5 g Rhodamine B in 250 mL water. Prepare in duplicate.
7. Working Rhodamine B solution, 0.01% in 0.5 M HCl. Dilute 25 mL Rhodamine B stock solution and 24 mL conc. HCl to 500 mL. Prepare fresh daily.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing two sections of $HgCl_2$-coated silica gel (front = 1.0 g; back = 0.5 g) separated and contained by silylated glass wool. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Visible spectrophotometer capable of measuring absorbance at 552 nm, with two matched 1-cm silica absorbance cells with tight-fitting PTFE caps.*
4. Separatory funnels, 125-mL.*
5. Beakers, Griffin, 50-mL.
6. Volumetric flasks, 25-, 50-, 250-, and 500-mL.
7. Pipets, 4-, 15-, and 20-mL.*
8. Graduated cylinders, 10- and 25-mL.*
9. Centrifuge, with centrifuge tubes, 15-mL, with plastic caps.*

* Clean all glassware with conc. HCl and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all concentrated acid handling in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove sampler caps immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: Use a cellulose ester membrane prefilter if particulate antimony compounds may be present.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 4 to 50 L.
4. Cap the sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front and back sorbent sections of the sampler tube in separate 50-mL beakers. Discard the glass wool.
6. Add 15.0 mL conc. HCl to each beaker.
7. Mildly agitate (swirl) the beaker contents every 10 min for a total desorption time of 30 min. Pour the solution into a 25-mL volumetric flask.
8. Add 4.0 mL conc. HCl to the sorbent in the beaker. Swirl and decant into the volumetric flask from step 7.
9. Repeat step 8. Dilute to volume with conc. HCl and swirl to mix.
   NOTE: Perform steps 10 through 15 within a 15-min period.
10. Pipet 15.0 mL of the sample extract into a separatory funnel.

11. Add 15 ± 5 mg ceric sulfate, swirl to dissolve and let stand unstoppered 60 s.
12. Add 15.0 mL isopropyl ether to the funnel, stopper, and shake 30 s, releasing pressure only at the beginning and end of that period.
13. Add 7.0 mL water, Shake 60 s. Wait 60 s to allow for separation. Remove and discard the aqueous layer. Be careful to remove all of the aqueous layer.
14. Add 20.0 mL working Rhodamine B solution, shake 60 s, releasing pressure only at the beginning and end of that period. Allow 60 s for the phases to separate. Remove and discard aqueous (lower) layer. Drain ca. 10 mL of the remaining solution into a 15-mL centrifuge tube and cap tightly.
15. Centrifuge 120 s at 2000 rpm. Transfer ca. 3 mL of the supernatant liquid to an absorption cell and cap. Proceed immediately to step 18.

CALIBRATION AND QUALITY CONTROL:

16. Calibrate daily with at least six working standards over the range 2 to 20 μg antimony per sample.
    a. Add known amounts of antimony stock solution and conc. HCl to cover the antimony concentration of 2 to 20 μg Sb per 15 mL and a reagent blank.
    b. Proceed as in steps 10 through 15 and 18 and 19.
    c. Prepare a calibration graph (absorbance vs. μg antimony/15 mL).
17. Analyze three quality control spikes to ensure that the calibration graph is in control.

MEASUREMENT:

18. Set the spectrophotometer to manufacturer's recommendations and to conditions given on page 6008-1.
19. Measure the absorbance using isopropyl ether as a blank.

CALCULATIONS:

20. Determine the mass, μg, of stibine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average blank front (B_f) and back (B_b) sorbent sections by multiplying the mass of antimony/15 mL found for each of these sections by 1.708, a combination conversion and dilution factor (MW SbH_3/MW Sb) · (25 mL/15 mL).
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
21. Calculate concentration, C, of stibine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)\ 1.708}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S243 was evaluated over the range 0.119 to 1.01 mg/m^3 using 20-L air samples [1]. Recovery averaged 98.6% in the range 0.12 to 1.0 μg SbH_3 per sample. The capacity of the sampling tubes (at a flow rate of 0.22 L/min, a SbH_3 concentration of 1.326 mg/m^3, and a relative humidity of 85%) was shown to be greater than 70 μg (as SbH_3). Previously, activated charcoal tubes were tried as a collection medium for stibine but were rejected because of poor collection efficiency [4].

REFERENCES:

[1] S243, Backup Data Report for Stibine, prepared under NIOSH Contract No. 210-76-123 (March 18, 1977), available as "Ten NIOSH Analytical Methods, Set 2," Order #PB271-464 from NTIS, Springfield, VA 22161.
[2] Ward, F.N. and H.W. Lakin. Anal. Chem., 26, 1168 (1954).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S243, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Failure Report S243, Stibine, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1977).

METHOD REVISED BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS.

STODDARD SOLVENT

See NAPHTHAS (Method 1550) for procedure

STRYCHNINE

$C_{21}H_{22}N_2O_2$ MW: 334.42 CAS: 57-24-9 RTECS: WL2275000

METHOD: 5016, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.15 mg/m^3
NIOSH: 0.15 mg/m^3/10 h; Group I Pesticide
ACGIH: 0.15 mg/m^3

PROPERTIES: solid; MP 268 °C; VP not significant

SYNONYMS: strychnidin-10-one

SAMPLING

SAMPLER: FILTER (glass fiber, 37-mm)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 70 L @ 0.15 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.073 to 0.34 mg/m^3 [3] (180-L samples)

BIAS: 4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.059 [1]

ACCURACY: ± 14.6%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: strychnine

DESORPTION: 5 mL mobile phase

INJECTION VOLUME: 20 µL

COLUMN: 25 cm x 4.2-mm ID, packed with µBondpack C18, 10-µm particle size

MOBILE PHASE: aqueous 1-heptane sulfonic acid + CH_3CN; pH 3.5; 1 mL/min @ ambient temperature

DETECTOR: UV absorption @ 254 nm

CALIBRATION: solutions of strychnine in mobile phase

RANGE: 10 to 70 µg per sample

ESTIMATED LOD: 0.8 µg per sample [1,2]

PRECISION ($\bar{S}_r$): 0.042 @ 13 to 62 µg per sample [1]

APPLICABILITY: The working range is 0.05 to 10 mg/m^3 for a 200-L air sample.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S302 [2].

REAGENTS:

1. Strychnine, 98%.*
2. Acetonitrile, chromatographic quality.
3. Water, chromatographic quality.
4. Acetonitrile:water, 1:1 (v/v). Mix equal volumes of acetonitrile and distilled water.
5. Acetic acid, glacial.*
6. Acetic acid, 0.01 N. Dilute 0.6 mL glacial acetic acid to 1 L with distilled water.
7. 1-Heptanesulfonic acid sodium salt, 95%.
8. Calibration stock solution, 1 mg/mL strychnine in 0.01 N acetic acid. Use an ultrasonic bath to aid dissolution.
9. Mobile phase: Dissolve 1.1014 g 1-heptanesulfonic acid sodium salt in 980 mL 1:1 acetonitrile:water. Adjust pH to 3.5 with glacial acetic acid. Dilute to 1 L with 1:1 acetonitrile:water. Filter through 0.45-μm PTFE filter and refrigerate. Prepare fresh weekly and if cloudiness appears.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filter, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. HPLC, UV absorption detector at 254 nm, recorder, integrator and column (page 5016-1).
4. Syringe filter, polypropylene housing, nylon membrane, 0.2-μm pore size.
5. Syringe, 20-μL.
6. Micropipets or syringes, 10- to 100-μL.
7. Jars, glass, squat-form ointment, with PTFE-lined screw caps.
8. Volumetric flasks, glass, 10-mL.
9. Pipet, 5-mL delivery, with pipet bulb.
10. Tweezers.
11. Ultrasonic bath.

SPECIAL PRECAUTIONS: Strychnine is a potent convulsant. Use impervious clothing, gloves and face shields when handling it [3,4].

Avoid skin contact with acetic acid as it may cause severe burns.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 70 to 1000 L.

SAMPLE PREPARATION:

3. Transfer the filter carefully using tweezers to an ointment jar.
4. Add 5.0 mL mobile phase. Seal and gently swirl the jar to wet the filter.
5. Filter the sample solution through a syringe filter.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 1 to 70 μg strychnine per sample (0.2 to 14 μg/mL).
   a. Add known amounts of calibration stock solution to mobile phase in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with the samples and blanks (steps 9, 10, and 11).
   c. Prepare calibration graph (peak area vs. μg strychnine).
7. Determine recovery (R) at least once for each lot of filters used for sampling in the calibration range. Prepare three filters at each of five levels plus three media blanks.

a. Deposit a known amount of calibration stock solution onto the filter. Allow filters to air dry.
b. Store samples overnight in ointment jars.
c. Prepare for analysis (steps 3 through 5) and analyze together with working standards (steps 9 through 11).
d. Prepare a graph of R vs. μg strychnine recovered.

8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control

MEASUREMENT:

9. Set HPLC system according to manufacturer's recommendations and to the conditions given on page 5016-1.
10. Inject sample aliquot using syringe, fixed volume sample loop or autosampler.
11. Measure peak area.

CALCULATIONS:

12. Determine the mass, μg (corrected for R) of strychnine found in the sample (W) and in the average media blank (B) from the calibration graph.
13. Calculate concentration, C, of strychnine in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S302 was issued on February 17, 1978 [2], and evaluated over the range 0.073 to 0.34 mg/m^3 using a 180-L sample [1,5]. Overall precision, $\hat{S}_{rT}$, was 0.059 with an average recovery of 100.9%, representing a non-significant bias. The concentration of strychnine was independently verified by analysis of filter samples with a UV spectrophotometer at 254 nm. Recovery was 0.98 in the range of 13.5 to 54.1 μg per sample. Collection efficiency was determined to be at least 98.8% for 180-L sample at a concentration to be 0.15 μg/mL. Average recovery for one-day old samples was 105% vs. 98.8% for seven-day old samples stored at room temperature.

Since the filter samples for the recovery and stability studies were prepared with strychnine acetate rather than the free base, the recovery of the free base and the stability of such samples is unknown.

REFERENCES:

[1] Back-up Data Report for Strychnine, NIOSH Contract No. 210-76-0123, available as "Ten NIOSH analytical Methods," Order Nol PB288-629 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S302, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
[5] NIOSH Research Report - Development and Validation of Methods for Sampling and analysis of Workplace and Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

M.J. Seymour, NIOSH/DPSE.

STYRENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

SULFUR DIOXIDE

SO_2 MW: 64.06 CAS: 7446-09-5 RTECS: WS4550000

METHOD: 6004, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 5 ppm
NIOSH: 2 ppm; STEL 5 ppm; Group I Pesticide
ACGIH: 2 ppm; STEL 5 ppm
(1 ppm = 2.62 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 2.26 (air = 1); BP −10 °C; MP −72.7 °C; nonflammable

SYNONYMS: none

SAMPLING

SAMPLER: FILTER + TREATED FILTER (cellulose + Na_2CO_3; preceded by 0.8-μm cellulose ester membrane)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 4 L @ 5 ppm
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: sulfite and sulfate ions

EXTRACTION: 10 mL 1.75 mM $NaHCO_3$/2.0 mM Na_2CO_3

INJECTION LOOP VOLUME: 50 μL

ELUENT: 1.75 mM $NaHCO_3$/2.0 mM Na_2CO_3, 2 to 3 mL/min

COLUMNS: Ion Pac AS4A separator, Ion Pac AG4A guard; micromembrane suppressor [2]

CONDUCTIVITY SETTING: 10 μS full scale

CALIBRATION: standard solutions of SO_3^{2-} and SO_4^{2-} in eluent

RANGE: 11 to 200 μg SO_2 per sample

ESTIMATED LOD: 3 μg SO_2 per sample [2]

PRECISION ($\bar{S}_r$): 0.042 [2]

APPLICABILITY: The working range is 0.2 to 8 ppm (0.5 to 20 mg/m^3) for a 100-L air sample. The method is applicable to STEL samples. SO_2 is collected on the back (treated) filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and may be quantitated as total particulate sulfate.

INTERFERENCES: Sulfur trioxide gas, if present in dry atmospheres, may give a positive interference for SO_2.

OTHER METHODS: This revises P&CAM 268 [3]. P&CAM 146 [4], P&CAM 163 [5], and S308 [6] use 0.3 N H_2O_2 for sampling, followed by titration with NaOH or barium perchlorate. P&CAM 160 [7] uses tetrachloromercurate solution and visible spectrophotometry. P&CAM 204 [8] uses a solid sorbent (molecular sieve 5A), thermal desorption, and mass spectrometry.

REAGENTS:

1. Water, deionized, filtered, specific conductance ≤ 10 μS/cm.
2. Fixative solution. Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol and dilute with deionized water to 1 L.
3. Eluent: 1.75 mM $NaHCO_3$/2.0 mM Na_2CO_3. Dissolve 0.588 g $NaHCO_3$ and 0.848 g Na_2CO_3 in 4 L filtered deionized water.
4. Calibration stock solutions, 1 mg/mL (as the anion). Prepare in duplicate.
   a. **Sulfite:** dissolve 0.1575 g Na_2SO_3 in water. Add 2 mL glycerol. Dilute to 100 mL. Prepare fresh daily.
   b. **Sulfate:** dissolve 0.1479 g Na_2SO_4 in deionized water. Dilute to 100 mL. Stable several weeks.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two 37-mm diameter cassette filter holders (connected in series by a M-M Luer adapter, e.g., Millipore XX1102503, or a short piece of plastic tubing) containing:
   a. (Front cassette) cellulose ester membrane filter, 0.8-μm pore size, supported by a backup pad.
   b. (Back cassette) cellulose filter (Whatman 40 or equivalent) which has been saturated with fixative solution and dried 20 to 30 min at 100 °C, supported by a porous plastic support pad.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Vials, glass, 20-mL, screw-cap, such as scintillation vials.**
4. Ion chromatograph, HPIC-AS4A anion separator and HPIC-AG4A guard, anion micromembrane suppressor, conductivity detector, and strip chart recorder. (Optional: integrator.)
5. Syringes, 10-mL, polyethylene, with luer tip.**
6. Filters, in-line, luer-tip holder with membrane filter, 13- or 25-mm, 0.45-μm pore size.
7. Micropipets, 50- to 1000-μL, with disposable tips.**
8. Volumetric flasks, 50- and 100-mL.**
9. Pipet, 10-mL.**
10. Polyethylene bottles, 250-mL.**

** Clean by rinsing thoroughly with deionized water.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove end caps of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 40 to 200 L. Do not exceed a total particulate loading of 2 mg on the front filter.
4. Seal the sampler and pack securely for shipment.
   NOTE: If determination of sulfuric acid is required, transfer the front (membrane) filter to a clean vial within 4 h to avoid low recovery of sulfate. Handle the filter with tweezers to avoid contamination.

SAMPLE PREPARATION:

5. Put the two filters from the sampler into separate, clean vials. Discard the backup pads. Add 10.0 mL eluent to each vial and let stand, with occasional vigorous shaking, for 30 min.

NOTE: The SO_2 collected on the treated (back) filter is present as sulfite, which oxidizes in air slowly (over several weeks) to sulfate. The contributions of sulfite and sulfate found on the back filter must be summed, with appropriate stoichiometric factors applied, to give the SO_2 concentration (step 11).

6. Pour each sample into a syringe fitted with an in-line filter.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards.
   a. Add known aliquots of sulfate calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to produce solutions containing 1 to 20 μg/mL SO_4^{2-}.
   b. Prepare sulfite standards in the same manner over the same range.
   c. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards daily.
   d. Analyze working standards with samples and blanks (steps 8 through 10). Prepare a calibration graph for each anion [peak height (mm or μS) vs. μg sulfite or sulfate].

MEASUREMENT:

8. Set ion chromatograph to conditions given on page 6004-1, according to manufacturer's instructions.
9. Inject sample aliquot. For manual operation, inject 2 mL of sample from syringe to ensure complete rinse of sample loop.
   NOTE: All samples, eluents, and water flowing through the ion chromatograph must be filtered to avoid plugging system valves or columns.
10. Measure peak heights of sulfite and sulfate peaks.
    NOTE: If peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

11. Determine the mass, μg, of sulfate equivalent found on the front (W_f) and back (W_b) filters and in the corresponding average media blanks (B_f and B_b).
    NOTE: The sulfate equivalent is the sum of the sulfate peak, μg, and 1.200 times the sulfite peak, μg, on the chromatogram (1.200 = MW SO_4^{2-}/MW SO_3^{2-}): $\mu g_{\text{sulfate equivalent}} = \mu g_{\text{sulfate}} + 1.200\ \mu g_{\text{sulfite}}$.
12. Calculate the concentration, C_{SO2}, of sulfur dioxide, applying the factor 0.667 (MW SO_2/MW SO_4^{2-}):

$$C_{SO_2} = \frac{(W_b - B_b)}{V} \cdot 0.667,\ \text{mg/m}^3.$$

13. Calculate the concentration, C_{SO4}, of particulate sulfate (including sulfuric acid) in the air volume sampled, V (L):

$$C_{SO_4} = \frac{(W_f - B_f)}{V},\ \text{mg/m}^3.$$

EVALUATION OF METHOD:

The sampler was adapted from that of Pate, et al. [9]. In experiments in which SO_2 was generated by permeation tube and collected in impingers containing H_2O_2, untreated 0.8-μm cellulose ester membrane filters were shown to allow complete passage of SO_2 [10]. In subsequent sampling of an atmosphere containing ca. 10 ppm SO_2 at 1 L/min for 30 min, two treated filters were placed in series following a cellulose ester membrane filter. Recoveries were: 0.667 mg SO_2 from the first treated filter, 0.02 mg SO_2 from the second treated filter, and less than 0.003 mg SO_2 in the backup impinger containing 0.3 N H_2O_2 [11]. Cellulose ester filters spiked with 0.2 mg H_2SO_4 gave the following recoveries: 83.5% using H_2O extraction, 98.5% using hot H_2O extraction, and 82.5% using 0.01 M HCl for extraction.

A study on filter impregnating solutions compared $NaHCO_3$ and KOH. The chromatograms of samples from the KOH-treated filters had noticeably flattened and broadened peak shapes as well as retention times reduced by approximately 10% when compared to the chromatograms of H_2SO_4 spiked on filters impregnated with $NaHCO_3$[1].

REFERENCES:

[1] Williamson, G.Y. NIOSH/MRSB Sequence 7452-B (unpublished, July 6, 1992).
[2] Williamson, G.Y. NIOSH/MRSB Sequence 7452-C (unpublished, July 22, 1992).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 268, U.S. Department of Health and Human Services, Publ. (NIOSH) 79-141 (1979).
[4] Ibid., 2nd ed., Vol. 1, P&CAM 146, Publ. (NIOSH) 77-157-A (1977).
[5] Ibid., 2nd ed., Vol. 1, P&CAM 163, Publ. (NIOSH) 77-157-A (1977).
[6] Ibid., 2nd ed., Vol. 4, S308, Publ. (NIOSH) 78-175 (1978).
[7] Ibid., 2nd ed., Vol. 1, P&CAM 160, Publ. (NIOSH) 77-157-A (1977).
[8] Ibid., 2nd ed., Vol. 1, P&CAM 204, Publ. (NIOSH) 77-157-A (1977).
[9] Pate, J.B., J.P. Lodge, Jr., and M.P. Neary. The Use of Impregnated Filters to Collect Traces of Gases in the Atmosphere, Anal. Chim. Acta, 28:341 (1963).
[10] Grote, A.A. (NIOSH, unpublished results, 1973).
[11] Eller, P.M. and M.A. Kraus. Methods for the Determination of Oxidized Sulfur and Nitrogen Species in Air, Internal Report, (unpublished, July 29, 1977).

METHOD REVISED BY:

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SULFUR HEXAFLUORIDE by portable GC 6602

SF_6 MW: 146.06 CAS: 2551-62-4 RTECS: WS4900000

METHOD: 6602 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
(1 ppm = 5.97 mg/m^3 @ NTP)

PROPERTIES: colorless, odorless gas; MP −50.8 °C; sublimes −63.8 °C; d = 5.0 (air = 1)

SYNONYMS: (none)

SAMPLING		MEASUREMENT	
SAMPLER:	GAS SAMPLING BAG	**TECHNIQUE:**	GAS CHROMATOGRAPHY (PORTABLE)
FLOW RATE:	0.02 to 0.1 L/min; fill bag ≤ 80% of capacity; spot samples (step 2.a.) or TWA samples (step 2.b.)	**ANALYTE:**	sulfur hexafluoride
		COLUMN:	38 cm x 6-mm OD stainless steel, packed with 100-120 mesh activated alumina
SAMPLE STABILITY:	stable 28 h in 5-layers bags; 8 h in Tedlar bags	**DETECTOR:**	electron capture
		CALIBRATION:	bag standards or calibrated gas mixtures
FIELD BLANKS:	in bag from a non-work area	**RANGE:**	0.1 to > 10,000 ppb
		ESTIMATED LOD:	0.05 ppb
		PRECISION ($\bar{S}_r$):	0.022

ACCURACY	
RANGE STUDIED:	0.1 to 200 ppb
BIAS:	− 0.4%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.022
ACCURACY:	± 4.8%

APPLICABILITY: The working range of this method is 0.1 to 10,000 ppb in relatively non-complex atmospheres where sulfur hexafluoride is known to be present, such as indoor environments where ventilation testing is being conducted by the release of SF_6.

INTERFERENCES: Any compound having the same or nearly the same retention time as sulfur hexafluoride on the column may cause a positive interference. Carbon dioxide, another common substance monitored to evaluate ventilation systems in indoor air quality studies, will not interfere.

OTHER METHODS: Method S244 [1] describes the determination of SF_6 by thermal conductivity detection after collection in bags, with a lower limit of 500 ppm, i.e., not sensitive enough for ventilation studies.

REAGENTS:

1. Sulfur hexafluoride in air at known concentration(s) for use in field calibration. Prepared in the field by filling sample bag (see "Equipment") with verified commercial standard compressed gas*, or by injecting known amount of pure (or high concentration) SF_6* into sample bag containing a metered volume of clean air.
2. Compressed argon or other gas* at approximately 30 psi for use as carrier gas.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with electron capture detector, gas sampling loop if desired (use of loop will limit variability of injection volume and therefore restrict range of method), and strip chart recorder if appropriate.
2. Personal sampling pump, 0.02 to 1 L/mim or other rate suitable for filling sample bags, with flexible connecting tubing.
   NOTE: Pumps lubricated with petroleum products should not be used.
3. Sample bags, 1 to 20 L or other appropriate sizes. Sources include: Calibrated Instruments, Inc., 200 Saw Mill River Rd., Hawthorne, NY 10532; SKC, Inc., 334 Valley View Rd., Eighty-Four, PA 15330-9614.
4. Syringes, gas-tight, of various sizes appropriate to the GC.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labeling bags.

SPECIAL PRECAUTIONS: Shipment of radioisotopes, calibration materials, and compressed gases must comply with 49CFR171-177 regulations regarding shipment of hazardous materials. Appropriate safety precautions should be followed when working with compressed gases.

SAMPLING AND MEASUREMENT:

1. Start GC and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A stable standing current and stable baseline should be attained at the highest sensitivity likely to be used.
2. Select either or both of the following sampling modes:
   a. **Spot sample** - Draw air sample into gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A potential source of random error in the method is imprecision of replicate injections. To reduce this error: i) use a gas sampling loop for injections; ii) make at least three replicate determinations per sample; iii) use an injection volume precisely readable, and consistent with that used in calibration.
   b. **Integrated air sample for time weighted average (TWA) determination** - Attach a clean sample bag to the outlet port of a personal sampling pump with a minimum length of flexible tubing.
      NOTE 1: To reduce memory effects and contamination, sample bags should be purged with clean air between samples. Ideally the bags should be filled with clean air prior to use, and an aliquot of that air from the bag injected into the GC to demonstrate that the bag is indeed clean prior to use. Pump the air sample into the bag at a rate calculated to fill <80% of the bag capacity over the desired sampling period.

NOTE 2: While it is not necessary to know precisely the sample flow rate, it is important that the flow rate be constant over the duration of the sample. Within eight hours after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2a above).

NOTE 3: Bag samples may be stored for longer periods if integrity has been demonstrated in the bag being used.

c. Obtain the peak height or area for the injected sample of sulfur hexafluoride.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph by at least three replicate determinations of at least five analyte volumes. Plot peak height (or area) vs. volume of sulfur hexafluoride.
   b. Determine detector drift, averaged over the time period expected to be used in the field.
   c. Determine the ability of the GC column to separate the sulfur hexafluoride from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph of peak height (or area) vs. volume of sulfur hexafluoride by triplicate determinations of working standards under the same conditions as for samples (step 2a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate volume of analyte in the sample, V_a (expressed in picoliters), by comparison of sample peak height or area with the daily calibration graph (step 5). Determine sulfur hexafluoride concentration, C (ppb) in the sample by dividing V_a by the volume of the injection, V_i (mL):

$$C = \frac{V_a}{V_i}, \text{ ppb.}$$

NOTE 1: Some GCs will perform some or all calculations electronically.]

NOTE 2: Determination of sulfur hexafluoride concentration expressed in pg/mL (i.e., mg/m^3) can be accomplished by establishing lab and field calibration graphs (Steps 4 and 5) of peak height or area vs mass of analyte in mg. "V_a" in Step 6 would then become "M_a", mass of analyte.]

EVALUATION OF METHOD:

This method was evaluated over the range 0.1 to 200 ppb (0.0006 to 1.2 pg/m^3) sulfur hexafluoride using an Ion Track Instruments (ITI) Model 505 portable SF_6 detector chromatograph modified by the addition of an injection port to allow syringe injections of samples. Mixtures of SF_6 in air were obtained from Scott Specialty Gases, Inc. at concentrations certified (±5%) of 1.02, 10.5, 36.6, 77.6, 105, 155, and 203 ppb. (The 10.5 ppb standard was diluted 1:100 to obtain a 0.105 ppb standard.) Calibration standards were prepared by dilution of sulfur hexafluoride (99.8% minimum purity, Union Carbide) with air from the laboratory compressed air supply. This dilution air was passed through activated charcoal to remove traces of hydrocarbons, but was tested prior to use since trace amounts of SF_6 may not be removed by the charcoal. The SF_6 was measured with the same type of gastight syringe used for sample injection, but the syringes used for the preparation of standards were not used for injections into the GC since they were shown to retain traces of SF_6 which would show up in such injections. The dilution air was metered into the same type of inert bags that were used for samples using a 2-L Hamilton syringe.

Packed column, ambient temperature isothermal gas chromatography provides rapid analysis of samples with little sample preparation, but at the expense of providing limited separation of the analyte of interest from potential interferences. The column used in the evaluation of this method was 38 cm x 0.6-cm (OD) stainless steel, packed with 100-120 mesh activated aluminum oxide, using an Argon carrier gas flow of approximately 30 mL/min. These conditions provided a retention time of approximately 1.4 minutes for SF_6, allowing replicate analyses of multiple samples and calibration standards during a work shift. Increasing the carrier gas flow provided a somewhat faster analysis, but resulted in a loss of sensitivity. Decreasing the carrier gas flow lengthened the retention time, but did not result in an increase in sensitivity. Baseline drift was typically less than 10% per hour. Relative standard deviations for replicate analyses ranged from 0.90 to 5.64%, with a mean of 2.2%. Analysis of certified commercial standards ranged from 97.6 to 102.8%, with a mean of 99.6%.

Samples in multi-layer 5.5-mil bags (Calibrated Instruments, Inc.) showed no detectable change in concentration over a 28-hr period. Samples in 4 mil Tedlar bags (SKC, Inc.) showed no detectable change in concentration after 28 hrs.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 79-141 (1979).

METHOD WRITTEN BY:

G.E. Burroughs, NIOSH/DPSE.

SULFURIC ACID

See ACIDS, INORGANIC (Method 7903) for procedure

SULFURYL FLUORIDE 6012

SO_2F_2 MW: 102.06 CAS: 2699-79-8 RTECS: WT5075000

METHOD: 6012, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 5 ppm
NIOSH: 5 ppm; STEL 10 ppm; Group I Pesticide
ACGIH: 5 ppm; STEL 10 ppm
(1 ppm = 4.17 mg/m^3 @ NTP)

PROPERTIES: gas; BP −55 °C; vapor density (air = 1) 3.5; nonflammable, colorless, odorless

SYNONYMS: sulfur difluoride, sulfuric oxyfluoride, Vikane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 800 mg/200 mg)

FLOW RATE: 0.05 to 0.1 L/min

VOL-MIN: 1.3 L @ 5 ppm
-MAX: 10 L

SHIPMENT: ship at 0 °C

SAMPLE STABILITY: at least 12 days @ 0 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	20 to 420 mg/m^3 (0.2- to 6-L samples)
BIAS:	−3.0%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.070 [1]
ACCURACY:	±16.7%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY CONDUCTIVITY DETECTION

ANALYTE: fluoride ion (F^-)

EXTRACTION: 20 mL 40 mN NaOH; sonicate 60 min

INJECTION VOLUME: 50 µL

ELUENT: 40 mN NaOH, 1.0 mL/min

COLUMN: Dionex IonPac-AG4A guard, IonPac-AS4A anion separator column; Dionex micromembrane-suppressor

DETECTOR: conductivity, 30 µS full scale

CALIBRATION: standard solutions of fluoride ion spiked onto sample media

RANGE: 10 to 80 µg fluoride per sample [2]

ESTIMATED LOD: 7 µg SO_2F_2 per sample [2]

PRECISION ($\bar{S}_r$): 0.052 (9 to 140 mg/m^3 SO_2F_2 per sample) [1]

APPLICABILITY: The working range is 2.2 to 17 ppm (9 to 75 mg/m^3) for a 3-L air sample. This method is applicable to STEL measurements using a 1.5 L sample. The method has been used to sample for sulfuryl fluoride at dwelling fumigation sites [2,3].

INTERFERENCES: Other fluoride compounds may interfere.

OTHER METHODS: This method is based on the method of Bouyoucos, et al. [4]. NIOSH Method #S245 uses gas bag samples, gas chromatography/FPD [5].

REAGENTS:

1. Sodium hydroxide*, ACS reagent grade.
2. Water, high purity.
3. Desorbing/extracting solution and eluent: 40 mN NaOH. Dissolve 3.2 g NaOH in 2 L of degassed high purity water.
4. Suppressor regenerant, 25 mN H_2SO_4*.
5. Calibration stock solution, 1 mg fluoride anion per mL. Dissolve 0.2210 g NaF in 100 mL deionized water.
6. Sulfuryl fluoride*, gas. Calibrated gas standards may be obtained from Scott-Marrin, Inc., Riverside, CA 92507.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 10-mm OD, 7-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 800 mg, back = 200 mg), separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.05 to 0.10 L/min, with flexible polyethylene or PTFE tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Filter, membrane, 0.45-μm pore size, 13-mm, with luer fitting.
5. Ion chromatograph, with a conductivity detector, chart recorder, integrator and columns (p. 6012-1).
6. Vials, glass, 20-mL, with plastic caps.
7. Vials, polyethylene, 20-mL, with plastic caps.
8. Micropipettes, with disposable plastic tips.
9. Volumetric flasks, 100-mL
10. Pipet, 10-mL, graduated in 0.1-mL intervals.
11. Pipet, volumetric, 20-mL.
12. Syringes, 10-mL, plastic, with luer tip.

SPECIAL PRECAUTIONS: Sulfuryl fluoride is a restricted use pesticide owing to its inhalation toxicity. It is extremely hazardous as vapor or liquid. Inhalation of vapors may be fatal. Read and follow all label precautions [6].

Sulfuric acid and sodium hydroxide are corrosive to skin, eyes, and mucous membranes. Handle all hazardous chemicals in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach a sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.1 L/min for a total sample volume of 1.3 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment, at 0 °C.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate 20-mL plastic vials. Discard the glass wool and foam plugs.
6. Add 20 mL 40 mN NaOH eluent to each plastic vial. Cap. Sonicate for 60 minutes.
7. Transfer a 5 to 7 mL aliquot to a tare weighted 20-mL glass vial using a plastic syringe fitted with a 0.45 μm membrane filter.
8. Re-weigh each glass vial and contents so that the net weight of the aliquot can be calculated.
9. Take each sample to complete dryness in an uncapped glass vial on a hot plate. Cool, then re-constitute to the original net weight with high-purity water.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    NOTE: Standards should be spiked onto charcoal tubes as follows to avoid high recoveries seen with liquid standards [3].
    a. Add known amounts of calibration stock solution onto charcoal tubes (5.0 to 80 μg F^-) and desorb in the same manner as field samples (steps 5 through 9).
    b. Analyze working standards together with samples and blanks (steps 12 through 14).
    c. Prepare a calibration graph of peak height vs. amount (μg) of fluoride per 20 mL of sample.
11. (Optional). Determine recovery (R) for each lot of tubes used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus three media blanks.
    a. Collect a known amount of SO_2F_2 gas onto each charcoal tube (steps 1 through 9).
    b. Analyze samples in the same manner as field samples (steps 12 through 14).
    c. Prepare graph of recovery vs. μg sulfuryl fluoride.

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 6012-1.
13. Re-filter sample if necessary, then inject a sample aliquot into the ion chromatograph.
14. Measure peak height.

CALCULATIONS:

15. Determine mass (μg) of fluoride found on the front (W_f) and back (W_b) sections, and in the average media blank front (B_f) and back (B_b) sorbent section.
16. Calculate concentration C of sulfuryl fluoride (mg/m^3) in the actual air volume, V(L), applying the conversion factor 2.686 (MW SO_2F_2/MW F^-; the reaction is $SO_2F_2 + 4NaOH \rightarrow 2NaF + Na_2SO_4 + 2H_2O$):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.686}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 20 to 420 mg/m^3. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.070 [1]. The average recovery of SO_2F_2 from charcoal was 99% when sampling atmospheres prepared in aluminized gas bags (Calibrated Instruments, Inc., Hawthorne, NY 10532). Recovery of fluoride from sampling media was 97% in the range 10 to 160 μg F^- per sample. Sample stability during storage was evaluated at 417 mg/m^3 SO_2F_2 per sample. Samples showed 101% recovery after twelve days of storage at 0-5 °C compared to one-day old samples.

REFERENCES:

[1] Williamson, G.Y. Backup Data Report for Sulfuryl Fluoride. NIOSH/MRSB Internal Report (unpublished) (1991).
[2] Analysis of NIOSH Samples for Sulfuryl Fluoride, NIOSH/MRSB Sequence #7161-A, (unpublished, May 13, 1991).
[3] Analysis of NIOSH Samples for Sulfuryl Fluoride, NIOSH/MRSB Sequence #7691-D (unpublished, January 27, 1993).
[4] Bouyoucos, S.A., Melcher, R.G., and Vaccaro, J.R., Collection and Determination of Sulfuryl Fluoride in Air by Ion Chromatography, Am. Ind. Hyg. J., 44, 57-61 (1983).
[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S245, U.S. Department of Health,

[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN BY:

George Y. Williamson, MRSB, DPSE.

SUPER ABSORBENT POLYMERS 5035

MW: Varies CAS: See Table 1 RTECS: None

METHOD: 5035, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solids; hygroscopic; form gels with water [1]

SYNONYMS: sodium polyacrylate, Sanwet IM-3500 (sodium polyacrylate grafted with starch), Water Lock A-100 (sodium acrylate-acrylamide copolymer grafted with starch), Water Lock B-204 (potassium acrylate-acrylamide copolymer grafted with starch), Water Lock G-400 (sodium acrylate-acrylamide copolymer).

SAMPLING

SAMPLER: MEMBRANE FILTER (PVC, 5-μm, 37-mm)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 50 L
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: >8 months @ 25 °C [2]

BLANKS: 2 to 10 field blanks per set

BULK SAMPLES: required (20 g)

ACCURACY

RANGE STUDIED: 0.02 to 0.15 mg/m^3 for Sanwet IM-3500

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ICP-AES OR AAS

ANALYTE: copper

EXTRACTION: 6 mL of 0.07 M cupric acetate; 14 mL of water; ultrasonic bath, 15 min.

ASHING REAGENTS: 70% HNO_3, 10 mL; 70% $HClO_4$, 1 mL (optional)

WAVELENGTH: 324. 7 nm

CALIBRATION: super absorbent polymer in sucrose

RANGES: see Table 1

ESTIMATED LODs: see Table 1

PRECISION ($\bar{S}_r$): 0.086 [2]

APPLICABILITY: This method has been used to measure Sanwet IM-3500 in air at a diaper manufacturing plant [2].

INTERFERENCES: Aerosols of copper compounds would interfere; however, this problem is uncommon.

OTHER METHODS: Super absorbent polymers in air can be determined by collection on PVC filters, treatment with hot HCl and measurement of sodium by flame AAS [2].

REAGENTS:

1. Super absorbent polymer (the type present in air samples), 99+% pure if water is only impurity. See step 15 to determine the amount of water present.
2. Copper acetate, 0.07 M. Dissolve 27.96 g of cupric acetate monohydrate in water to make 2 L of solution. Solution may be stored at least 6 months. Filter solution through 0.45-μm cellulose ester filter immediately (<4 h) before use.
3. Water, deionized.
4. Sucrose, 99+% pure.
5. Calibration stock mixture, ca. 4% super absorbent polymer by weight. Mix ca. 380 mg of polymer with 8000 mg of sucrose (do not use polymer which has been heated). Shake mixture 5 min by hand. Grind mixture to fine powder with freezer mill for 12 min (mill cooled with liquid nitrogen).
6. Nitric acid, 70%.
7. Perchloric acid, 70% (optional).*
8. Argon (for ICP-AES).
9. Acetylene (for AAS).
10. Air (for AAS).
11. Dilution acid, 2.8% HNO_3:0.7% $HClO_4$. Add 40 mL of 70% HNO_3 and 10 mL of 70% $HClO_4$ to deionized water to make 1 L of solution.
12. Dilution acid, 3.5% HNO_3. Add 50 mL of 70% HNO_3 to deionized water to make 1 L of solution.

* See Special Precautions

EQUIPMENT:

1. Sampler: PVC filter, 37-mm membrane filter, 5-μm pore size, in two-piece filter cassette.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Instrument for measurement of copper (LOD <2 μg per sample); e.g., inductively coupled plasma-atomic emission spectrometer or atomic absorption spectrophotometer.
4. Vacuum filtration apparatus, two units (product XX10 025 00, Millipore Corp., Bedford, MA, or equivalent).
5. Filters, cellulose ester, 25-mm diameter, 0.45-μm pore size.
6. Vials, 20-mL.
7. Pipets, 5- and 6-mL, with pipet bulb.
8. Balance, readable to five decimal places.
9. Ultrasonic bath.
10. Beakers, 50- and 250-mL.
11. Beakers, Phillips, 125-mL, with watch glass covers.**
12. Forceps.
13. Spatulas.
14. Freezer mill, or mortar and pestle.
15. Stirring rod, glass.
16. Hot plate, surface temperature, 150 °C.

** Clean Phillips beakers with 70% nitric acid, and rinse thoroughly with deionized water before use.

SPECIAL PRECAUTIONS: Work with perchloric acid should be performed only in a perchloric acid hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 50 to 1500 L. Limit the loading of particulate matter on the filter to a maximum of about 1 mg.
3. Seal the inlet and outlet of the sampler with plugs. Pack securely for shipment. Separately ship a bulk sample (20 g) of the super absorbent polymer.

SAMPLE PREPARATION:

4. Transfer the 37-mm PVC filter to a 20-mL vial, and allow the exposed side of the filter to face inward.
5. Add 6 mL of 0.07 M copper acetate solution (filtered through a 0.45-μm cellulose ester filter

within about 4 h before use).

6. Add 14 mL of deionized water. Cap the vial.
7. Place the vial into an ultrasonic bath for 15 min.
8. Collect the copper-polymer precipitate on a 25-mm cellulose ester filter (0.45-μm pore size) by vacuum filtration.
   NOTE: The copper-polymer precipitate should be collected within about 4 h after the addition of copper acetate solution to samples and blanks. Particles containing copper may appear in copper acetate solution if the solution stands for a few days. These particles would cause a positive interference.
9. Rinse the vial with two 12-mL portions of deionized water, and add the rinses to the filtration apparatus. If blue particles of copper-polymer precipitate are observed in the vial after the two rinses, rinse the vial with additional water until blue particles are not observed in the vial. Add the additional rinses to the filtration apparatus.
10. Recover super absorbent polymer from the interior surface of the front piece of the cassette filter holder.
    a. Seal inlet of front piece of the cassette filter holder with a plug.
    b. Add 5 mL of 0.07 M copper acetate to this cassette piece.
    c. Place this cassette piece into a clean ultrasonic bath for about 30 sec.
       NOTE: If a visible coating of copper-polymer precipitate does not become dislodged during ultrasonic treatment, the coating may be dislodged with a glass stirring rod.
    d. Pour solution from cassette piece to the vacuum filtration apparatus.
    e. Rinse cassette piece with 5 mL of deionized water.
11. Transfer the 25-mm cellulose ester filter with collected precipitate to a 125-mL Phillips beaker. Cover with a watch glass.
12. Rinse the bottom part of the top piece of the filtration apparatus with deionized water in a 50-mL beaker.
13. Assemble the vacuum filtration apparatus with a clean 25-mm cellulose ester filter. Add the rinse from the 50-mL beaker to the filtration apparatus. Transfer the 25-mm filter to the same Phillips beaker (step 10).
    NOTE: Steps 12 and 13 are applicable if the vacuum filtration apparatus is the type that sandwiches the filter between the top piece (vertical column) and the bottom piece. When the vertical column is separated from the filter, water with copper-polymer precipitate may travel by capillary action to the underside of the vertical column. Also, precipitate may cling to the inside wall of the vertical column.
14. Add 10 mL of 70% nitric acid and 1 mL of 70% perchloric acid to filters in the Phillips beaker.
    NOTE: Use of perchloric acid is optional.
    a. Cover the beaker with the watch glass.
    b. Place the beaker onto a hot plate at 150 °C, and reflux overnight.
    c. Remove the watch glass, and heat the mixture just to dryness at 150 °C.
    d. Remove the beaker from the hot plate. Add 0.5 mL of 4:1 70% nitric acid:70% perchloric acid (v/v) or 0.5 mL of 70% nitric acid (choice depends on whether the standard solutions contain perchloric acid).
    e. Dilute the mixture to 10 mL with deionized water.

CALIBRATION AND QUALITY CONTROL:

15. Determine the amount of water present in a bulk sample of the super absorbent polymer. Place an accurately weighed 20-g sample of the super absorbent polymer into an oven at 130 °C for about 16 hours. Determine the weight loss, and calculate the amount of water in the original sample (percent by weight).
16. Calibrate with at least six working standards.
    a. Prepare a series of working standards of super absorbent polymer in sucrose by dilution of portions of the calibration stock mixture with sucrose. Calculate the quantities of calibration stock mixture which will be diluted with about 8 g of sucrose in order that 50 to 300 mg of each working standard contains a desirable quantity of anhydrous super absorbent polymer

in the calibration range (8 to 1000 μg is an approximate calibration range). Shake each dilution in a 20-mL vial by hand for about 5 min, and then grind each mixture in a freezer mill (cooled with liquid nitrogen) for 12 min or with a mortar and pestle.

NOTE: Although the super absorbent polymer in the calibration stock mixture and working standards may contain water, it is convenient to express a quantity of super absorbent polymer on the basis of anhydrous super absorbent polymer.

b. Prepare six samples at each level and six blanks. For each sample, accurately weigh 50 to 300 mg of a working standard (polymer-sucrose mixture) in a 20-mL vial with a five-place balance.
c. Add 5 mL of deionized water to each vial. Agitate each vial to dissolve the sucrose.
d. Add 6 mL of 0.07 M copper acetate solution [filtered (see step 5)].
e. Place each vial into an ultrasonic bath for 10 min.
f. Collect the copper-polymer precipitates (steps 8 and 9), prepare samples (step 14), and analyze samples (steps 18 and 19).
g. Prepare a calibration graph of instrument response for copper versus μg of anhydrous super absorbent polymer.

17. Estimate recovery (R) of super absorbent polymer from 37-mm PVC membrane filters.
a. Prepare six samples at each level. For each sample, accurately weigh 50 to 300 mg of a working standard polymer-sucrose mixture) in a 20-mL vial on a five-place balance. Place a 37-mm PVC filter into each vial.
b. Follow steps 9, 11 through 14, and 18 and 19.
c. Determine each quantity of super absorbent polymer found from the calibration graph (step 16. g).
d. Calculate the recovery for each sample by dividing the quantity of super absorbent polymer found by the original quantity of polymer.
NOTE: Each recovery is an estimate because the PVC filters have not been fortified with super absorbent polymer.

MEASUREMENT:

18. Set instrument for measurement of copper according to conditions specified by the manufacturer.
19. Analyze samples and standards.
NOTE: If the concentrations of the samples are above the range of the standards, dilute the samples with dilution acid, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

20. Determine the quantity (corrected for recovery) of anhydrous super absorbent polymer in μg, W, in the air sample from the calibration graph (step 16. g).
21. Calculate the concentration, C, of the super absorbent polymer in the air volume sampled, V (L):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated with Sanwet IM-3500, Water Lock A-100, Water Lock B-204, and Water Lock G-400. Average ratios of quantity of copper found to quantity of anhydrous Sanwet IM-3500 were 0.66, 0.78, 0.69, 0.72, 0.63 and 0.57 for 8-, 16-, 32-, 63-, 515-, and 1466-μg quantities of anhydrous polymer (values of S_r for the average ratios were 0.34, 0.12, 0.13, 0.05, 0.05, and 0.03, respectively; pooled $\bar{S}_r$

was 0.086). A second method for calculation of precision involved division of the standard error of the calibration curve by the average y value (average value of copper); precision for the analytical method ($\bar{S}_r$) = 16.7/247 = 0.068.

This sampling and analytical method (Method 5035, Cu-SAP method) was compared with the sodium method [2] for determination of Sanwet IM-3500 in area air samples at a diaper manufacturing plant.

Comparison of Cu-SAP Method (Filters Only) with Sodium Method

Set	Analytical Method	Volume of Air (liters)	Average Concentration of Sanwet IM-3500 (mg/m^3)	Relative Standard Deviation
1a	Cu-SAP	840	0.0673	0.19
1b	sodium	908	0.108	0.023
2a	Cu-SAP	425	0.0978	0.35
2b	sodium	420	0.162	0.052

Air samples for each method were collected at 2 liters/min. Sets 1a and 1b had three samples each; sets 2a and 2b had two samples each. Although PVC filters and interior surfaces of front pieces of cassette filter holders were analyzed in the Cu-SAP method, interior surfaces were not analyzed in the sodium method; thus, the comparisons above are for PVC filters only. Quantities of Sanwet IM-3500 found on interior surfaces of front pieces of cassettes ranged from 12 to 39% of the total quantities found. A bulk sample of Sanwet IM-3500 from the diaper plant contained 7.20% water. See additional information in reference [2].

The average of six blanks was 2.95 μg of copper, and the standard deviation of these blanks was 1.04 μg of copper (cellulose ester filters will retain small quantities of copper during filtration of copper acetate solutions and rinses with deionized water). Average recoveries of 8-, 17-, 63-, and 526-μg quantities of Sanwet IM-3500 from 37-mm PVC filters were 1.27, 0.84, 0.83 and 1.01, respectively. A standard mixture of Sanwet IM-3500 in sucrose (4.48% Sanwet IM-3500 by weight) was stable during storage in a vial for a period of more than eight months at room temperature. Digestion procedures involving (a) nitric and perchloric acids and (b) nitric acid only were evaluated for digestion of copper-polymer precipitate prepared from 500-μg quantities of Sanwet IM-3500. The two procedures were found to be equally effective.

REFERENCES:

[1] Masuda, F., "Super Absorbent Polymers--Characteristics and Trends in Development of Applications," Chemical Economy & Engineering Review, 15(11):19-22 (1983).

[2] Tucker, S.P., M.B. Millson, and D.D. Dollberg, "Determination of Polyacrylate Super Absorbent Polymers in Air," Analytical Letters, 26(5):965-980 (1993).

METHOD WRITTEN BY:

Samuel P. Tucker, Ph.D., Mark B. Millson, and Donald D. Dollberg, Ph.D., NIOSH/DPSE

Table 1

CAS Numbers, Detection Limits, and Analytical Ranges for Super Absorbent Polymers

Super Absorbent Polymer	CAS Number	Detection Limit* (μg/sample)	Analytical Range (μg/sample)
Sanwet IM-3500	60323-79-7	4	15 to 1000
Water Lock A-100	65930-07-6	14	45 to 1000
Water Lock B-204	72162-30-2	13	42 to 1000
Water Lock G-400	61788-39-4	8	28 to 1000

* The detection limit is defined as three times the standard deviation of blanks. The standard deviation of six blanks was 1.04 μg of copper per sample. The average blank value was 2.95 μg of copper. Detection limits in Table 1 are quantities of anhydrous super absorbent polymer per sample.

2,4,5-T
See 2,4-D (Method 5001) for Procedure

$C_8H_5Cl_3O_3$ MW: 255.49 CAS: 93-76-5 RTECS: AJ8400000

METHOD: 5001, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 10 mg/m^3 (2,4-D or 2,4,5-T)
NIOSH: 10 mg/m^3; Group I Pesticide
ACGIH: 10 mg/m^3

PROPERTIES: solid; MP 153 °C (2,4,5-T); VP not significant

SYNONYMS: 2,4,5-T: (2,4,5-trichlorophenoxy)acetic acid; Esterone 245; Trioxone; Weedone

SAMPLING

SAMPLER: FILTER (glass fiber, binderless)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 15 L @ 10 mg/m^3
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 5 to 20 mg/m^3 [1,2] (100-L samples)

BIAS: 4.78%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.053 (2,4,5-T) [2]

ACCURACY: ± 14.2%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4,5-T anion

DESORPTION: 15 mL CH_3OH; stand 30 min

INJECTION VOLUME: 50 µL

ELUENT: 0.003 M $NaClO_4$-0.001 M $Na_2B_4O_7$

FLOW RATE: 1.7 mL/min

DETECTOR: UV @ 289 nm

COLUMN: stainless steel, 50 cm x 2-mm ID, packed with Zipax SAX (DuPont) ambient temperature; 6900 kPa (1000 psi)

CALIBRATION: solutions of analyte in methanol

RANGE: 0.15 to 2 mg per filter

ESTIMATED LOD: 0.030 mg per filter [2]

PRECISION ($\bar{S}_r$): 0.025 [2]

APPLICABILITY: This method determines 2,4-D, 2,4,5-T, and their salts, but not their esters. The working range is 1.5 to 20 mg/m^3 of either compound for a 100-L air sample.

INTERFERENCES: High concentrations of esters of either compound do not interfere but require the use of a pre-column to prevent degradation of the HPLC column.

OTHER METHODS: This method combines and replaces Methods S279 [3] and S303 [3] which are the same except for eluent composition and UV detector wavelength.

TELLURIUM

See ELEMENTS (Method 7300) for procedure

o-TERPHENYL 5021

$C_{18}H_{14}$ MW: 230.31 CAS: 84-15-1 RTECS: WZ6472000

METHOD: 5021, Issue 2 **EVALUATION:** PARTIAL **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : C 1 ppm (o-, m-, and p-isomers)
NIOSH: C 0.5 ppm (o-, m-, and p-isomers)
ACGIH: C 0.53 ppm (o-, m-, and p-isomers)
(1 ppm = 9.42 mg/m^3)

PROPERTIES: solid; MP 58 °C; BP 332 °C; VP 0.035 Pa (0.00026 mm Hg; 0.35 ppm) @ 22 °C [1]

SYNONYMS: o-diphenyl benzene; o-triphenyl; 1,2-diphenyl benzene

SAMPLING

SAMPLER: FILTER (2.0 µm, PTFE)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 4.5 to 20 mg/m^3 [1] (15-L samples)

BIAS: − 4.4%

OVERALL PRECISION : 0.097 [1]

ACCURACY ($\hat{S}_{rT}$): ± 20.0%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: o-terphenyl

DESORPTION: CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-DETECTOR: 230 °C
-INJECTOR: 220 °C
-COLUMN: 185 °C

CARRIER: N_2, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 5% SE-30 on 80/100 mesh Gas Chrom W

CALIBRATION: standard solutions of o-terphenyl in CS_2

RANGE: 0.015 to 0.5 mg per sample

ESTIMATED LOD: 0.002 mg per sample

PRECISION ($\bar{S}_r$): 0.052 @ 0.07 to 0.27 mg per sample [1]

APPLICABILITY: The working range is 0.5 to 60 mg/m^3 for a 30-L air sample. The method has been tested only with o-terphenyl.

INTERFERENCES: None identified.

OTHER METHODS: This revised Method S27 [2].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. ortho-Terphenyl, reagent grade.*
3. Hexane, chromatographic quality.*
4. Calibration stock solution, 1 mg/mL. Dissolve an accurately weighed 100 mg o-terphenyl in hexane and dilute to 100 mL.
5. Air, filtered, compressed.
6. Nitrogen, purified.
7. Hydrogen, prepurified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE laminated membrane filters, 2.0-μm, 37-mm (Zefluor, Membrana Corp., Pleasonton, CA, or equivalent) backed by a gasket (37-mm OD, 32-mm ID) cut from a cellulose acetate support pad (available SKC, Inc. #225-23) in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Vials, scintillation, screw cap, 20-mL.
4. Tweezers.
5. Gas chromatograph, FID, integrator, and column (page 5021-1).
6. Beakers, 50-mL.
7. Centrifuge tubes, graduated, calibrated at 0.5 mL.
8. Volumetric flasks, 10- and 100-mL.
9. Pipets, 1.0 to 100-μL.
10. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Exposure to terphenyls may cause eye, skin, and respiratory irritation [3]. Carbon disulfide presents a severe hazard owing to its toxic properties and fire and explosion potential (flash point = −30 °C). All work with this solvent should be performed in a fume hood. Hexane has a flash point = −22 °C.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 2 to 30 L.
3. Transfer the filter from the cassette within 1 h of sampling to a clean vial. Handle the filter only with clean tweezers.

SAMPLE PREPARATION:

4. Remove filter from vial and place in 50-mL beaker. Rinse vial with 1 mL CS_2.
5. Extract filter three times with 1-mL portions of CS_2.
6. Transfer the extracts and vial rinsing to a graduated centrifuge tube. Gently evaporate the solution with a stream of nitrogen to a final volume of 0.5 mL.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.002 to 0.5 mg o-terphenyl per sample.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. Prepare calibration graph (peak area vs. mg of o-terphenyl).

8. Determine recovery (R) at least once for each lot of filters used for sampling in the calibration range (step 7). Prepare three filters at each of five levels plus three media blanks.
   a. Spike a known amount of calibration stock solution directly onto the filter with a microliter pipet or syringe.
   b. Allow to stand overnight in the dark.
   c. Extract (steps 4 through 6) and analyze together with working standards (steps 10 and 11).
   d. Prepare graph of recovery vs. mg o-terphenyl recovered.
9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5021-1. Inject 5-μL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
11. Measure peak area.

CALCULATIONS:

12. Determine the mass, mg (corrected for recovery) of o-terphenyl found in the sample (W) and in the average media blank (B) from the calibration graph.
13. Calculate concentration, C, of o-terphenyl in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S27 was issued on November 8, 1974, and was validated for o-terphenyl with both spiked filters and an aerosol generated from a 0.25% (w/v) solution of o-terphenyl in toluene by an aspiration/spray dry technique [1]. The collection efficiency for o-terphenyl of a mixed cellulose ester membrane filter was 1.00 ± 0.01 when sampling an atmosphere containing 18.8 mg/m^3 at 1 L/min for 15 min. No o-terphenyl was detected on charcoal tubes preceded by glass fiber filters when sampling an atmosphere containing 17 mg/m^3 o-terphenyl. Storage stability of the samples was not determined.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S27, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

B. R. Belinky, NIOSH/DPSE; S27 originally validated under NIOSH Contract CDC-99-74-45.

1,1,2,2-TETRABROMOETHANE 2003

$Br_2CHCHBr_2$ MW: 345.70 CAS: 79-27-6 RTECS: KI8225000

METHOD: 2003, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1985 **Issue 2:** 15 August 1994

OSHA : 1 ppm
NIOSH: no REL
ACGIH: 1 ppm
(1 ppm = 14.14 mg/m^3 @ NTP)

PROPERTIES: liquid; d 2.964 g/mL @ 20 °C; BP 243.5 °C; MP 0 °C; VP 13 Pa (0.1 mm Hg) @ 20 °C

SYNONYMS: acetylene tetrabromide; Muthmann's liquid; sym-tetrabromoethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 50 L @ 1 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 6.5 to 23 mg/m^3 [1] (98-L samples)

BIAS: − 9.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.096 [1]

ACCURACY: ± 23.6%

MEASUREMENT

METHOD: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,2,2-tetrabromoethane

DESORPTION: 1 mL tetrahydrofuran; 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 220 °C
-DETECTOR: 270 °C
-COLUMN: 105 °C

CARRIER GAS: N_2, 50 mL/min

COLUMN: 0.9 m x 6.4-mm OD glass; 5% SE-30 on 80/100 mesh Gas Chrom W

CALIBRATION: 1,1,2,2-tetrabromoethane in tetrahydrofuran

RANGE: 0.7 to 4 mg per sample

ESTIMATED LOD: 0.08 mg per sample

PRECISION ($\bar{S}_r$): 0.041 [1]

APPLICABILITY: The working range is 0.5 to 2.8 ppm (7 to 40 mg/m^3) for a 100-L air sample. High humidity during sampling will reduce breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S117 [2] in a revised format.

REAGENTS:

1. Tetrahydrofuran (THF), chromatographic quality and free from peroxides.*
2. 1,1,2,2-Tetrabromoethane, ≥98% pure.*
3. Hexane, chromatographic quality.*
4. Calibration stock solution, 89 mg/mL. Dissolve 0.89 g (300 μL at 20 °C) 1,1,2,2-tetrabromoethane in tetrahydrofuran to make 10 mL of solution. Prepare fresh daily.
5. Desorption efficiency (DE) stock solution, 237 μg/μL. Dissolve 2.37 g (800 μL at 20 °C) 1,1,2,2-tetrabromoethane in hexane to make 10 mL of solution.
6. Nitrogen, purified.
7. Hydrogen, purified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh silica gel (front = 150 mg; back = 75 mg) separated by a 2-mm plug of urethane foam. A plug of silylated glass wool precedes the front section. A 3-mm plug of urethane foam follows the backup section. Pressure drop across tube must be <3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2003-1).
4. Vials, 2-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with pipet bulb.
6. Volumetric flasks, 10-mL.
7. Syringes, 500-μL, readable to 10 μL.
8. Syringes, 10-μL, readable to 0.1 μL.
9. U-tube, 25 cm x 15-mm ID, with glass stopcocks.
10. Temperature bath, 75 °C.

SPECIAL PRECAUTIONS: THF is a serious fire risk [flash point (open cup) = −15 °C]. Explosive peroxides can form in THF during exposure to air in the absence of an inhibitor. THF vapor irritates the eyes and respiratory tract and cause headache, dizziness and narcosis. THF liquid can irritate the skin. If THF is distilled, distill in the presence of ferrous sulfate or other reducing agent. Store THF under nitrogen in a dark glass or metal container.

1,1,2,2-Tetrabromoethane is toxic, narcotic and can irritate the eyes and skin [3].

n-Hexane is a serious fire risk [flash point (closed cup) = −30 °C]. Inhalation of n-hexane vapor can irritate the upper respiratory tract and cause depression of the central nervous system. n-Hexane as a liquid can cause dermatitis and irritate the eyes.

Work in a well-ventilated fume cabinet, wear gloves, avoid inhalation of vapors and protect solvents from sparks and open flame.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 50 to 100 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL THF to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 4 mg 1,1,2,2-tetrabromoethane per sample. Working standard should be prepared fresh daily.
   a. Add known amounts of calibration stock solution to THF in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. mg 1,1,2,2-tetrabromoethane).
9. Determine desorption efficiency (DE) at least once for each batch of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Place aliquots of DE stock solution into a U-tube partly immersed in a temperature bath at about 75 °C, and draw air through the U-tube into media blank samplers with a pump at 0.2 to 1 L/min.
      NOTE: Although values of DE for the original method [2] are based on liquid spikes, values of DE should be determined for vapor spikes. Values of DE for liquid and vapor spikes may be different [4].
   b. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
      NOTE: If breakthrough occurs with the vapor spikes, determine DE using liquid spikes.
   c. .Prepare a graph of DE vs. mg 1,1,2,2-tetrabromoethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with THF, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1,2,2-tetrabromoethane found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1,1,2,2-tetrabromoethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S117 [2] was evaluated with controlled atmospheres of 1,1,2,2-tetrabromoethane [1]. Overall precision ($\hat{S}_{rT}$) was 0.096 for 98-L samples (18 samples, pooled) at 6.5 to 23 mg/m^3. Concentrations found by this method, 6.5, 14 and 23 mg/m^3, were 7, 4 and 17% lower than the corresponding concentrations based on the delivery rate of the syringe pump and flow rates of dilution air in the generation system. The discrepancies were attributed to difficulties in generating the atmospheres. Breakthrough from front sections of sorbent was not observed during passage of 220 L of dry air at 0.9 L/min when the concentration was 23 mg/m^3. Breakthrough at high relative humidity was not tested. Portions of silica gel were fortified with solutions of 1,1,2,2-tetrabromoethane in hexane. Average values of desorption efficiency were 0.79, 0.92 and 0.98 after applications of 0.70-, 1.4- and 2.8-mg quantities of 1,1,2,2-tetrabromoethane; precision ($\hat{S}_r$) was 0.041 (18 samples, pooled). A storage study to determine the stability of 1,1,2,2-tetrabromoethane on silica gel was not performed. Peroxides in tetrahydrofuran may cause rapid deterioration of standard solutions of 1,1,2,2-tetrabromoethane; thus, standards should be prepared daily.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S117, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S117, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Acetylene Tetrabromide, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] Tucker, S. P., and G. J. Deye. Anal. Lett., 14 (A12), 959-976 (1981).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; S117 originally validated under NIOSH Contract CDC-99-74-45.

(1) 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and (2) 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

(1): CCl_3CClF_2 MW: 203.83 CAS: (1) 76-11-9 RTECS: (1) KI1425000
(2): CCl_2FCCl_2F (2) 76-12-0 (2) KI1420000

METHOD: 1016, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 500 ppm
NIOSH: 500 ppm
ACGIH: 500 ppm
(1 ppm = 8.34 mg/m^3 @ NTP)

PROPERTIES: solids; MP (1) 40.6 °C; (2) 25 °C; BP (1) 91.5 °C, (2) 93 °C; VP 5.3 kPa (40 mm Hg; 5.2% v/v) @ 20 °C; not combustible

SYNONYMS: (1): Refrigerant 112a.
(2): Refrigerant 112.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.035 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2 L

SHIPMENT: routine

SAMPLE STABILITY: not tested

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1): 2160 to 9020 mg/m^3 [1]
(2): 1880 to 8060 mg/m^3 [1]

BIAS: (1) 0.17%
(2) 2.0%

OVERALL PRECISION ($\hat{S}_{rT}$): (1): 0.069;
(2): 0.054 [1]

ACCURACY: (1) ± 32.4%
(2) ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,1,2-tetrachloro-2,2-difluoroethane; 1,1,2,2-tetrachloro-1,2-difluoroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

	(1)	(2)
TEMPERATURE-INJECTION:	185 °C	50 °C
-DETECTOR:	250 °C	240 °C
-COLUMN:	50 °C	50 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions in CS_2

RANGE: 2 to 20 mg per sample

ESTIMATED LOD: 0.3 mg per sample

PRECISION ($\bar{S}_r$): (1): 0.27 @ 4 to 17 mg per sample [1];
(2): 0.005 @ 4 to 17 mg per sample [1]

APPLICABILITY: The working range for either analyte is 120 to 1400 ppm (1000 to 12,000 mg/m^3) for a 2-L air sample. These compounds are used as degreasing solvents, refrigerants, foaming agents and corrosion inhibitors. Capillary columns may be used (DB-Wax or Nukol on fused silica, 3 m x 0.32-mm, 0.5 µm film) with appropriate changes in instrumental conditions.

INTERFERENCES: None reported.

OTHER METHODS: This combines and revises Methods S131 and S132 [2].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,1,2-Tetrachloro-2,2-difluoroethane and 1,1,2,2-tetrachloro-1,2-difluoroethane, reagent grade.*
3. Hexane, chromatographic quality.
4. Calibration stock solution, 0.2 mg/μL. Dissolve 2 g analyte in CS_2 to prepare 10 mL solution. Prepare in duplicate.
5. DE stock solution, 1 mg/μL. Dissolve 10 g analyte in hexane to prepare 10 mL solution. Prepare in duplicate.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.035 L/min, with flexible connecting tubing.
3. File, triangular.
4. Gas chromatograph, flame ionization detector, integrator and column (page 1016-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipets, 10- to 1000-μL.

SPECIAL PRECAUTIONS: Tetrachloro-1,2-difluoroethane has been determined to be a carcinogen [3]. Both analytes react with chemically-active metals such as sodium, potassium and beryllium or with powdered magnesium, aluminum and zinc.

Hazardous products such as hydrogen chloride, hydrogen fluoride and carbon monoxide may be released when either analyte decomposes. Both analytes will attack some forms of plastics, rubber and coatings.

Carbon disulfide is toxic and flammable; work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.035 L/min for a total sample size of 0.5 to 2 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain analyte concentrations in the range 0.3 to 20 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interests. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1016-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peaks area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

1,1,1,2-Tetrachloro-2,2-difluoroethane: Method S131 was issued on May 9, 1975 [2], and was validated at 2.08, 4.17 and 8.35 mg/m^3 [1]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 103.6% over the range 4 to 17 mg per sample. The breakthrough volume was 2.7 L when sampling 14,300 mg/m^3 at 0.035 L/min.

1,1,2,2-Tetrachloro-1,2-difluoroethane: Method S132 was issued on May 9, 1975 [2], and was validated at 20.05, 4.15 and 8.35 mg/m^3 [1]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 105% over the range 4 to 17 mg per sample. Breakthrough had not occurred after 3 h sampling 6990 mg/m^3 at 0.041 L/min. The test was stopped after 3 h.

REFERENCES:

[1] Documentation for the NIOSH Validation Tests, S131 and S132, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S131 and S132, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S.Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

Yvonne T. Gagnon, NIOSH/DPSE.

1,1,2,2-TETRACHLOROETHANE

$Cl_2CHCHCl_2$ M.W.: 167.85 CAS: 79-34-5 RTECS: KI8575000

METHOD: 1019, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: 1 ppm; carcinogen; Group I Pesticide
ACGIH: 1 ppm (skin)
(1 ppm = 6.86 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.5866 g/mL @ 25 °C; BP 146.5 °C; MP −44 °C; VP 0.8 kPa (6 mm Hg; 0.8% v/v) @ 25 °C; nonflammable

SYNONYMS: acetylene tetrachloride; bonoform; 1,1-dichloro-2,2-dichloroethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L @ 5 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 18 to 74 mg/m^3 [1] (10-L samples)

BIAS: 6.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 16.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,2,2-tetrachloroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 230 °C
-COLUMN: 160 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: stainless steel, 3 m x 3-mm OD, packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 0.1 to 1 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.016 @ 0.16 to 0.64 mg per sample [1]

APPLICABILITY: The working range is 1.5 to 15 ppm (10 to 100 mg/m^3) for a 10-L air sample. Capillary columns may be substituted for the packed column, with appropriate changes in instrumental conditions.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S124 [3] and the method which appears in the criteria document [4].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,2,2-Tetrachloroethane, reagent grade.*
3. DE stock solution, 50 mg/mL. Dilute 0.5 g 1,1,2,2-tetrachloroethane to 10 mL with CS_2.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated petroleum-based charcoal* (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (SKC 226-38, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1019-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: 1,1,2,2-Tetrachloroethane is a powerful narcotic, liver poison, and suspected carcinogen, and can be absorbed through the skin [4-6]. Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). Work with these substances only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of 1,1,2,2-tetrachloroethane to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 1,1,2,2-tetrachloroethane concentrations in the range 0.01 to 1 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg 1,1,2,2-tetrachloroethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg 1,1,2,2-tetrachloroethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1019-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1,1,2,2-tetrachloroethane found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1,1,2,2-tetrachloroethane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S124 was issued on May 9, 1975 [3], and validated with generated atmospheres which were calibrated by gas chromatography [1]. Average recovery was 106% at 5 ppm. Breakthrough did not occur after sampling 4 h at 0.185 L/min from an atmosphere containing 101 mg/m^3 in dry air. Desorption efficiency for SKC Lot 104 petroleum-based charcoal was 0.83, 0.87, and 0.88 at 0.16, 0.32, and 0.64 mg 1,1,2,2-tetrachloroethane per sample, respectively. Lower recoveries were observed for coconut shell charcoal (SKC Lot 105). In subsequent work, 1,1,2,2-tetrachloroethane was observed to degrade rapidly into trichloroethylene during storage on Pittsburgh activated carbon; 19% converted during one day and 63% converted during eight days at ambient conditions [7]. Therefore, the analyte is sensitive to the sorbent type; only the recommended sorbent should be used. Breakthrough at high relative humidity was not tested, nor was sample stability.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S124, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] UBTL Report for Sequence 1977 (NIOSH, unpublished, September 7, 1979).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S124, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Criteria for a Recommended Standard...Occupational Exposure to 1,1,2,2-Tetrachloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-121 (1976), available as PB 273-802 from NTIS, Springfield, VA 22161.
[5] NIOSH Current Intelligence Bulletin 27, Chloroethanes: Review of Toxicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-181 (1978).
[6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[7] Arnold, J. Internal memo (NIOSH, unpublished, May 8, 1984).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

TETRACHLOROETHYLENE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

TETRAETHYL LEAD (as Pb)

$Pb(C_2H_5)_4$ MW: 323.44 CAS: 78-00-2 RTECS: TP4550000

METHOD: 2533, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.075 mg/m^3 (as Pb; skin)
NIOSH: 0.075 mg/m^3 (as Pb; skin)
ACGIH: 0.1 mg/m^3 (as Pb; skin)

PROPERTIES: liquid; d = 1.653 g/mL @ 20 °C; BP 200 °C (dec.); MP −130 to −138 °C; VP 27 Pa (0.2 mm Hg; 2.2 g/m^3) @ 20 °C

SYNONYMS: TEL; lead tetraethyl

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2 resin, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 30 L
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.045 to 0.20 mg/m^3 (as Pb) (120-L samples) [1]

BIAS: 5.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 [1]

ACCURACY: ± 20.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetraethyl lead

DESORPTION: 1 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 20 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of tetraethyl lead in pentane

RANGE: 2 to 30 µg (as Pb) per sample

ESTIMATED LOD: 0.1 µg (as Pb) per sample [1]

PRECISION ($\hat{S}_r$): 0.067 @ 4.3 to 17 µg (as Pb) per sample

APPLICABILITY: The working range is 0.017 tp 0.23 mg/m^3 (as Pb) for a 120-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S383 [2].

REAGENTS:

1. Pentane (reagent grade).
2. Tetraethyl lead.*
3. XAD-2 resin (Rohm & Haas Co.)(optional, if commercial tubes are used). Extract, in order, for 24 h each in Soxhlet or Giant extractor with: water, methanol, diethylether, and n-pentane. Dry 24 h under vacuum (0.1 to 1 kPa) at low heat.
4. Calibration stock solution, 2 mg/mL (as Pb). Dissolve 31.2 mg tetraethyl lead (ca. 19 μL) in pentane to make 10 mL solution. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tubes, 10-cm long, 6-mm OD, and 4-mm ID with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 100 mg, back = 50 mg), separated and contained by silylated glass wool plugs. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min, with flexible connecting tubing.
3. Gas chromatograph, with photoionization detector, integrator, and column.
4. Vials, 2-mL, glass, with PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-μL, readable to 0.1 μL.
7. Pipet, 1 mL, with bulb.

SPECIAL PRECAUTIONS: Tetraethyl lead is extremely poisonous. Acute or chronic poisoning may occur if inhaled or absorbed through skin [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 30 to 200 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Add 1.0 mL pentane to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as 0.1% (v/v) dodecane, may be added to samples, blanks, and working standards at this step [2].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetraethyl lead (as Pb) concentrations in the range 0.1 to 30 μg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area vs. μg tetraethyl lead (as Pb)].

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg tetraethyl lead (as Pb) recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2533-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, t_r = 4.5 min for tetraethyl lead; dodecane elutes later.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of tetraethyl lead (as Pb) found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of tetraethyl lead (as Pb) in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S383 was issued on March 18, 1977 [2], and validated with generated atmospheres in the range 0.045 to 0.2 mg/m^3 for eighteen 120-L samples [1,4]. Partial breakthrough (effluent = 2.5% of test concentration) occurred after sampling for 240 min at 1.0 L/min from an atmosphere containing 0.156 mg/m^3 tetraethyl lead (as Pb) at 90% RH. Desorption efficiency for eighteen spiked samples in the range 4.3 to 17 μg tetraethyl lead (as Pb) averaged 1.05 with S_r = 0.04.

REFERENCES:

[1] A.D. Little, Inc. Backup Data Report S383 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S383, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

TETRAETHYL PYROPHOSPHATE 2504

$[(CH_3CH_2O)_2PO]_2O$ MW: 290.19 CAS: 107-49-3 RTECS: UX6825000

METHOD: 2504, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.05 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.05 mg/m^3 (skin)
(1 ppm = 11.86 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.185 g/mL @ 20 °C;
BP 124 °C @ 1 mm Hg; MP 32 °C;
VP 0.063 kPa (0.00047 mm Hg; 0.62 ppm)
@ 30 °C

SYNONYMS: diphosphoric acid tetraethyl ester; pyrophosphoric acid tetraethyl ester; TEPP

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 Chromosorb 102 tubes in series,
100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 20 L @ 0.05 mg/m^3
-MAX: 48 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 0.102 mg/m^3 [1]
(48-L samples)

BIAS: − 0.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.086 [1]

ACCURACY: ± 17.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD

ANALYTE: TEPP

DESORPTION: 1 mL toluene; stand 60 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 200 °C
-COLUMN: 115 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 2 m x 2-mm ID glass; Super-Pak 20M

CALIBRATION: TEPP in toluene

RANGE: 1 to 6 µg per sample [1]

ESTIMATED LOD: 0.1 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.039 [1]

APPLICABILITY: The working range is 0.025 to 0.15 mg/m^3 for a 40-L air sample. The method is useful for both area and personal samples.

INTERFERENCES: None identified.

OTHER METHODS: This is P&CAM 336 [2] in a revised format.

REAGENTS:

1. TEPP, purified*.
   NOTE: TEPP is hygroscopic and easily hydrolyzed.
2. Tripropyl phosphate, reagent grade, or other suitable internal standard.
3. Toluene, reagent grade.
4. Eluent: Dilute a weighed amount of tripropyl phosphate to 100 mL with toluene. Concentration of solution must be within the linear range of the FPD.
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered.
8. Calibration stock solution, 1.18 mg/mL. Dilute 11.8 mg (10 μL) TEPP to 10 mL with eluent. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes, 10-cm long, 8-mm OD, 6-mm ID, flame-sealed ends, front tube containing a 100-mg section of extracted resin and a back containing a 50-mg section, retained by silylated glass wool plugs in each tube. Pressure drop across the tubes in series at 1 L/min airflow must be less than 3.4 kPa. (Tubes commercially available as SKC, Inc. ST 226-105).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector, phosphorus filter, integrator and column (page 2504-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, volumetric, 10- and 100-μL.
6. Flasks, volumetric, 10-mL.
7. Pipettes, volumetric, 1-mL, with pipet bulb.
8. File.

SPECIAL PRECAUTIONS: TEPP is a cholinesterase inhibitor and can be absorbed through the skin. Wear protective gloves and suitable protective clothing when handling the pure material [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 20 to 48 L.
4. Separate the front and backup tubes. Cap the tubes with plastic (not rubber) caps. This prevents migration of TEPP between sorbent sections. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 6 μg TEPP per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg TEPP).

9. Determine desorption efficiency (DE) at least once for each batch of Chromosorb 102 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg TEPP recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2504-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of TEPP found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of TEPP in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 336 [2] was evaluated over the range 0.025 to 0.102 mg/m^3 at 21.5 °C and 735.3 mm Hg using 48-L samples [1,4]. Overall precision, $\hat{S}_{rT}$, was 0.086 with an average recovery of 99.4%, representing a non-significant bias. The concentration of TEPP was independently verified by sampling the generator with toluene-filled bubblers and analysis by GC/FPD. Desorption efficiency averaged 0.994 in the range 1.1 μg to 4.8 μg per sample. After sampling an atmosphere containing 0.41 μg/m^3 at 0.18 L/min at 90% RH for 300 min, only 0.2% of the influent concentration was detected breaking through the sorbent bed.

REFERENCES:

[1] Backup Data Report S305, TEPP, prepared under NIOSH Contract No. 210-76-0123 (August, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 336, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).

[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE; P&CAM 336 originally developed under NIOSH Contract No. 210-76-0123.

TETRAHYDROFURAN 1609

C_4H_8O MW: 72.11 CAS: 109-99-9 RTECS: LU5950000

METHOD: 1609, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 200 ppm
NIOSH: 200 ppm; STEL 250 ppm
ACGIH: 200 ppm; STEL 250 ppm
(1 ppm = 2.95 mg/m^3 @ NTP)

PROPERTIES: liquid; MP −108 °C; BP 66 °C; d 0.886 g/mL @ 20 °C; VP 19.3 kPa (145 mm Hg; 19% v/v) @ 20 °C; explosive range 2 to 11.8% v/v in air

SYNONYMS: diethylene oxide; THF

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 9 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 323 to 1240 mg/m^3 [1] (9-L samples)

BIAS: − 3.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 12.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: tetrahydrofuran

DESORPTION: 0.5 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 190 °C
-DETECTOR: 250 °C
-COLUMN: 185 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: tetrahydrofuran in CS_2

RANGE: 0.5 to 13 mg per sample

ESTIMATED LOD: 0.05 mg per sample

PRECISION ($\bar{S}_r$): 0.016 @ 3 to 11.8 mg per sample [1]

APPLICABILITY: The working range is 100 to 2600 mg/m^3 (34 to 880 ppm) for a 5-L air sample.

INTERFERENCES: High humidity may reduce the breakthrough volume of the charcoal tube. The column specified may not be appropriate for large numbers of samples. CS_2 tends to dissolve some porous polymers. An alternate GC column is 30 m x 0.32-mm ID fused silica capillary coated with 0.5 µm DBWAX at 60 °C [2].

OTHER METHODS: This revises Method S78 [3].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Tetrahydrofuran (THF), reagent grade.*
3. Hydrogen, prepurified,
4. Nitrogen, purified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less then 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1609-1).
4. Vials, glass, 1-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Pipet, 0.5-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Tetrahydrofuran and carbon disulfide are toxic and extremely flammable (flash points −17 °C and −30 °C, respectively) [4]. All work should be performed in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 9 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 0.5 mL CS_2 to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.05 to 13 mg THF per sample.
   a. Add known amounts of THF to CS_2 in 10-mL volumetric flasks and dilute to the mark with CS_2 to produce concentrations in the range 0.1 to 26 mg THF/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg THF).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (1 to 20 μL) of THF or a standard solution of THF in CS_2 directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg THF recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1609-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of THF found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of THF in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S78 was issued on February 14, 1975 [3]. The precision and bias were determined by analyzing generated atmospheres of tetrahydrofuran in dry air containing 323, 636 and 1240 mg/m^3 at 22.5 °C and 763 mm Hg using 9-L samples [1]. The concentrations were determined by comparison with a "bag" standard using a hydrocarbon analyzer. Storage stability was not assessed. Breakthrough of the front section of the charcoal tube was observed after sampling 13.32 L of dry test atmosphere containing 1140 mg/m^3 for 72 min at 0.185 L/min. Desorption efficiencies for samples spiked with tetrahydrofuran were 0.91 to 0.95 in the range 3 to 11.8 mg tetrahydrofuran per sample.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S78, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2, from Superintendent of Documents, Washington, DC 20402.
[2] User check, UBTL, Inc., NIOSH Sequence #4585-S (NIOSH, unpublished, March 21, 1985).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S78, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-0037-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Julie R. Okenfuss, NIOSH/DPSE; S78 originally validated under NIOSH Contract CDC-99-74-45.

TETRAMETHYL LEAD (as Pb) 2534

$Pb(CH_3)_4$ MW: 267.34 CAS: 75-74-1 RTECS: TP4725000

METHOD: 2534, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.075 mg/m³ (as Pb; skin)
NIOSH: 0.075 mg/m³ (as Pb; skin)
ACGIH: 0.15 mg/m³ (as Pb; skin)
(1 ppm = 8.47 mg/m³ as Pb)

PROPERTIES: liquid; d 1.995 g/mL @ 20 °C; BP 110 °C; MP −27.5 °C; VP 2.9 kPa (22 mm Hg; 245 g/m³ as Pb) @ 20 °C; lower explosive limit 1.8% v/v in air

SYNONYMS: TML; lead tetramethyl; tetra methyl plumbane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2 resin, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 15 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 98% recovered after 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.04 to 0.18 mg/m³ (as Pb) (24-L samples) [1]

BIAS: − 0.27%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.112

ACCURACY: ± 22.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetramethyl lead

DESORPTION: 2 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 17 mL/min

COLUMN: 6 m x 3-mm OD stainless steel packed with 10% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solution of tetramethyl lead in pentane

RANGE: 1 to 10 µg (as Pb) per sample

ESTIMATED LOD: 0.4 µg (as Pb) per sample [2]

PRECISION ($\bar{S}_r$): 0.0763 @ 0.9 to 3.6 µg (as Pb) per sample [1]

APPLICABILITY: The working range is 0.04 to 0.4 mg/m³ (as Pb) for a 24-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S384 [2].

REAGENTS:

1. Pentane (reagent grade).
2. Tetramethyl lead.*
3. Calibration stock solution, 0.4 mg/mL (as Pb). Dissolve 5.16 mg tetramethyl lead (ca. 2.6 μL) in pentane to make 10 mL solution. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD and 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 400 mg, back = 200 mg), separated and contained by silylated glass wool plugs. Pressure drop <3.4 kPa @ 1 L/min airflow. Tubes are commercially available (SKC, Inc. ST226-30-06).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with photoionization detector, integrator, and column (page 2534-1).
4. Vials, 4-mL, glass, and PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-μL, readable to 0.1 μL.
7. Pipets, 1- and 2-mL.

SPECIAL PRECAUTIONS: Tetramethyl lead is extremely poisonous with delayed symptoms [3]. Acute or chronic poisoning may occur if inhaled or absorbed through skin.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 15 to 100 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 2.0 mL pentane to each vial containing 400 mg sorbent, and 1.0 mL pentane to each vial containing 200 mg sorbent. Cap each vial.
   NOTE: A suitable internal standard (e.g., 0.1% v/v nonane) may be added to samples and blanks at this step [1].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetramethyl lead concentrations in the range 0.2 to 5 μg/mL (as Pb).
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area or peak height vs. μg tetramethyl lead (as Pb)].
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject a known amount (2 to 20 μL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. μg tetramethyl lead (as Pb) recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2534-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, t_r = 6 min for tetramethyl lead.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of tetramethyl lead (as Pb) found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of tetramethyl lead (as Pb) in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S384 was issued on April 15, 1977 [2], and validated with generated atmospheres [1,3]. Average recovery was 97.4% ± 6.5% (18 samples) in the range 0.04 to 0.18 mg/m^3 for 24-L samples. No breakthrough occurred after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.312 mg/m^3 tetramethyl lead (as Pb) at 82% RH. Desorption efficiency for eighteen spiked samples in the range 0.89 to 3.6 μg per sample averaged 0.84 with $\bar{S}_r$ = 0.091. Sample migration between front and back sorbent sections was found to be negligible after storage for 10 days at room temperature.

REFERENCES:

[1] A. D. Little, Inc. Backup Data Report S384 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S384, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

TETRAMETHYL THIOUREA 3505

$(CH_3)_2NC(=S)N(CH_3)_2$ MW: 132.23 CAS: 2782-91-4 RTECS: YU2750000

METHOD: 3505, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: no recommended exposure limit
ACGIH: no standard

PROPERTIES: solid; MP 78 °C; BP 245 °C

SYNONYMS: 1,1,3,3-tetramethyl-2-thiourea; TMTU

SAMPLING

SAMPLER: IMPINGER (water)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 50 L @ 0.3 mg/m³
-MAX: 250 L

SHIPMENT: ship impinger contents in vial

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; high-volume air or settled dust

ACCURACY

RANGE STUDIED: generated atmospheres not studied

BIAS: unknown

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: tetramethyl thiourea-pentacyanoamine-ferrate coordination complex

WAVELENGTH: 590 nm

CALIBRATION: solutions of tetramethyl thiourea-pentacyandamine ferrate coordination complex in water

RANGE: 15 to 150 µg per sample

ESTIMATED LOD: 3 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.02 @ 15 to 150 µg per sample [1,2]

APPLICABILITY: The working range is 0.15 to 10 mg/m³ for a 100-L air sample. Tetramethyl thiourea is used in the manufacture of adhesives and polychloroprene rubber. The method was also applied to ethylene thiourea [1].

INTERFERENCES: Compounds containing a thione (C=S) group will complex with the pentacyanoamineferrate reagent and may interfere with the analyte absorbance band at 590 nm. Other compounds that absorb at 590 nm may interfere.

OTHER METHODS: This method was originally designated P&CAM 282 [1], which it replaces.

REAGENTS:

1. Bromine, Br_2, ACS reagent grade.*
2. Disodium pentacyanonitrosyl ferrate dihydrate (sodium nitroferricyanide; sodium nitroprusside), $Na_2Fe(CN)_5NO \cdot 2H_2O$, ACS reagent grade.
3. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, ACS reagent grade.
4. Sodium bicarbonate, $NaHCO_3$.
5. Water, distilled or deionized.
6. Complexing reagent (see APPENDIX).
7. Dilute complexing reagent. Mix one volume complexing reagent with two volumes water. Prepare fresh daily.
8. Tetramethyl thiourea (TMTU), reagent grade.*
9. TMTU stock solution, 1000 μg/mL.* Dilute 0.250 g TMTU to 250 mL with distilled water.
10. Calibration stock solution, 20 μg/mL. Dilute 5 mL TMTU stock solution to 250 mL with distilled water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget impinger with 15 mL water.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing and splashover protection (empty impinger or glass wool in tube between sampler and pump).
3. Spectrophotometer to operate at 590 nm with matched glass cuvettes, 5-cm optical path length.
4. Analytical balance, 0.1 mg.
5. Mortar and pestle.
6. Test tubes, 20-mL, calibrated at 15.0 mL.
7. Vials, glass, 20-mL, with PTFE-lined screw caps.
8. Beaker, 50-mL.
9. Pipets, adjustable (0.1- to 5-mL), with disposable tips.
10. Volumetric flasks, 25- and 250-mL.
11. Tweezers.
12. Microspatula.
13. Rubber suction bulb.
14. Weighing paper.
15. Filter funnel, stand and filter paper.

SPECIAL PRECAUTIONS: Bromine is very corrosive and causes severe burns; vapors are extremely irritating and toxic. Wear gloves and handle only in a hood.

Tetramethyl thiourea is an animal teratogen and carcinogen [3]. Avoid inhalation, ingestion or skin contact. Keep TMTU in a bottle labelled "animal carcinogen" and place the bottle in a resealable thick-walled plastic bag in locked storage.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 50 to 250 L. Transfer the sample solution to a 20-mL vial for shipment.
3. Collect a high-volume air sample or rafter dust sample. Ship in a glass vial in a separate container.

SAMPLE PREPARATION:

4. Transfer contents of the vial to a test tube. Add water to the 15-mL mark.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards over the range 3 to 150 μg TMTU per sample.
   a. Pipet 0- to 10-mL aliquots of calibration stock solution into clean vials. Bring the total volume to 15 mL with distilled water.

b. Analyze together with the samples and blanks (steps 6 through 8).
c. Prepare calibration graph (absorbance vs. μg TMTU).

MEASUREMENT:

6. Complexation.
   NOTE: Perform this step at the same time for both working standards and samples. Color degradation occurs at the rate of ca. 2% in 3 h.
   a. Pipet 1.5 mL dilute complexing reagent into each test tube or vial.
   b. Allow to stand for at least 30 min with occasional shaking to ensure full color development.
      NOTE: The color of the complex varies with increasing concentration from yellow to light green to turquoise. Very high concentrations have Prussian blue color; dilute these with distilled water before analysis and use the appropriate dilution factor in calculations.
7. Transfer the solution to a clean 5-cm cuvette. Remove droplets from cuvette windows with lens paper.
8. Measure absorbance at 590 nm vs. reference cell containing 15 mL distilled water and 1.5 mL dilute complexing reagent.
   NOTE 1: Sensitivity is ca. 0.006 absorbance unit/μg.
   NOTE 2: Scan the absorbance of the bulk sample (several mg of bulk sample dissolved in 15 mL water and treated as in steps 6 through 8) in the range 350 to 700 nm. Compare to spectrum of TMTU to detect possible interferences.

CALCULATIONS:

9. Determine the mass of TMTU (μg) for the sample (M) and average media blank (B).
10. Calculate the concentration of TMTU, C, in the air volume sampled, V (L):

$$C = \frac{(M - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was tested with 35 standards in the range 15 to 150 μg per sample with an average $\bar{S}_r$ of 2% [1,2]. All calibration graphs indicated a minimum linear correlation coefficient of 0.9999 [2]. TMTU spiked on VM-1 (PVC) filter samples could not be recovered with water or methanol in waterbath temperatures up to 60 °C because it reacted with the filter material [2]. The method was also used on 42 field samples collected in midget impingers in a survey [2]. The amounts of TMTU found ranged from 9 to 302 μg per sample.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 282, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[2] Palassis, J. Sampling and Analytical Determination of Airborne Tetramethyl and Ethylene Thiourea, Am. Ind. Hyg. Assoc. J., 41, 91-97 (1980).
[3] Registry of Toxic Effects of Chemical Substances, V. 3, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-107 (1983).

METHOD WRITTEN BY:

John Palassis, NIOSH/DTMD.

APPENDIX:

PREPARATION OF COMPLEXING REAGENT

1. Weigh 0.500 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in a 50-mL beaker. Dissolve in 10 mL distilled water.
2. Grind together 0.500 g $NH_2OH \cdot HCl$ and 1.00 g $NaHCO_3$ in a mortar.
3. In a hood, add the ground mixture to the solution from step 1 above. When bubbling ceases, add 0.10 mL bromine. When reaction stops, add ca. 10 mL distilled water. Filter. Rinse beaker with 4 mL distilled water and filter. Transfer filtrate to a 25-mL volumetric flask and dilute with distilled water to the mark. Refrigerate.

TETRANITROMETHANE 3513

$C(NO_2)_4$ MW: 196.0 CAS: 509-14-8 RTECS: PB4025000

METHOD: 3513, Issue 1 **EVALUATION:** FULL **Issue 1:** 15 August 1994

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: 1 ppm
(1 ppm = 8.02 mg/m^3)

PROPERTIES: colorless liquid, pungent odor; BP = 125.7 °C; MP = 12.5 °C; sp. gravity = 1.650 (13 °C)

SYNONYMS: TNM; Tetan

SAMPLING

SAMPLER: IMPINGER (ethyl acetate, 15 mL)

FLOW RATE: 0.5 to 1.0 L/min

VOL-MIN: 20 L @ 1 ppm
-MAX: 250 L

SHIPMENT: refrigeration recommended

SAMPLE STABILITY: 14 days refrigerated

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.70 to 11.5 mg/m^3 [1] (250-L sample)

BIAS: 0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 21.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NPD

ANALYTE: tetranitromethane

DILUTION: ethyl acetate

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 160 °C
-DETECTOR: 200 °C
-COLUMN: 40 °C

COLUMN: 30 m, 0.32-mm ID, 1-µm film thickness DB-1 capillary column [2]

CALIBRATION: solutions of tetranitromethane in ethyl acetate

RANGE: 17 to 660 µg per sample

ESTIMATED LOD: 5 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.011 [2]

APPLICABILITY: The working range is 0.02 to 2.5 ppm (0.2 to 20 mg/m^3) for a 100-L air sample. A flame ionization detector can be used but has less sensitivity. A Stabilwax-DB capillary column can be used as an alternate to a DB-1 capillary column [2].

INTERFERENCES: Any nitrogen or phosphorus compound with a similar retention time as tetranitromethane.

OTHER METHODS: This method revises and modifies S224 [1].

REAGENTS:

1. Tetranitromethane.
2. Ethyl acetate, nanograde.
3. Helium, purified.
4. Nitrogen, purified.
5. Hydrogen, purified.
6. Compressed air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget impinger containing 15 mL ethyl acetate.
2. Personal sampling pump, 0.5 to 1.0 L/min, with flexible connecting tubing and splash over protection.
3. Gas chromatograph, NPD, integrator and column (page 3513-1).
4. Vials, 20-mL, with PTFE screw caps.
5. Syringes, 10-μL, and other convenient sizes.
6. Volumetric flasks, 25-mL, 10-mL.

SPECIAL PRECAUTIONS: Tetranitromethane is highly toxic and extremely explosive [3]. Use fume hood and protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler inline.
2. Pipette 15 mL of ethyl acetate into each impinger. Attach midget impinger to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.5 to 1.0 L/minute for a total sample size of 20 to 250 L.
   NOTE: Routinely check and fill impingers to insure that the level of ethyl acetate remains at a volume of 10 to 15 mL.
4. Transfer the sample solution to 20-mL vial. Rinse impinger stem and body with 1 to 2 mL ethyl acetate, and add to the 20-mL vial.
5. Pack securely for shipment.

SAMPLE PREPARATION:

6. Transfer samples into 25-mL volumetric flasks and dilute to volume with ethyl acetate.
7. Transfer 1 mL aliquot to autosampler vials and immediately cap vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 17 to 660 μg tetranitromethane per sample.
   a. Add known amounts of tetranitromethane to ethyl acetate in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. Prepare calibration graph (peak area vs. μg tetranitromethane).
9. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 3513-1. Inject 1-μL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethyl acetate,

reanalyze and apply the appropriate dilution factor in calculations.

11. Measure peak area.

CALCULATIONS:

12. Determine the mass, μg, of tetranitromethane found in the impinger sample (W) and average media blank (B).
13. Calculate concentration, C (mg/m^3), of tetranitromethane in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method was validated over the range of 2.70 to 11.5 mg/m^3 at 19 °C and 763 mm Hg using a 250-L sample [1]. Collection efficiency was 0.895 ± 0.01 at 11.5 mg/m^3; this was used as a correction factor in the validation experiments. The overall precision ($\hat{S}_{rT}$) was 0.076 and the bias was not significant [1]. In a later study, the LOD was determined to be 5 μg per sample and the analytical precision was 0.011 [2]. Tetranitromethane was stable for 14 days in 15-mL ethyl acetate solution. However, it is recommended that the samples be stored under refrigeration.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2 ed., Vol. 3, S224, DHEW (NIOSH) Publication No. 77-157-C (1977).

[2] Pendergrass, S.M. Method Development for Tetranitromethane, MRSB, DPSE, NIOSH (unpublished, 1991).

[3] Hawley's Condensed Chemical Dictionary, 11th ed., N.I. Sax and R.J. Lewis, Eds. Van Nostrand Reinhold Co., New York (1987).

METHOD REVISED BY:

Stephanie M. Pendergrass, NIOSH/DPSE.

THALLIUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

THIRAM

$((CH_3)_2NC(=S)S-)_2$ MW: 240.43 CAS: 137-26-8 RTECS: JO1400000

METHOD: 5005, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group I Pesticide
ACGIH: 1 mg/m^3

PROPERTIES: white crystalline powder; d 1.29 g/mL; MP 155 °C; VP not significant

SYNONYMS: bis(dimethylthiocarbamoyl)disulfide; tetramethylthiuram disulfide; tetramethylthioperoxydicarbonic diamide

SAMPLING

SAMPLER: FILTER (1-μm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days at 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable; 1 to 5g

ACCURACY

RANGE STUDIED: 3 to 12 mg/m^3 [1] (240-L samples)

BIAS: − 0.18%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 10.67%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Thiram

EXTRACTION: (filter) 10 mL CH_3CN, 30 min; (cassette top) 10 mL CH_3CN rinse

INJECTION VOLUME: 5 μL

MOBILE PHASE: 60% acetonitrile/40% water, 1 mL/min

COLUMN: μ-Bondapak C_{18} (30 cm x 3.9-mm-ID stainless steel); ambient temperature

DETECTOR: UV @ 254 nm, 1-cm cell

CALIBRATION: standard solutions of Thiram in acetonitrile

RANGE: 0.1 to 3 mg per sample [1]

ESTIMATED LOD: 0.005 mg per sample [1]

PRECISION ($\hat{S}_r$): 0.012 [1]

APPLICABILITY: The working range is 0.5 to 15 mg/m^3 for a 200-L air sample. NIOSH researchers have used this method at facilities that use Thiram as an insecticide.

INTERFERENCES: None known.

OTHER METHODS: This is Method S256 [2] in a revised format. An earlier spectrophotometric method, P&CAM 228 [3], has not been revised because of excessive analytical variability [4].

REAGENTS:

1. Acetonitrile, HPLC grade.*
2. Water, distilled, deionized.
3. Thiram, reagent grade.*
4. Air or nitrogen, compressed, for drying syringes.
5. Calibration stock solution, 0.75 mg/mL. Dissolve an accurately weighed 7.5 mg Thiram in acetonitrile and dilute to 10 mL. Prepare fresh daily in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 1-μm PTFE membrane filter (Millipore FA or equivalent), 37-mm diameter, two-piece polystyrene cassette filter holder with backup pad, sealed with tape or a shrinkable band. Filter holders made of Tenite should not be used.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Liquid chromatograph, UV detector at 254 nm,integrator and column (page 5005-1).
4. 13 mm x 5 μm PTFE filters and stainless steel filter holder to protect the LC column.
5. Vials, 20-mL, glass, PTFE-lined screw caps.
6. Syringe, 1-mL, with Luer-Lok fitting.
7. Pipets, 10-mL, with pipet bulb.
8. Tweezers.
9. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetonitrile is toxic and flammable; work with it only in a hood.

Thiram is an irritant of skin and mucous membranes, a skin sensitizer, and suspected teratogen [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 4 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Collect a bulk sample (1 to 5 g) in a glass vial with PTFE-lined cap; ship separately from filters.

SAMPLE PREPARATION:

4. Remove filter from cassette with tweezers and place in 20-mL vial.
5. Add 10 mL acetonitrile. Cap the vial.
6. Rinse the inside top of cassette with 10 mL acetonitrile into a 20-mL vial. Cap the vial.
7. Agitate samples during the 30-min desorption period.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.005 to 3 mg Thiram per sample.
   a. Add known amounts of calibration stock solution to acetonitrile in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg Thiram).

MEASUREMENT:

9. Set liquid chromatograph to conditions on page 5005-1. Inject 10-μL sample aliquot. Rinse and dry syringe between injections.
10. Measure peak area.

CALCULATIONS:

11. Read the mass, mg, of Thiram found in the sample filter (W_f) and top rinse (W_t) and in the average media blank (B) from calibration graph.
12. Calculate the concentration of Thiram, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_f + W_t - B) \cdot 10^3}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S256 was issued on June 8, 1979 [2], and validated by collecting 18 samples (six each at one-half, one and two times the OSHA standard) from dynamically-generated test atmospheres using Thiram 65 (65% Thiram; Mayer Chemical Co.), as well as a set of six samples which was stored at room temperature for seven days to establish stability [1,4]. The stored sample results were within 2.1% of samples analyzed after one day, indicating adequate storage stability for seven days. Eighteen more samples were spiked directly (six each at one-half, one and two times the OSHA standard). The pooled relative standard deviation for these three sets of samples was found to be 0.012. The average recovery for all three levels was 99.8%; therefore, there is no bias for this method. The pooled relative standard deviation for the three sets of samples collected from test atmospheres was 0.022. Test atmospheres at 12 mg/m^3 Thiram were sampled with PTFE filters followed by bubblers containing acetonitrile; no detectable Thiram (LOD = 0.005 mg) was found in the bubblers indicating that vapor pressure of Thiram was insignificant.

REFERENCES:

[1] Backup Data Report S256, NIOSH Contract 210-76-0123, available as Order No. PB 81-244634 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] Ibid, V. 1, P&CAM 228, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Failure Report S256, NIOSH Contract CDC-99-74-45 (unpublished, 1976).
[5] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Yvonne T. Gagnon, NIOSH/DPSE; S256 originally validated under NIOSH Contract 210-76-0123.

TITANIUM

See ELEMENTS (Method 7300)

METALS IN URINE (Method 8310)

TOLUENE (passive)

$C_6H_5CH_3$ MW: 92.14 CAS: 108-88-3 RTECS: XS5250000

METHOD: 4000, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : 200 ppm; C 300 ppm; P 500 ppm
NIOSH: 100 ppm; STEL 150 ppm
ACGIH: 50 ppm (skin)
(100 ppm = 3.77 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.866 g/mL @ 20 °C; BP 110.6 °C; MP −95 °C; VP 3.8 kPa (28 mm Hg; 3.7% v/v) @ 25 °C; explosive range 1.3 to 7.1% v/v in air

SYNONYMS: methylbenzene; phenyl methane; toluol

SAMPLING

SAMPLER: PASSIVE (activated carbon)

SAMPLE TIME-MIN: 15 min @ 200 ppm
-MAX: 8 h @ 20 to 200 ppm

SHIPMENT: see step 2 - if necessary, transfer sorbent pad to septum-capped vial; otherwise, routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C if stored in septum-capped vial

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: desirable

ACCURACY

RANGE STUDIED:	75 to 2250 mg/m^3 [1]
BIAS:	not significant [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.038 [1]
ACCURACY:	± 7.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: toluene

DESORPTION: 1.5 mL carbon disulfide; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 200 °C
-COLUMN: 100 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: 3.6 m x 3-mm OD SP-1000 on 80/100 mesh Chromosorb WHP

CALIBRATION: analyte solutions in CS_2

RANGE: 0.5 to 15 mg per sample

ESTIMATED LOD: 0.01 mg per sample

PRECISION ($\hat{S}_r$): 0.022 [1]

APPLICABILITY: The working range is 13 to 660 ppm (50 to 2500 mg/m^3) for a 4-hour sample. The method is applicable to STEL determinations. The method determines toluene vapor only (not aerosol). Competitive adsorption by water vapor and other volatile organic solvents affects sampler capacity.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: NIOSH Methods 1500 and 1501 [2] employ active sampling on charcoal tubes with overall sensitivity about the same as this method.

REAGENTS:

1. Eluent: carbon disulfide (CS_2), chromatographic quality.*
2. Toluene, reagent grade.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: passive monitor with activated charcoal collection element. Monitors must be of known sampling rate for toluene.
2. Gas chromatograph, FID, integrator and column (page 4000-1).
3. Vials, glass, 2-mL, with PTFE-lined septum caps.
4. Pipet, TD, 1.5-mL, and pipet bulb.
5. Syringes, 5-, 10-, 25- and 100-μL.
6. Volumetric flasks, 10-mL.
7. Tweezers.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = −30 °C); work with it only in a fume hood.

SAMPLING:

1. Remove sampler from package and remove caps, if applicable. Attach sampler in worker's breathing zone. Make sure sampler inlets are unobstructed. Record start of sampling time. Follow manufacturer's recommendations to estimate appropriate sampling time based on relative humidity and suspected concentration of toluene.
   NOTE: The uptake constant is only valid for samplers in air with ambient velocity higher than ca. 10 cm/sec. For area samples, ensure adequate air movement.
2. Terminate sampling by sealing the sampler as recommended by the manufacturer or by transferring, in a toluene-free environment, the activated charcoal collection element to a vial and sealing the vial with a septum cap. Use tweezers for handling the collection element, taking care not to touch any activated charcoal.
   NOTE: Some sampler designs (e.g., 3M 3500 [3]) do not require transfer of the collection element; others (e.g., Gilian Trace Air OVM-1 and OVM-2) require transfer of sorbent pad to a sealed vial. Some sampler designs (e.g., Draeger ORSA-5) use granular sorbent.

SAMPLE PREPARATION:

3. Add 1.5 mL CS_2 to each collection element.
4. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards.
   a. Add known amounts of toluene to CS_2 in 10-mL volumetric flasks and dilute to the mark to produce toluene concentrations in the range 0.01 to 10 mg/mL.
   b. Analyze with samples and blanks (steps 8 through 10).
   c. Prepare calibration graph (peak area vs. mg toluene).
6. Determine desorption efficiency (DE) in the calibration range at least once for each lot of samplers used. Prepare three samplers at each of five concentrations plus three media blanks.
   a. Place the collection element of a media blank sampler into a vial and cap.
   b. Inject a known amount of toluene directly onto the collection element with a microliter syringe.
   c. Allow to stand overnight.

d. Desorb (steps 3 and 4) and analyze with working standards.
e. Prepare a graph of DE vs. mg toluene recovered.

7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

8. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 4000-1.
9. Inject sample aliquot manually using solvent flush technique or with an autosampler.
   NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
10. Measure peak area.

CALCULATIONS:

11. Determine the mass, mg (corrected for DE), of toluene found on the sample collection element (W) and on the average media blank (B).
    NOTE: If W > sampler capacity x 0.33, the sampler may be saturated [4]. Evaluate each result on the basis of other organics present in the sampled atmosphere, the concentrations of all the adsorbable organics present, the ambient relative humidity, the sampling rate for the organics present and the sampling time.
12. Calculate concentration, C (mg/m^3), of toluene in the air sampled:

$$C = \frac{(W - B) \cdot 10^6}{t \cdot K}.$$

where: t = length of sampling period (min)
K = uptake constant (cm^3 toluene/min).

NOTE: The uptake constant must be known accurately (either be supplied by the sampler manufacturer or determined by the user by calibration with standard toluene-in-air mixtures [5]). K can be estimated from the diffusion coefficient, D (cm^2/min), the cross-sectional area, A (cm^2), and the diffusion pathlength, L (cm), of the sampler:

$$K = \frac{D \cdot A}{L}.$$

EVALUATION OF METHOD:

Precisions and biases listed in the method were determined by analyzing generated atmospheres containing various concentrations of toluene at a range of humidities and in the presence of other volatile organics [3]. Generated concentrations were independently verified.

REFERENCES:

[1] Perkins, J. B., N. H. Price, L. Eggenberger and J. A. Burkart. Evaluation of Passive Organic Vapor Monitors, available as PB83-221028 from NTIS, Springfield, VA 22161 (1981).

[2] NIOSH Manual of Analytical Methods, 3rd ed., V. 2, NMAM 1500, 1501. U.S. Department of Health and Human Services, Publ. (NIOSH) 84-100 (1984).

[3] Rodriguez, S. T., D. W. Gosselink, and A. E. Mullins. "Determination of Desorption Efficiencies in the 3M 3500 Organic Vapor Monitor," Am. Ind. Hyg. Assoc. J., 43, 569-574 (1982).

[4] Woebkenberg, M. L. Unpublished data (1982).

[5] Cassinelli, M.E.; R.D. Hull; J.V. Crable; A.W. Teass, "Protocol for the Evaluation of Passive Monitors," In: Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring. A. Berlin, R.H. Brown; K.J. Saunders; Royal Society of Chemistry, Burlington House, London (1987).

METHOD WRITTEN BY:

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2,4- AND 2,6-TOLUENEDIAMINE (in the presence of isocyanates)

$CH_3C_6H_3(NH_2)_2$ MW: 122.17 CAS: 2,4-: 95-80-7 2,6-: 823-40-5 RTECS: 2,4-: XS9625000 2,6-: XS9750000

METHOD: 5516, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989** **Issue 2: 15 August 1994**

OSHA : no PEL
NIOSH: 2,4-: lowest feasible; carcinogen
ACGIH: no TLV

PROPERTIES: 2,4-: solid; MP 99 °C
2,6-: solid; MP 106 °C

SYNONYMS: 2,4-: 4-methyl-1,3-benzenediamine; 2,4-diaminotoluene
2,6-: 2-methyl-1,3-benzenediamine; 2,6-diaminotoluene

SAMPLING

SAMPLER: IMPINGER (solution of 1-(2-methoxyphenyl)-piperazine in toluene, 15 mL)

FLOW RATE: 1 L/min

VOL-MIN: 30 L @ 10 $\mu g/m^3$
-MAX: 500 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C in the dark [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTES: 2,4- and 2,6-bisacetamidotoluene

PREPARATION: acetylate 4 hour, evaporate, redissolve in 1.5 mL methanol

INJECTION VOLUME: 10 μL

MOBILE PHASE: programmed; sodium acetate in acetonitrile/water at pH 6.0; 1.0 mL/min; ca. 20 °C

COLUMN: 10 cm x 8-mm octadecylsilylated silica (C_{18}), 5-μm particle size, in Waters RCM-100 radial compression module

CALIBRATION: standard solution of analytes in methanol

RANGE: 0.3 to 3 μg per sample [1]

ESTIMATED LOD: 0.1 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.06 @ 0.74 to 0.89 μg per sample [1]

APPLICABILITY: The working range is 3 to 30 $\mu g/m^3$ for a 100-L air sample. This method, based on that of Warwick et al. for isocyanates [2], determines 2,4- and 2,6-toluenediamine in air in the presence of isocyanates. Samples from polyurethane foam plants were analyzed simultaneously for 2,4- and 2,6-toluenediamine and 2,4- and 2,6-toluene diisocyanate [1].

INTERFERENCES: m-Phenylenediamine interferes in the determination of 2,4-toluenediamine.

OTHER METHODS: Holdren et al. [3] reported a similar method using N-(4-nitrobenzyl)propylamine in toluene for sampling and HPLC with electrochemical detection. Other methods are: (a) absorb on Tenax GC, desorb in toluene, GC [4]; (b) absorb on silica gel, desorb in 2-butanone, GC [5]; (c) sample in aqueous acid, work up, GC of free amines [6] or bis(heptafluorobutyryl)amides [7,8]; (d) sample in ethanolic KOH, workup, LC of free amine [9,10] or GC of bis(pentafluoropropionyl) amides [11]; (e) sample with sulfuric acid-coated filter, work up, GC of bis(heptafluorobutyrl)amides [12]. Some of these methods [3,9-11] can be used for the simultaneous determination of toluenediamines and toluene diisocyanates.

REAGENTS:

1. Toluene, reagent grade.
2. 1-(2-Methoxyphenyl)piperazine, purified (see APPENDIX A).
3. Sampling medium: 43 μg/mL 1-(2-methoxyphenyl)piperazine in toluene.
4. 2,4-Toluenediamine*, reagent grade.
5. 2,6-Toluenediamine*, reagent grade.
6. Acetic anhydride, reagent grade.
7. Methanol, reagent grade.
8. Mobile phase A: Dissolve 60 mg anhydrous sodium acetate in 1 L of 12% acetonitrile in distilled water. Add 17% (V/V) aqueous acetic acid. Bring pH to 6.0.
9. Mobile phase B: Acetonitrile, chromatographic quality.
10. Water, distilled deionized.
11. Sodium acetate, anhydrous.
12. 2,4-Bisacetamidotoluene, See APPENDIX B).
13. 2,6-Bisacetamidotoluene, (See APPENDIX B).
14. Calibration stock solution, 0.5 μg/μL. Dissolve 5 mg each of 2,4- and 2,6-bisacetamidotoluene in methanol. Dilute to 10 mL.
15. Nitrogen, prepurified.
16. Pentane*, purified.

* See SPECIAL PRECAUTIONS

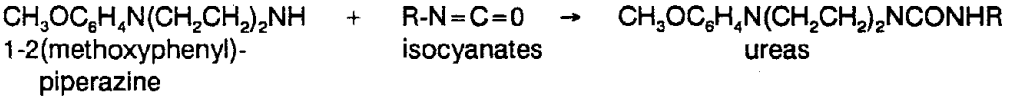
EQUIPMENT:

1. Sampler: midget impinger, 25-mL.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. Liquid chromatograph (HPLC) with 229-nm UV detector, recorder, integrator, and column (page 5516-1).
4. Vials, 4-mL and 20-mL, glass, with PTFE-lined caps.
5. Pipets, pasteur, 14.6-cm, glass disposable.
6. Volumetric flasks, 10-mL.
7. Syringes, 10- and 100-μL.
8. Pipets, 2-mL (graduated) and 15-mL, glass, with pipet bulb.
9. Water bath.
10. Hotplate, spark-free, 35 to 50 °C.
11. Evaporator, Mini-Vap, six-port, or equivalent.
12. pH meter.
13. Beakers, 250-mL.
14. Flask, filtration, 500-mL.
15. Funnel, Buchner, fritted glass, 100-mL.
16. Vacuum pump.
17. Vacuum desiccator.
18. Watchglass.

SPECIAL PRECAUTIONS: 2,4-Toluenediamine is a cancer suspect agent [13]; 2,6-Toluenediamine may be mutagenic [14]. Handle these chemicals carefully in a hood or glove box, and avoid working-surface contamination which might occur by spillage or by dissipation of fine powder from opening of containers or making transfers.
Pentane is highly volatile and flammable. Take adequate precautions while handling pentane.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15.0 mL sampling medium to an impinger.
3. Connect the assembled impinger to a sampling pump.
4. Sample 30 to 500 L of air at an accurately measured sampling rate of 1 L/min. When it is necessary to add solvent for proper impinger operation during sampling, add only toluene.
   NOTE: The reagent in the sampling medium reacts with isocyanates present to form ureas, thus preventing reaction of the isocyanate with the toluenediamines.



5. Transfer sample solution, including condensed water, to a 20-mL vial for shipment. Rinse impinger with 1 to 2 mL toluene. Add rinsings to sample solution.

SAMPLE PREPARATION:

6. Add 25 μL acetic anhydride to acetylate the 2,4- and 2,6-toluenediamine and excess 1-(2-methoxyphenyl)piperazine. Allow 4 hours for completion of reactions. Evaporate sample to dryness under a gentle stream of nitrogen while warming to 40 to 50 °C on a hotplate. Redissolve residue in 1.5 mL methanol.
   NOTE: The acetylation reaction for 2,4-toluenediamine to produce 2,4-bisacetamidotoluene is:

$$\underset{\text{2,4-toluenediamine}}{CH_3C_6H_3(NH_2)_2} + \underset{\text{acetic anhydride}}{2CH_3COOCOCH_3} \rightarrow \underset{\text{2,4-bisacetamidotoluene}}{CH_3C_6H_3(NHCOCH_3)_2} + \underset{\text{acetic acid}}{2\ CH_3COOH.}$$

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards.
   a. Using aliquots of calibration stock solution, prepare working standards of 2,4- and 2,6-bisacetamidotoluene in methanol covering the range 0.1 to 3 μg/mL each.
   b. Analyze these with the unknown and blank samples (steps 9 through 11).
   c. Prepare calibration graphs (peak height vs. μg 2,4- and 2,6-toluenediamine per sample). Multiply the concentration (μg/mL) of bisacetamidotoluene by 0.889 mL to obtain the quantity (μg) of toluenediamine per sample.
      NOTE: The factor 0.889 includes the MW of toluenediamine (122.17), the MW of bisacetamidotoluene (206.24), and the 1.5-mL solution volume from step 6.
8. Prepare three quality control samples by adding known quantities of 2,4- and 2,6-toluenediamine to 15 mL of sampling medium and analyze (steps 9 through 11).

MEASUREMENT:

9. Set up the HPLC system according to the manufacturer's recommendations and to the conditions given on page 5516-1. The mobile phase program is:
   a. Linear gradient 100% A to 90% A over t = 0 to 8 min.
   b. 90% A to 40% A over t = 8 to 19 min following the convex gradient % A = $90 - 31\ (t - 8)^{1/5}$.
   c. Hold at 40% A for 1 min, or as long as necessary to clear the column.
   d. Return to 100% A and hold for 7 min before the next run.
   NOTE: If only 2,4- and 2,6-toluenediamine are to be quantified, the mobile phase program may be modified to hasten elution of the ureas derived from the isocyanates.
10. Inject a 10-μL aliquot of solution from step 6 or step 7b.
11. Measure the peak heights. Adjusted retention times for some compounds of interest are:

2,6-bisacetamidotoluene	5.2 min
1,4-bisacetamidobenzene	7.8 min
1,3-bisacetamidobenzene	9.4 min
2,4-bisacetamidotoluene	9.7 min
1-acetyl-4-(2-methoxyphenyl)piperazine	14.3 min
urea derivative of 2,6-toluene diisocyanate	17.0 min
urea derivative of 2,4-toluene diisocyanate	18.3 min

CALCULATIONS:

12. Using the calibration graphs, determine the mass, μg, of 2,4- and of 2,6-toluenediamine in each sample (W) and in the average media blank (B).
13. Calculate the concentration, C, of 2,4- and of 2,6-toluenediamine in the air volume sample, V (L):

$$C = \frac{(W - B)}{V},\ mg/m^3.$$

EVALUATION OF METHOD: [1]

The relationship of peak height and concentration of 2,4- and 2,6-bisacetamidotoluene in methanol was found to be essentially linear over the ranges 0.05 to 141 μg/mL and 0.14 to 84 μg/mL, respectively. The time required for completion of the acetylation reaction was determined using samples equivalent to 0.7 μg of 2,4-toluenediamine and 0.9 μg of 2,6-toluenediamine in 15 mL of sampling medium. Aliquots (2 mL) were treated with 10 μL of acetic anhydride and allowed to stand 0.25 to 6 hrs before further workup and analysis. The acetylation of 2,6-toluenediamine was the slower reaction, but it appeared complete after 4 h. Sample stability was studied using solutions of 2,4- and 2,6-toluenediamine in sampling medium at levels corresponding to 0.89 and 0.74 μg per sample, respectively. The recoveries, ranging from 97% to 106%, suggested the samples were stable under the conditions of storage -- 1, 7, and 14 days at room temperature in the dark. The potential for interference from isocyanates was investigated by drawing air containing 7.3 μg each of 2,4- and 2,6-toluene diisocyanate through samples of 0.9 μg each of 2,4- and 2,6-toluenediamine in 15 mL of sampling medium. The recoveries from these samples, averaging 95%, suggested that, when compared to identical samples not treated with toluene diisocyanate, a small but statistically significant negative bias was caused by the isocyanate. Using the data from all of the recovery experiments, the relative standard deviation (S_r) for 2,4-toluenediamine (0.74 and 0.83 μg per sample) ranged from 0.01 to 0.08 with a pooled average ($\bar{S}_r$) of 0.05 and for 2,6-toluenediamine (0.89 μg per sample) ranged from 0.02 to 0.14 with a pooled average ($\bar{S}_r$) of 0.06.

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METHOD WRITTEN BY:

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APPENDIX A:

PURIFICATION OF 1-(2-METHOXYPHENYL)PIPERAZINE:

Place 25 g 1-(2-methoxyphenyl)piperazine (yellowish white solid) in a 250-mL beaker. Add ca. 125 mL pentane. Bring to a boil (CAUTION: Pentane is FLAMMABLE) on a water bath and allow to boil until all but a small amount of yellow oil is in solution. The 1-(2-methoxyphenyl)piperazine will melt as it is warmed in the pentane. Decant the solution into a clean beaker, cover with a watchglass, and cool in the freezer for 2 to 3 h. Collect the resulting white needles in a Buchner funnel using suction filtration and dry them in a vacuum desiccator. The crystals are hygroscopic and melt at 26 to 29 °C. Store them in an airtight container in a refrigerator.

APPENDIX B:

SYNTHESIS OF 2,4- AND 2,6-BISACETAMIDOTOLUENE:

Place 0.5 g of 2,4- or 2,6-toluenediamine in a 250-mL beaker. Add ca. 100 mL of distilled water and warm to dissolve the compound. Filter the solution, if necessary. Chill the solution in an ice bath, then slowly add 5 mL acetic anhydride and stir. After keeping the mixture at least 1 h in the ice bath, collect the solid product by suction filtration. Recrystallize the product from water by dissolving it in boiling water, filtering the hot solution, chilling the filtrate in a refrigerator, and collecting the precipitate by suction filtration. Dry the precipitate in a vacuum desiccator.

2,4-Bisacetamidotoluene recrystallizes as white needles and melts at 230 °C.

2,6-Bisacetamidotoluene recrystallizes as brownish needles and melts at ca. 318 °C.

TOLUENE-2,4-DIISOCYANATE

$C_9H_6N_2O_2$ MW: 174.16 CAS: 584-84-9 RTECS: CZ6300000

METHOD: 2535, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : C 0.02 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 0.005 ppm; STEL 0.02 ppm
(1 ppm = 7.12 mg/m^3 @ NTP)

PROPERTIES: liquid; MP 19.5-21.5 °C; BP 251 °C; density 1.2244 g/mL @ 20 °C; VP ca. 1.3 Pa (0.01 mm Hg; 0.96 mg/m^3) @ 20 °C

SYNONYMS: 2,4-TDI; 2,4-bis(carbonylamino)toluene; 2,4-tolylene diisocyanate

SAMPLING

SAMPLER: TUBE WITH REAGENT-COATED GLASS WOOL (N-[(4-nitrophenyl)methyl]-propylamine on glass wool)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 2 L @ 0.02 ppm
-MAX: 170 L

SHIPMENT: protect from light

SAMPLE STABILITY: at least 14 days @ 25 °C [1]

STABILITY OF REAGENT ON GLASS WOOL: ≤ 7 days @ 25 °C; ≥ 4 weeks @ −21 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.039 to 0.53 mg/m^3 [1] (67-L samples)
BIAS:	− 0.5% [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.033 [1]
ACCURACY:	± 7.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 3,3'-bis[(4-nitrophenyl)methyl]-3,3'-dipropyl-1,1'-(4-methyl-1,3-phenylene) diurea (2,4-TDIU)

DESORPTION: 2 mL CH_3OH; ultrasonic bath, 3 min

INJECTION VOLUME: 50 µL

MOBILE PHASE: 55:45 (v/v) CH_3CN:H_2O with 0.08% Et_3N and 0.16% H_3PO_4; 1.0 mL/min

COLUMN: 25 cm x 4.6 mm; octadecylsilylated silica, 5-µm particle size

DETECTOR: UV @ 254 nm

CALIBRATION: standard solutions of 2,4-TDIU in CH_3OH

RANGE: 0.3 to 25 µg 2,4-TDI per sample

ESTIMATED LOD: 0.1 µg 2,4-TDI per sample

PRECISION ($\bar{S}_r$): 0.067 [1]

APPLICABILITY: The working range is 0.004 to 0.35 ppm (0.03 to 2.5 mg/m^3) for a 10-L air sample. This method is applicable to isocyanate vapors (2,4-TDI vapor, 2,6-TDI vapor, and hexamethylene diisocyanate (HDI) vapor) [2,3], but not aerosols because of inefficient collection of aerosols and incomplete reaction of aerosol isocyanates with reagent.

INTERFERENCES: The reagent is slightly unstable in the dark at 25 °C. Tailing during HPLC, a result of reagent deterioration, may raise detection limits .

OTHER METHODS: This revises P&CAM 326 [4]. Sangö used similar HPLC conditions [5]. Melcher reviewed methods for isocyanates [6]. Method 5521 (Isocyanates, Monomers), using collection in an impinger, is an alternative method.

REAGENTS:

1. 2,4-TDI* (see APPENDIX A).
2. N-[(4-nitrophenyl)methyl]-propylamine hydrochloride.
3. 2,4-TDIU (see APPENDIX B).
4. Methanol, chromatographic quality.
5. Calibration stock solution, 10 mg/mL. Dissolve 50 mg 2,4-TDIU in methanol to make 5 mL solution.
6. Water, distilled.
7. NaOH, 1 M.
8. Toluene, reagent grade.
9. Dichloromethane, reagent grade.
10. Hexane, reagent grade.*
11. Nitrogen, purified, compressed.
12. Mobile phase. Mix 0.8 mL triethylamine and 1.6 mL H_3PO_4 with 1 L 55:45 CH_3CN:H_2O (v/v).*
13. Dibutylamine, 99% pure.
14. Tetrahydrofuran, reagent grade.*
15. Bromocresol purple indicator solution.
16. HCl, 0.05 M, standardized.
17. 2,4-TDI stock solution, 100 mg/mL. Dissolve 500 mg 2,4-TDI in dichloromethane to make 5 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 4 cm x 6-mm ID, containing two sections of tightly compressed, reagent-coated glass wool (see Appendix C) (front = 7 mm; back = 5 mm), wrapped entirely with black tape; open ends with plastic caps.
   NOTE: Protect sampler from light. Store sampler in the dark at -21 °C up to 4 weeks, or at 25 °C up to 7 days.
   Pressure drop across the tube must be <3.4 kPa at 1 L/min air flow. Tubes available commercially by special order (SKC, Inc.).
2. Separatory funnels, 125-mL.
3. Beakers, 50- and 125-mL.
4. Aluminum foil.
5. Glass wool, silanized.
6. Glass rod, 15 cm x 4 mm.
7. Tweezers.
8. Rubber tubing, opaque 1.5 cm x ca. 8-mm ID.
9. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
10. High pressure liquid chromatograph, 254-nm UV detector, integrator, and column (page 2535-1).
11. Vials, glass, 2-mL, caps lined with PTFE.
12. Pipets, 2-, 15-, and 25-mL.
13. Ultrasonic bath.
14. Syringes, 100-µL, readable to 1 µL.
15. Syringes, 10-µL, readable to 0.1 µL.
16. Volumetric flasks, 5-mL.
17. Buret, 50-mL.
18. U-tube, glass, 25 cm x 15-mm ID, glass stopcocks.
19. Sorbent tube, glass, 7 cm x 6 mm, coconut shell charcoal, ca. 150 mg.

SPECIAL PRECAUTIONS: 2,4-TDI can irritate the eyes and skin, and can cause bronchial asthma and allergic eczema. Flash points of hexane, tetrahydrofuran and triethylamine are −26 °C, −17 °C, and −6 °C, respectively.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove plastic caps from sampler. Attach sampler to personal sampling pump with flexible tubing.
3. Sample 2 to 170 L of air at 0.2 to 1 L/min.
4. Seal ends of sampler with plastic caps. Pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer front and back sections of reagent-coated glass wool to separate vials. Add 2 mL methanol. Seal vials.
6. Place vials into ultrasonic bath for 3 min.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.3 to 80 μg 2,4-TDIU per sample (equivalent to 0.1 to 25 μg 2,4-TDI per sample).
   a. Prepare a series of standard solutions of 2,4-TDIU in methanol over the range of 0.15 to 40 μg/mL.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. μg 2,4-TDIU).
8. Determine recoveries from samplers in the range 0.3 to 25 μg 2,4-TDI per sample. Prepare three samples at each of three levels plus three media blanks.
   NOTE: Recoveries should be quantitative. If recoveries are not quantitative, determine the reason for error.
   a. Prepare a series of standard solutions of 2,4-TDI in dichloromethane in the range 0.06 to 5 mg/mL.
   b. Connect a U-tube to the inlet of a sampler with a short piece of tubing.
      NOTE: The length of tubing should be minimal to prevent losses of TDI by adsorption or reaction on the inside wall of the tubing.
   c. Connect charcoal sorbent tube to inlet of U-tube (charcoal can adsorb contaminants of air which would react with 2,4-TDI).
   d. Draw ambient air through the charcoal tube, U-tube, and sampler with a sampling pump at 1 L/min.
   e. Place 5 μL of a standard solution of 2,4-TDI into the U-tube.
   f. Allow operation of the pump to continue for 20 min.
   g. Desorb (steps 5 and 6) and analyze with working standards (steps 9 and 10).

MEASUREMENT:

9. Establish chromatographic conditions indicated on page 2535-1.
10. Inject sample aliquot manually or with autosampler. Measure peak area.

CALCULATIONS:

11. Determine the mass (μg) of 2,4-TDIU found on the sample front (W_f) and back (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
12. Calculate concentration, C, of 2,4-TDI in the air volume sampled, V (L):

$$C = \frac{0.310\ (\ W_f + W_b - B_f - B_b\ )}{V},\ mg/m^3,$$

where 0.310 = MW of 2,4-TDI/MW of 2,4-TDIU.

EVALUATION OF METHOD:

A variation of this method which involved normal-phase HPLC (Method P&CAM 326) was tested with fortified samplers and atmospheres generated with a diffusion cell [1,4]. Average recoveries of 2,4-TDIU from front sections of reagent-coated glass wool were 0.97 to 0.99 after applications of 1.0-, 2.1-, 9.9-, and 20.0-μg quantities of 2,4-TDI from a U-tube; $\bar{S}_r$ was 0.067 (21 samples, pooled). $\bar{S}_r$ was 0.033 (29 samples, pooled) for 67-L samples at 0.039 to 0.53 mg/m^3. The independent method used for evaluation was that of Meddle and Wood [7]. Average concentrations ranged from 0.054 to 0.46 mg/m^3 by the independent method [1]. Conclusive evidence for bias in the reagent-coated glass wool method was not found. Breakthrough volume was 71 L (0.53 mg/m^3, 1 L/min); breakthrough volume was 279 L (0.14 mg/m^3, 1 L/min). 2,4-TDIU was stable on coated glass wool at room temperature in the dark for 14 days. The reagent, N-[(4-nitrophenyl)methyl]propylamine, is unstable [1].

Evaluation of samplers with 2,4-TDI aerosols was not performed. However, samplers were inefficient collectors when aerosol particles were present in an atmosphere of 4,4'-methylenediphenylisocyanate (MDI). The collection efficiency of each sampler for MDI was about 90% (flow rate, 1 L/min; total concentration of MDI in vapor and aerosol forms, about 0.52 mg/m^3; mass median diameter of MDI particles, about 0.6 μm; geometric standard deviation, about 2.2) [1].

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METHOD WRITTEN BY:

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APPENDIX A: Determination of Purity of 2,4-TDI

Dissolve 480 μL (365 mg, 0.00282 mole) dibutylamine in 10 mL tetrahydrofuran. Add 100 μL (122 mg, 0.000701 mole) 2,4-TDI. Stir the mixture and allow to stand 6 min. Add a few drops of bromocresol purple indicator solution. Prepare two additional samples in this manner. Titrate excess dibutylamine with 0.05 M HCl. Calculate percent purity, P, of 2,4-TDI for each sample:

$$P = \frac{B - (V \cdot M)}{2W} \cdot 100.$$

where: B = Molar quantity of dibutylamine before reaction (0.00282)
V = Volume of 0.05 M HCl (L)
M = Concentration of HCl (0.05 M)
2 = Number of moles of dibutylamine required to react with 1 mole of 2,4-TDI
W = Molar quantity of 2,4-TDI added to tetrahydrofuran solution (0.000701)

APPENDIX B: Preparation of 2,4-TDIU [8]

Dissolve 1.03 g (0.00446 mole) N-[(4-nitrophenyl)methyl]-propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)methyl]propylamine with 50 mL toluene, and separate the phases. Add a solution of 262 µL (321 mg, 0.00184 mole) 2,4-TDI in 30 mL toluene to the solution of N-[(4-nitrophenyl)methyl]propylamine. Collect the precipitate by filtration. Purify the product by dissolving it in a small volume of dichloromethane and precipitating it with hexane. Dry the product in vacuo (MP = 136 to 139 °C).

APPENDIX C: Preparation of Reagent-Coated Glass Wool

Dissolve 300 mg (0.00130 mole) N-[(4-nitrophenyl)methyl]propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)-methyl]propylamine with 50 mL hexane. Transfer 40 mL of the hexane solution to a 50-mL beaker which is wrapped with aluminum foil and contains 1.82 g silanized glass wool. Under dim light, evaporate hexane from the beaker with the aid of a stream of nitrogen. Knead the glass wool with a glass rod to produce a uniform coating. Continue to evaporate hexane until the glass wool appears dry. Protect the coated glass wool from bright light. The quantity of coated glass wool is sufficient for the preparation of the front and back sections for twenty samplers.

o-TOLUIDINE

See AMINES, AROMATIC (Method 2002) for procedure

TRIBUTYL PHOSPHATE 5034

$(C_4H_9O)_3P=O$ MW: 266.32 CAS: 126-73-8 RTECS: TC7700000

METHOD: 5034, Issue 1 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1994

OSHA : 0.5 ppm
NIOSH: 0.2 ppm
ACGIH: 0.2 ppm
(1 ppm = 10.9 mg/m^3 @ NTP)

PROPERTIES: liquid; boiling point 293 °C; density 0.98 g/mL @ 20 °C; VP very low @ 20 °C; vapor density 9.2 (air = 1); flash point 166 °C (closed cup)

SYNONYMS: phosphoric acid, tributyl ester; tri-*n*-butyl phosphate; TBP; Celluphos 4

SAMPLING

SAMPLER: FILTER (0.8-μm mixed cellulose ester membrane); above 23 °C, use two filter cassettes in series

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 0.5 ppm
-MAX: 100 L

SHIPMENT: separate front and backup cassettes if two were used; seal cassettes firmly with plugs

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.7 to 12.6 mg/m^3 [1] (100-L samples)

BIAS: − 0.3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 16.8%

MEASUREMENT

TECHNIQUE: GC, FPD with a phosphorus filter

ANALYTE: tributyl phosphate

EXTRACTION: 10 mL diethyl ether

INJECTION VOLUME: 5 μL

DETECTOR: H_2, 70 mL/min; Air 150 mL/min

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 240 °C
-COLUMN: 150 °C

CARRIER GAS: N_2, 50 mL/min

COLUMN: 6-ft x ⅛-in ID stainless steel, with 3% OV-101 on 100/120 mesh Supelcoport

CALIBRATION: standard solutions of tributyl phosphate in diethyl ether

RANGE: 6 to 1500 μg per sample

ESTIMATED LOD: 2 μg per sample [1]

PRECISION ($\hat{S}_r$): 0.0146 @ 234 to 973 μg per sample [1]

APPLICABILITY: The working range is 0.006 to 1.4 ppm (0.06 to 15 mg/m^3) for a 100-L air sample. This method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions.

INTERFERENCES: Any phosphorus-containing compound that has the same retention time as the analyte is an interference. A non-polar capillary column may be used for better resolution.

OTHER METHODS: This revises Method S208 [2]. Analytical methods for tributyl phosphate (TBP) have been reviewed [3]. Another packed-column GC procedure has been described recently [4]. TBP has been determined in air by capillary-column GC/NPD preceded by sampling on a glass fiber filter or XAD-7 resin [5]. GC/MS [6], LC/MS [7], and LC/TID (thermionic detection) [8] have all been shown to be useful methods for the analysis of TBP in environmental samples. Finally, a continuous phosphorus gas analyzer has been used to monitor TBP in air [9].

REAGENTS:

1. Diethyl ether*, anhydrous, reagent grade.
2. Tributyl phosphate*, reagent grade.
3. Hydrogen, purified
4. Compressed air, prefiltered
5. Nitrogen, purified
6. Calibration stock solution, tributyl phosphate in diethyl ether

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm mixed cellulose ester membrane filter (0.8-μm pore size) supported by cellulose backup pad in three-piece filter holder.
   NOTE: Backup filter unit is needed when sampling at temperatures above 23 °C.
2. Personal sampling pump, 1 to 3 L/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph equipped with a flame photometric detector, phosphorus filter, and column (p. 5034-1).
4. Electronic integrator or some other suitable method for measuring peak areas.
5. Tweezers.
6. Jars: 2 oz ointment jars for sample extraction, squat form with aluminum-lined screw caps.
7. Syringes, 10-μL and other convenient sizes.
8. Volumetric flasks, 10-mL and other convenient sizes.
9. Pipets, 10-mL and other convenient sizes.

SPECIAL PRECAUTIONS: Store diethyl ether away from heat, light, and sources of ignition in a well-ventilated area. Do not leave container open. Diethyl ether can oxidize in air to form explosive peroxides, a reaction accelerated by light. Distillation and evaporation can concentrate unstable peroxides in the residue, a potentially explosive condition [10].

Avoid inhalation of tributyl phosphate vapors and contact with eyes, skin, and clothing [11,12]. Handle only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with the representative filter cassettes in line.
2. Remove cassette plugs and connect cassette filter to the personal sampling pump with flexible tubing.
   NOTE: If ambient temperature is above 23 °C, use two filter cassettes connected in series with a short piece of flexible tubing for sample collection. Some tributyl phosphate may exist as vapor above 23 °C.
3. Sample at an accurately known flow rate of 1 to 3 L/min for a total sample size of 2 to 100 L.
4. Separate front and backup filter cassettes (if two cassettes were used). Firmly seal collected sample cassettes with plugs, and pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the filter and backup pad to an ointment jar using tweezers.
6. Pipet 10.0 mL of diethyl ether into each jar. Seal the jar immediately to minimize evaporation.
7. Allow samples to stand for at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 2 to 1000 μg per sample.
   a. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with diethyl ether.
   b. Analyze working standards together with samples and blanks (steps 11 and 12). This will minimize the effect of variations in FPD response with time.
      NOTE 1: The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards be carefully interspersed with the samples.
      NOTE 2: Use of an internal standard is recommended to minimize errors caused by sample solvent evaporation and FPD response variations.
   c. Prepare a calibration graph of area vs. μg of tributyl phosphate per 10 mL of sample.
9. Determine recovery in the concentration range of interest for each lot of filters used for sampling. Prepare three filters at each of five levels plus three media blanks.
   a. Spike aliquot of calibration solution onto each filter.
   b. After air-drying, extract filters with 10 mL diethyl ether (steps 5 through 7).
   c. Analyze together with working standards (steps 11 and 12).
   d. Prepare graph of recovery vs. μg tributyl phosphate.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5034-1. Inject 5-μL sample aliquot using solvent flush technique or with autosampler.
    NOTE: If peak area is above linear range of the calibration graph, dilute with diethyl ether, analyze, and apply appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, μg (corrected for recovery), of tributyl phosphate found in the sample (W) and the average media blank (B).
14. Calculate concentration of tributyl phosphate in the actual air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 2.7 to 12.6 mg/m^3 at 19 °C and pressure of 761 mm Hg with 100-L air samples [1]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.076. The average collection efficiencies for test concentrations of 12.6 mg/m^3 and 9.3 mg/m^3 were 100.0% and 99.6%, respectively. The average recovery from filters spiked in the range 234 μg to 973 μg per filter was 100.4%. Therefore, there is no significant bias in the method. No tests of sample stability during storage were conducted.

REFERENCES:

[1] Backup Data Report for Tributyl Phosphate, in Documentation of the NIOSH Validation Tests, prepared under NIOSH Contract CDC-99-74-45 (1977).

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S208, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

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[4] Kuno, Y., Hina, T., Akiyama, T., and Matsui, M., Simultaneous Determination of Tributyl Phosphate and Dibutyl Phosphate in Spent Fuel Reprocessing Streams by Gas Chromatography, J. Chromatogr., 537 (1-2): 489 (1991).

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[6] Ishikawa, S., Taketomi, M., and Shinohara, R., Determination of Trialkyl and Triaryl Phosphates in Environmental Samples, Water Res., 19 (1): 119 (1985).

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[10] Material Safety Data Sheet for Diethyl Ether, No. 343, General Electric Company, Schenectady, N.Y., August, 1979.

[11] Material Safety Data Sheet for Tributyl Phosphate, No. 521, General Electric Company, Schenectady, N.Y., October, 1983.

[12] Material Safety Data Sheet for Tributyl Phosphate, No. P1180.2, Van Waters & Rogers, Inc. (U.S.), Seattle, Washington, August 27, 1989.

METHOD REVISED BY:

Robert P. Streicher, Ph.D., NIOSH/DPSE.

1,1,2-TRICHLOROETHANE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

TRICHLOROETHYLENE

$CCl_2=CHCl$ MW: 131.39 CAS: 79-01-6 RTECS: KX4550000

METHOD: 1022, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 100 ppm; C 200 ppm; P 300 ppm
NIOSH: 25 ppm; C 2 ppm/1 h (waste anesthetic); suspect carcinogen; Group 1 Pesticide
ACGIH: 50 ppm; STEL 200 ppm; suspect carcinogen
(1 ppm = 5.37 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.46 g/mL @ 20 °C; BP 87 °C; MP −86 °C; VP 9.9 kPa (74 mm Hg; 9.8% v/v) @ 25 °C; explosive range 11 to 41% v/v in air

SYNONYMS: trichloroethene; ethylene trichloride; triclene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 477 to 2025 mg/m^3 (3.4-L samples) [1]

BIAS: − 7.19%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.082 [1]

ACCURACY: ± 19.78%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: trichloroethylene

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel, packed with 10% OV-101 on 100/200 mesh Chromosorb WHP

CALIBRATION: standard solutions of trichloroethylene in CS_2

RANGE: 0.5 to 10 mg per sample

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.038 @ 1.6 to 6.4 mg per sample [1]

APPLICABILITY: The working range is 27 to 875 ppm (150 to 4700 mg/m^3) for a 3.4-L air sample. The method is applicable to STEL determinations. The method was used for samples containing 0.5 to 5 mg trichloroethylene from a tool-degreasing operation [2].

INTERFERENCES: None studied. Alternate columns which have been used are stainless steel, 6 m x 3 mm OD, packed with 10% SP-1000 on 80/100 mesh Supelcoport [2] and fused silica capillary, 60 m x 0.32 mm, coated with 0.25 µm OV-351 [3].

OTHER METHODS: This combines and revises methods S336 [4] and P&CAM 127 [5]. The criteria document method is similar [6]. NIOSH Method 3701 uses a portable gas chromatograph for field readout.

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. Trichloroethylene (TCE), reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1022-1).
4. Vials, 2-mL, PTFE-lined septum caps.
5. Syringes, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). Trichloroethylene is a suspect carcinogen and a narcotic [6,7,8]. Work with these substances only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as ethylbenzene [1], undecane [2], or octane [3] at 0.1% (v/v) may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of TCE to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain TCE concentrations in the range 0.01 to 10 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg TCE).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of TCE, or a standard solution thereof in CS_2, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg TCE recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1022-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of TCE found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of TCE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S336 was issued on June 6, 1975 [4], and validated with generated atmospheres using a calibrated syringe drive [1]. Average recoveries were 92 to 94% (16 samples) in the range 477 to 2025 mg/m^3 for 3.4-L samples. Breakthrough volume of 18.5 L (effluent = 5% of test concentration) occurred after sampling for 99 min at 0.187 L/min from an atmosphere containing 2266 mg/m^3 trichloroethylene in dry air. Desorption efficiency for SKC Lot 105 activated coconut charcoal in the range 1.6 to 6.4 mg per sample averaged 96.4% with $\bar{S}_r$ = 0.7% (18 samples). n-Octane was used as an internal standard in the chromatographic measurements. The semi-quartile ranges of desorption efficiencies in two rounds of the Proficiency Analytical Testing (PAT) program were 0.97 to 1.0 for charcoal tubes spiked with 0.6 to 1.1 mg trichloroethylene [9].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S336, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available at Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] UBTL Report for NIOSH Sequence #4266-R (NIOSH, unpublished, March 26, 1984).
[3] UBTL Report for NIOSH Sequence #4266-N (NIOSH, unpublished, March 14, 1984).

[4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S336, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
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[8] Special Occupational Hazard Review with Control Recommendations -- Trichloroethylene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-130 (1978).
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METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

TRICHLOROETHYLENE by portable GC 3701

$Cl_2C=CHCl$ MW: 131.39 CAS: 79-01-6 RTECS: KX4550000

METHOD: 3701, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 August 1987 **Issue 2:** 15 August 1994

OSHA : 100 ppm; C 200 ppm; P 300 ppm
NIOSH: 25 ppm; C 2 ppm/1 h; carcinogen
ACGIH: 50 ppm; 200 ppm STEL; suspect carcinogen
(1 ppm = 5.37 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.46 g/mL @ 20 °C; BP 87 °C; MP −86 °C; VP 7.7 kPa (58 mm Hg; 7.6% v/v) @ 20 °C; explosive range 11 to 41% v/v in air

SYNONYMS: trichloroethane

SAMPLING

SAMPLER: AIR BAG (Tedlar)

FLOW RATE: 0.02 to 0.05 L/min or higher; fill bag to ≤80% of capacity; spot samples possible (step 2.1.)

SAMPLE STABILITY: bags should be analyzed as soon after collection as possible (≤4 h)

BLANKS: clean air, either in bag or from a non-work area

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: trichloroethylene (TCE)

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 10 to 1000 ppm

ESTIMATED LOD: 0.25 ng per injection (0.1 ppm for a 1-mL injection

PRECISION ($\bar{S}_r$): 0.078

ACCURACY

RANGE STUDIED: 25 to 100 ppm

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.078

ACCURACY: > ± 15%

APPLICABILITY: The working range is 10 to 1000 ppm (54 to 5400 mg/m^3) in relatively non-complex atmospheres where trichloroethylene is known to be present (see EVALUATION OF METHOD).

INTERFERENCES: None found.

OTHER METHODS: Method 1022 [1] uses activated charcoal sampler tubes.

REAGENTS:

1. Trichloroethylene (TCE)* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure trichloroethylene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 0.05 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
3. Bags, Tedlar, 2- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC, and for preparation of bag standards.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labelling bags.

SPECIAL PRECAUTIONS: TCE is a suspect carcinogen [2]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A straight line baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. **Spot sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections, if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration; and
      (4) set conditions such that peaks are at least 50% of full scale.
   b. **Integrated air sample for TWA determination.**
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
         NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to a personal sampling pump suitable for bag filling with a minimum length of flexible tubing.
      (3) Pump the air to be sampled into the sample bag at a rate calculated to fill $\leq$ 80% of the sample bag capacity over the sampling period.
         NOTE: The flow rate must remain within $\pm$ 5% of the initial setting throughout the sampling period.

(4) Within 4 hrs after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2.a).

3. Obtain the TCE peak height of the injected sample.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph by at least three replicate determinations of at least six working standards. Plot peak height vs. mass of TCE.
   b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
   c. Determine the ability of the GC column to separate the TCE peak from other substances known or predicted to be present in the field samples.
5. Establish a daily calibration graph (peak height vs. ng of TCE) by triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of TCE in sample by comparison of peak height with daily calibration graph (step 5). Determine concentration, C, of TCE in the injected sample, V (mL):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

NOTE: Some GCs perform this calculation electronically.

EVALUATION OF METHOD:

This method was evaluated using an AID Model 590 portable GC. Gas bags containing known amounts of TCE in air were used to establish the calibration graph. The response of the portable GC was then compared to the concentration obtained from analysis of replicate charcoal tube samples taken from the same bag. A six-inch strip chart recorder was used to obtain peak height data from the portable GC.

A limitation in the use of this type of portable GC (e.g., packed column, room temperature isothermal) is the limited ability to separate the analyte from any interferences present. In the evaluation of this method, a six-foot DC 200 column was used. Its ability to separate the TCE peak from other contaminants was not evaluated. However, the use of this or any other packed column operated at room temperature to separate complex mixtures is severely limited. Therefore, the application of this method should be confined to relatively uncomplicated atmospheres.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 3rd ed., V. 2, NMAM 1022. U.S. Department of Health and Human Services, Publ. (NIOSH) 84-100 (1984).

[2] NIOSH Current Intelligence Bulletin 2, Trichloroethylene, NIOSH (June 6, 1975), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-127 (1979).

METHOD WRITTEN BY:

J.C. Posner, Ph.D., NIOSH/DPSE

1,2,3-TRICHLOROPROPANE

See HYDROCARBONS, HALOGENATED (Method 1003) for procedure

1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE 1020

CCl_2F - $CClF_2$ MW: 187.38 CAS: 76-13-1 RTECS: KJ4000000

METHOD: 1020, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1000 ppm; STEL 1250 ppm
NIOSH: 1000 ppm; STEL 1250 ppm
ACGIH: 1000 ppm; STEL 1250 ppm
(1 ppm = 7.66 mg/m^3 NTP)

PROPERTIES: clear liquid; d = 1.55 g/mL @ 20 °C; BP = 47.6 °C; MP −35 °C; vapor pressure = 38 kPa (384 mm Hg, 51% v/v) @ 20 °C

SYNONYMS: Freon 113, Refrigerant 113, Freon TF

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 1000 ppm
-MAX: 3 L

SHIPMENT: refrigerated

SAMPLE STABILITY: undetermined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3300 to 14,200 mg/m^3 [1] (1.5-L samples)

BIAS: − 2.3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 [1]

ACCURACY: ± 14.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPH, FID

ANALYTE: 1,1,2-trichloro-1,2,2-trifluoroethane

DESORPTION: 1 mL CS_2; stand 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 32° to 90° @ 5°/min °C

CARRIER GAS: He; 1 to 2 mL/min

COLUMN: DB-Wax/Stabilwax fused silica capillary, 30 m x 0.32-mm ID, split injection 5:1; (<500 µg, splitless).

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 0.015 to 14 mg per sample [2]

ESTIMATED LOD: 0.005 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.02 [2]

APPLICABILITY: The working range is 10 to 18000 mg/m^3 (1.3 to 2350 ppm) for a 1.5-L air sample. This method may be used with diffusive sampler collection, but a larger volume of CS_2 may be needed for desorption.

INTERFERENCES: None studied.

OTHER METHODS: This is a revision of NIOSH 3rd ed. Method 1020 (8/15/90). This method was updated for sequences 6937, 6956, and 6916A [1]. Method S129 [3] was originally evaluated under NIOSH Contract CDC-99-74-45.

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,2-Trichloro-1,2,2-Trifluoroethane (TTE), reagent grade.*
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, with flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged, and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1020-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10- to 100-μL, readable to 0.5%.
7. Volumetric flasks, 10-mL.
8. Pipet, TD 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). 1,1,2-Trichloro-1,2,2-Trifluoroethane is a narcotic [4]. Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 3 L.
4. Cap the samplers. Pack securely for shipment in a refrigerated container.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards in the range of 0.1 to 20 mg/mL.
   a. Add known amounts of TTE to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg TTE).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of TTE or a standard solution of TTE in CS_2 directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg TTE.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1020-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of TTE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of TTE in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S129 was issued on May 9, 1975 [3], and validated with generated atmospheres using calibrated syringe drive and independent verification by gas chromatography [2]. Average recovery was 100.3% (18 samples) in the range 3300 to 14,200 mg/m^3 for 1.5-L samples. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 60 min at 0.046 L/min from an atmosphere containing 14,500 mg/m^3 1,1,2-Trichloro-1,2,2-Trifluoroethane in dry air. Desorption efficiency for 18 samples of SKC lot 105 activated coconut charcoal spiked with 5.6 to 23 mg 1,1,2-Trichloro-1,2,2-Trifluoroethane averaged 1.01 with $\bar{S}_r$ = 0.02. Sample stability was not determined.

REFERENCES:

[1] Pendergrass, S.M., Method Development Efforts, NIOSH/DPSE Analytical Sequence #6937, 6956, and 6916A (unpublished) NIOSH/MRSB (1989).

[2] Documentation of the NIOSH Validation Tests, S129, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S129, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

S.M. Pendergrass, NIOSH/DPSE; S129 originally validated under NIOSH Contract CDC-99-74-45.

TRIETHYLENETETRAMINE
See ETHYLENEDIAMINE, Method 2540, for Procedure

$(NH_2CH_2CH_2NHCH_2)_2$ MW: 146.2 CAS: 112-24-3 RTECS: YE6650000

METHOD: 2540, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm = 5.98 mg/m^3)

PROPERTIES: liquid; d 0.98 g/mL @ 20 °C; BP 277.4 °C; VP unknown; flash point 118 °C

SYNONYMS: triethylenetetramine: TETA; trientine; N,N-bis(2-aminoethyl)-1,2-diaminoethane; 3,6-diazaoctane-1,8-diamine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (1-naphthylisothiocyanate-coated XAD-2, 80 mg/40 mg)

FLOW RATE: 0.01 to 0.1 L/min [1]

VOL-MIN: 1 L @ 10 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: >30 days @ 20 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.016 to 8 mg/m^3; (10-L samples)
OVERALL PRECISION ($\hat{S}_{rT}$):	0.06 [1]
BIAS:	−1.9%
ACCURACY:	±13.7%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: naphthylisothiourea derivative of analytes

DESORPTION: 2 mL dimethylformamide (DMF), ultrasonic 30 min

INJECTION VOLUME: 10 µL

COLUMN: 10-µm radial cyano, 10 cm x 8-mm ID in Waters RCM-100 radial compression mode

MOBILE PHASE: 50/50 isoctane/isopropanol at 3 mL/min

CALIBRATION: standard solutions of derivatives in DMF

RANGE: 1 to 119 µg per sample

ESTIMATED LOD: 0.3 µg per sample

PRECISION ($\bar{S}_r$): 0.018

APPLICABILITY: The working range for TETA is 0.08 to 160 mg/m^3 for a 10-L air sample. This method is the result of evaluation [2] of OSHA Method #60 for DETA, EDA, TETA [1]. The theoretical capacity of each front section is 1.6 mg of TETA.

INTERFERENCES: Other primary or secondary amines may react with the sampler coating reagent, and thereby reduce the sampler capacity.

OTHER METHODS: This replaces NIOSH Method P&CAM 276 [3]. The method of Anderson, et al., for EDA [4] is an alternate method using thiourea derivatization and HPLC analysis.

TRIFLUOROBROMOMETHANE

$CBrF_3$ MW: 148.92 CAS: 75-63-8 RTECS: PA5425000

METHOD: 1017 , Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1000 ppm
NIOSH: 1000 ppm
ACGIH: 1000 ppm
(1 ppm = 6.09 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 5 (air = 1); BP −57.8 °C; MP −168 °C; nonflammable

SYNONYMS: Refrigerant 13B1; bromotrifluoromethane.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 1000 ppm
-MAX: 1 L

SHIPMENT: separate front and back tubes; in dry ice

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2890 to 11,500 mg/m^3 [1] (1-L samples)

BIAS: − 2.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.065 [1]

ACCURACY: ± 13.46%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: trifluorobromomethane

DESORPTION: 5 mL methylene chloride; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 170 °C
-COLUMN: 105 °C
-DETECTOR: 230 °C

CARRIER GAS: N_2, 50 mL/min

COLUMN: stainless steel, 1.2 x 6-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of analyte in methylene chloride

RANGE: 0.5 to 18 mg per sample [1]

ESTIMATED LOD: 0.05 mg per sample

PRECISION ($\hat{S}_r$): 0.038 @ 3 to 12 mg per sample [1]

APPLICABILITY: The working range is 80 to 3000 ppm (500 to 18,000 mg/m^3) for a 1-L air sample.

INTERFERENCES: None reported.

OTHER METHODS: This revises Method S125 [2].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality.*
2. Trifluorobromomethane, 99%.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8-mm OD, 6-mm ID, followed by 7 cm long, 6-mm OD, 4-mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1017-1).
4. Vials, 10-mL, PTFE-lined caps.
5. Syringes, gas tight, 10-μL to 3-mL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 5-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows at ca. 200 mL/min, with T-connection and septum. Wrap outlet of tubing with heating tape and connect tubing to inlet of test sampler.

SPECIAL PRECAUTIONS: Methylene chloride is a suspect carcinogen and is metabolized to carbon monoxide, a toxic gas [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 1 L.
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with dry ice.

SAMPLE PREPARATION:

5. Pipet 5.0 mL chilled CH_2Cl_2 into a series of vials.
6. Place the front and back sorbent sections of the front sampler tube in a vial. Discard the glass wool and foam plugs. Immediately cap the vial. Similarly place the front and back sorbent sections of the back sampler tube in a separate vial.
7. Allow to stand 30 min with occasional agitation. Analyze within 6 h.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known volumes of trifluorobromomethane gas with a gas-tight syringe to 5.0 mL CH_2Cl_2 in 10-mL volumetric flasks by slowly bubbling the gas through the liquid with the tip of the syringe needle near the bottom of the volumetric flask. Dilute to the mark. Use serial dilutions as needed to obtain trifluorobromomethane concentrations in the range 0.01 to 3.6 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg trifluorobromomethane).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Connect a large charcoal tube (400 mg/200 mg) to the outlet of the DE apparatus. Start nitrogen flow (ca. 200 mL/min) through the DE apparatus and into the charcoal tube. Inject a known amount (0.01 to 3 mL; 0.05 to 18 mg @ NTP) of trifluorobromomethane gas into the septum. Allow the N_2 flow to continue for 20 sec.
   b. Cap the tube. Allow to stand overnight at −10 °C.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. mg trifluorobromomethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1017-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CH_2Cl_2 reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of trifluorobromomethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of trifluorobromomethane in the air volume sample, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S125 was issued on May 9, 1975 [2], and validated over the range 2890 to 11,500 mg/m^3 at 25 °C and 760 mm Hg using 1-L samples [1]. Generated concentrations were produced by calibrated gas flows and verified by a total hydrocarbon analyzer, standardized with gas standards. Overall precision, s_r, was 0.065, with average recovery of 100%. Desorption efficiency was 0.81 in the range 3 to 12 mg per sample. Breakthrough (effluent = 5% of test concentration) occurred in 90 min when a concentration of 12,370 mg/m^3 was sampled at a rate of 0.046 L/min. The stability of trifluorobromomethane on charcoal was not determined.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S125, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S125, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

METHOD REVISED BY:

Y. T. Gagnon and G. David Foley, NIOSH/DPSE.

TRIMELLITIC ANHYDRIDE

$C_9H_4O_5$ MW: 192.13 CAS: 552-30-7 RTECS: DC2050000

METHOD: 5036, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : No PEL
NIOSH: 0.005 ppm/10 h
ACGIH: 0.005 ppm
(1 ppm = 7.86 mg/m^3 @ NTP)

PROPERTIES: solid; MP 161 to 163 °C;
VP 5.3 x 10^{-4} Pa (4 x 10^{-6} mm Hg)
@ 20 °C

SYNONYMS: anhydrotrimellitic acid; 1,3-dioxo-phthalancarboxylic acid; 1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid; 1,2,4-benzenetricarboxylic acid anhydride; 1,2,4-benzenetricarboxylic acid cyclic-1,2-anhydride.

SAMPLING

SAMPLER: FILTER (0.8-μm PVC-copolymer)

FLOW RATE: 1.5 to 2.0 L/min

VOL-MIN: 400 L
-MAX: not specified

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.048 to 0.24 mg/m^3 [1] (400-L samples)

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

EXTRACTION: methanol, 3 mL

DERIVATIZATION: boron trifluoride/methanol

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 315 °C
-DETECTOR: 325 °C
-COLUMN: 250 °C, 2 min; 16 °C/min; 310 °C, 4 min

COLUMN: stainless steel, tenax 60/80 mesh, (9 ft x 2-mm)

CARRIER GAS: Helium, 35 mL/min

CALIBRATION: standard solutions of trimethyl trimellitate (derivative) in a mixture of pyridine, diethyl ether, and pentane

RANGE: 19 to 96 μg per sample

ESTIMATED LOD: 2 μg per sample

PRECISION ($\bar{S}_r$): 0.087 @ 19.2 to 96 μg per sample

APPLICABILITY: The working range is 0.048 to 0.24 mg/m^3 for a 400-L air sample. The method was used for analysis of bulk samples and air (field samples) [2,3]. This method will not differentiate between trimellitic anhydride and trimellitic acid [1].

INTERFERENCES: Any compound with the same retention time is an interference. The interference may be eliminated by changing the temperature program or carrier gas flow rate.

OTHER METHODS: This revises Method P&CAM 322 [1], which was based on a procedure by Biondi and Cagnosso [4].

REAGENTS:

1. Methanol; ACS reagent grade.
2. Pentane, ACS reagent grade.*
3. Diethyl ether, ACS reagent grade.*
4. Boron trifluoride/methanol, 14° (w/v) mixture* (commercially available from GC suppliers).
5. Pyridine, ACS reagent grade.
6. Pyridine mixture,* prepare a 7:3 pyridine/pentane mixture in a screw-cap tube.
7. Trimellitic anhydride.
8. Calibration stock solution, 1.92 μg/μL. Dissolve 0.4803 g of trimellitic anhydride in methanol and dilute to 250 mL.
9. Hydrogen, prepurified.
10. Air, compressed, filtered.
11. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, PVC-copolymer filter (0.8-μm pore size) supported by a cellulose backup pad in a three-piece plastic filter holder.
2. Personal sampling pump, 1.5 to 2 L/min with flexible polyethylene or PTFE tubing.
3. Gas Chromatograph, FID, integrator and column.
4. Test tubes, glass, (13 x 100-mm) with teflon-lined screw caps.
5. Syringe, 10-μL.
6. Pipettes, 10-μL, 25-μL, and 0.25 - 5-mL.
7. Volumetric flask, 250-mL.
8. Beakers, 50-mL and 250-mL.
9. Hotplate, variable heat settings.
10. Watch Glasses, for 50-mL beakers.
11. Ultrasonic bath.
12. Septa, high temperature (350 °C), GC injection.
13. Analytical balance, to ± 0.01 mg.
14. Tweezers
15. Applicator stick.
16. Weighing paper.

SPECIAL PRECAUTIONS: Diethyl ether and pentane are extremely flammable. Boron trifluoride and pyridine are toxic. Work with these substances only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the filter holder to the pump with a piece of flexible tubing.
3. Sample at an accurately known flow rate between 1.5 and 2 L/min for a total sample size of 400 L or greater. Collect a larger sample if a qualitative analysis is to be performed.
4. Replace filter plugs, and pack securely for shipment.

SAMPLE PREPARATION:

5. Extraction:
   a. Place a field sample or spiked filter sample in a 50-mL beaker.
   b. Add 3 mL of methanol.
   c. Cover the beaker with a watch glass and place on a hot plate (65 °C) for one minute.
   d. Remove the beaker with the watch glass still in place and place in the ultrasonic bath for one minute.
   e. Rinse the bottom of the watch glass with 1 mL of methanol, collect the rinse in the beaker.
   f. Lift the filter with tweezers above the methanol level and rinse both sides of the filter slowly with two 3-mL aliquots of methanol, collecting the rinse in the beaker.
   g. Roll and squeeze the filter with tweezers against the inside wall of the beaker to remove methanol retained by the filter.
   h. Discard the filter.

i. Place the beaker on the hot plate (55 °C) and evaporate the methanol to volume less than 5 mL.
j. Transfer the methanol extract to a test tube.
k. Rinse the beaker two or three times with small amounts of methanol and combine the rinsings in the test tube.
l. Evaporate the methanol in the test tube to dryness.

6. Derivatization:
   a. Add 125 μL of BF_3/methanol to each sample or standard tube and screw the cap tightly.
   b. Place in a water bath (97 °C) for 20 min.
   c. Remove the tube and allow to cool to room temperature.
   d. Add 50 μL of diethyl ether to the tube. Screw the cap on and shake mildly.
   e. Add 50 μL of pentane, replace cap and shake mildly.
   f. Add 50 μL of pyridine, replace cap and shake mildly.
   g. Allow to stand for a few minutes until the white material precipitates.

CALIBRATION AND QUALITY CONTROL:

7. Prepare at least six working standards over the range of 19.2 to 96 μg (10 to 50 μL) of trimellitic anhydride.
   a. Add known amounts of calibration stock solution to test tubes.
   b. Derivatize according to step 6.
   c. Prepare a calibration graph (peak area vs. μg analyte).
8. Determine recovery (R) for each lot of filters used for sampling in the concentration range of interest (step 7). Prepare three filters at each of five levels plus three media blanks.
   a. Spike aliquots of calibration solution onto the center of each filter. Allow to dry overnight.
   b. Extract and derivatize (steps 5 and 6) and analyze (steps 10 through 12).
9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and recovery graphs are in control.

MEASUREMENT:

10. Set gas chromatographic conditions as given on page 5036-1.
11. Inject a 5 μL aliquot.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass of trimellitic anhydride, μg (corrected for recovery), for sample (W) and average media blank (B).
14. Calculate the concentration of trimellitic anhydride, C (mg/m^3) in the air volume sampled, V(L):

$$C = \frac{(W - B)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The extraction efficiency was evaluated over the range of 19.2 to 96 μg/sample levels with an average recovery of 103.3% and a measurement precision of 0.087.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, V.6, P&CAM 322. U.S. Department of Health, Education and Welfare, (NIOSH) Publication No. 80-125 (1980).
[2] Sequence 1607, NIOSH (unpublished, 1979).
[3] Sequence 3632, Utah Biomedical Research Laboratory, Salt Lake City, Utah (unpublished, 1982).
[4] Biondi, P.A., and M. Cagnosso. Journal of Chromatography:109, 389 (1975).

METHOD REVISED BY:

Robert Kurimo, DPSE, NIOSH.

2,4,7-TRINITROFLUOREN-9-ONE 5018

$C_{13}H_5N_3O_7$ MW: 315.20 CAS: 129-79-3 RTECS: LL9100000

METHOD: 5018, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 May 1985 **Issue 2:** 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solid yellow needles; MP 176 °C

SYNONYMS: TNF

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.5-μm, PTFE membrane)	**TECHNIQUE:**	HPLC, UV DETECTION
FLOW RATE:	1 to 3 L/min	**ANALYTE:**	2,4,7-trinitrofluoren-9-one
VOL-MIN:	100 L @ 2 μg/m^3	**PREPARATION:**	extract with 2 mL toluene; centrifuge
-MAX:	500 L	**INJECTION VOLUME:**	100 μL
SHIPMENT:	routine	**MOBILE PHASE:**	20% isooctane/80% methylene chloride; 2 mL/min; ambient temperature
SAMPLE STABILITY:	at least 2 weeks @ 25 °C	**COLUMN:**	Waters Radial PAK B (packed with 10-μm silica) with Radial Compression Module, or equivalent
BLANKS:	2 to 10 field blanks per set	**DETECTOR WAVELENGTH:**	280 nm
		CALIBRATION:	standard solutions of TNF in toluene
		RANGE:	0.2 to 4 μg per sample
		ESTIMATED LOD:	0.04 μg per sample [1]
		PRECISION ($\hat{S}_r$):	0.056 [1]

ACCURACY	
RANGE STUDIED:	not studied
BIAS:	none identified
OVERALL PRECISION ($\hat{S}_{rT}$):	not evaluated
ACCURACY:	not determined

APPLICABILITY: The working range is 0.4 to 100 μg/m^3 for a 500-L air sample. This method was developed for the determination of TNF in spent toner from business copy machines.

INTERFERENCES: None known.

OTHER METHODS: This revises P&CAM 348 [1].

REAGENTS:

1. Isooctane, HPLC grade.
2. Methylene chloride, HPLC grade.
3. Toluene.
4. Calibration stock solution, 0.05 mg/mL. Dissolve 0.5 mg 2,4,7-trinitrofluoren-9-one* (TNF)* in 10 mL toluene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: PTFE filter, 0.5-μm pore size, 37-mm diameter, with backup pad and in polystyrene cassette.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tube.
3. Liquid chromatograph with UV detector, recorder, integrator, autosampler or syringe, and column (page 5018-1)
4. Ultrasonic waterbath.
5. Centrifuge.
6. Test tubes, glass, 10-mL, screw-cap.
7. Pasteur pipets.
8. Volumetric flasks, 10-mL
9. Syringes or micropipets, 5- to 100-μL
10. Pipets, 2-mL, glass, delivery, with pipet bulb.
11. Tweezers

SPECIAL PRECAUTIONS: Trinitrofluorenone is a suspect carcinogen and mutagen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove cassette plugs and attach cassette to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 100 to 500 L.
4. Plug the inlet and outlet of the cassette. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove filter from cassette. Fold or roll the filter and slide it to the bottom of a test tube with tweezers.
6. Add 2.0 mL toluene to each test tube and seal.
7. Suspend test tube with filter in an ultrasonic bath. Agitate for 5 min.
8. Centrifuge sample at ca. 2500 rpm for 30 min.
9. Transfer an aliquot of clear sample liquid to a clean test tube or autosampler vial.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.04 to 4 μg TNF per sample.
    a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark to produce concentrations of 0.02 to 2 μg/mL.
    b. Analyze together with samples and blanks (steps 13 through 15).
    c. Prepare calibration graph (peak area vs. μg TNF).

11. Determine recovery (R) over the calibration range (step 10) at least once for each lot of filters used for sampling. Prepare three filters at each of five levels plus three blanks.
    a. Add a known amount of TNF in toluene to media blank filters. Allow to dry.
    b. Place filters in test tubes and allow to stand overnight.
    c. Extract filters (steps 5 through 9) and analyze together with working standards (steps 13 through 15).
    d. Prepare a graph of R (mass recovered/mass added) vs. μg TNF recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph and recovery graph are in control.

MEASUREMENT:

13. Set up the liquid chromatograph according to manufacturer's recommendations and to the conditions given on page 5018-1.
14. Inject sample aliquot using syringe, fixed volume sample loop or autosampler.
15. Measure peak area.
    NOTE: If peak area is above the range of the standards, dilute with toluene, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, μg (corrected for R) of TNF found in the sample (W) and in average media blank (B).
17. Calculate concentration, C, of TNF in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

Lab-tested with 2,4,7-trinitrofluoren-9-one spiked filters. The average recovery was 95% over the range 0.2 to 4.0 μg per sample and had a pooled precision ($\bar{S}_r$) of 0.056. PTFE filters with a loading of 0.4 μg were stored for two weeks at room temperature with no loss of analyte [1,2].

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 348, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
[2] Seymour, M. J. J. Chrom., 236, 530-534 (1982).

METHOD WRITTEN BY:

Martha J. Seymour, NIOSH/DPSE.

TRIORTHOCRESYL PHOSPHATE

$(C_6H_4(CH_3)O)_3P=O$ MW: 368.37 CAS: 78-30-8 RTECS: TD0350000

METHOD: 5037, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 0.1 mg/m³
NIOSH: 0.1 mg/m³ (skin)
ACGIH: 0.1 mg/m³ (skin)

PROPERTIES: liquid; melting point 11 °C; boiling point 410 °C 1.20 g/mL; VP very low at 20 °C; vapor density 12.7 (air = 1); flash point 210 °C (closed cup)

SYNONYMS: phosphoric acid, tri-o-cresyl ester; phosphoric acid, tri-o-tolyl ester; phosphoric acid, tri(2-tolyl) ester; phosphoric acid, tris(2-methylphenyl) ester; o-cresyl phosphate; o-tolyl phosphate; tricresyl phosphate; tris(o-cresyl)phosphate; tris(o-tolyl)phosphate; tris(o-methylphenyl)phosphate; TOCP; TOTP; Phosflex 179-C

SAMPLING

SAMPLER: FILTER (0.8-μm MIXED CELLULOSE ESTER MEMBRANE)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 0.1 mg/m³
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 29 to 170 μg/m³ (100-L samples) [1]

BIAS: − 1.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.086 [1]

ACCURACY: ± 16.9%

MEASUREMENT

TECHNIQUE: GC, FPD in phosphorus mode

ANALYTE: triorthocresyl phosphate

EXTRACTION: 10 mL diethyl ether

INJECTION VOLUME: 5 μL

CARRIER GAS: N_2, 50 mL/min

DETECTOR: H_2, 70 mL/min
Air, 150 mL/min

TEMPERATURES-INJECTION: 250 °C
-DETECTOR: 250 °C
-COLUMN: 220 °C

COLUMN: 6-ft x ⅛-in ID stainless steel, with 3% OV-101 on 100/120 mesh Supelcoport

CALIBRATION: standard solutions of triorthocresyl phosphate in diethyl ether

RANGE: 0.15 to 24 μg per sample

ESTIMATED LOD: 0.05 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.0236 [1]

APPLICABILITY: The working range of this method is 0.002 to 2 mg/m³ for a 100-L air sample. This method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions.

INTERFERENCES: Any phosphorus-containing compound that has the same retention time as the analyte is an interference. Triorthocresyl phosphate may be a minor component in a product containing numerous isomeric tricresyl phosphates. When dealing with such products, it must be verified that the chromatographic parameters employed result in separation of the triorthocresyl phosphate isomer from the other tricresyl phosphate isomers. A non-polar capillary column may be used for better resolution.

OTHER METHODS: This revises Method S209 [2]. The separation of aryl phosphate isomers by capillary-column GC has been investigated [3,4]. A GC/FID method has been reported that determines triorthocresyl phosphate (TOCP) in the presence of other isomeric tricresyl phosphates (TCPs) in edible oils [5]. GC/MS has been used to determine total TCP in water [6]. Reversed-phase (RP) LC/UV [7], RPLC/MS [8], and RPLC/TID (thermionic detection) [9] have been shown to be useful analytical methods for TOCP, but all were evaluated in the absence of other TCP isomers. Normal-phase (NP) LC/UV has been used to determine total TCP in edible oils [10]. NPLC has been used to quantify low levels of TOCP in commercial TCP products [11].

REAGENTS:

1. Diethyl ether*, anhydrous, reagent grade.
2. Triorthocresyl phosphate*, reagent grade.
3. Hydrogen, purified.
4. Compressed air, prefiltered.
5. Nitrogen, purified.
6. Calibration stock solution, triorthocresyl phosphate in diethyl ether.

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm mixed cellulose ester membrane filter (0.8-μm pore size) supported by cellulose backup pad in three-piece filter holder.
2. Personal sampling pump with flexible polyethylene or PTFE tubing.
3. Gas chromatograph equipped with a flame photometric detector, phosphorus filter, and column (p. 5037-1).
4. Electronic integrator or some other suitable method for measuring peak areas.
5. Tweezers.
6. Jars: 2-oz ointment jars for sample extraction, squat form with aluminum-lined screw caps.
7. Syringes, 10-μL and other convenient sizes.
8. Volumetric flasks, 10-mL and other convenient sizes.
9. Pipets, 10-mL and other convenient sizes.

SPECIAL PRECAUTIONS: Store diethyl ether away from heat, light, and sources of ignition in a well-ventilated area. Do not leave container open. Diethyl ether can oxidize in air to form explosive peroxides, a reaction accelerated by light. Distillation and evaporation can concentrate unstable peroxides in the residue, a potentially explosive condition [12].

Triorthocresyl phosphate is more toxic than other tricresyl phosphate isomers and readily absorbed through the skin. Avoid contact of triorthocresyl phosphate with eyes, skin, and clothing [13,14]. Handle only in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with the representative filter cassette in line.
2. Remove cassette plugs and connect cassette filter to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 1 to 3 L/min for a total sample size of 2 to 100 L.
4. Firmly seal collected sample cassettes with plugs. Pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the filter and backup pad to an ointment jar using tweezers.
6. Pipet 10.0 mL of diethyl ether into each jar. Seal the jar immediately to minimize evaporation.
7. Allow samples to stand for at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 0.05 to 24 μg per sample.
   a. Prepare a stock solution by weighing an appropriate quantity of triorthocresyl phosphate into a volumetric flask and diluting to volume with diethyl ether.

NOTE: Triorthocresyl phosphate is very viscous and thus difficult to measure with a microliter syringe.

b. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with diethyl ether.

c. Analyze working standards together with samples and blanks (steps 11 and 12). This will minimize the effect of variations in FPD response with time.

NOTE 1: The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards be carefully interspersed with the samples.

NOTE 2: Use of an internal standard is recommended to minimize errors caused by sample solvent evaporation and FPD response variations.

d. Prepare a calibration graph of area vs. μg of triorthocresyl phosphate per 10 mL of sample.

9. Determine recovery in the concentration range of interest for each lot of filters used for sampling. Prepare three filters at each of five levels plus three media blanks.
   a. Spike aliquot of calibration solution onto each filter.
   b. After air-drying, extract filters with 10 mL diethyl ether (steps 5 through 7).
   c. Analyze together with working standards (steps 11 and 12).
   d. Prepare graph of recovery vs. μg triorthocresyl phosphate.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5037-1. Inject 5-μL sample aliquot using solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the calibration graph, dilute with diethyl ether, analyze, and apply appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, μg (corrected for recovery), of triorthocresyl phosphate found in the sample (W) and the average media blank (B).
14. Calculate concentration (C) of triorthocresyl phosphate in the actual air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 29 to 170 μg/m^3 at 19 °C and pressure of 761 mm Hg with 100-L air samples [1]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.086. The average collection efficiencies for test concentrations of 0.17, 0.19, and 3.8 mg/m^3 were 98.8%, 98.7%, and 99.5%, respectively. The average recovery from filters spiked in the range 5.85 μg to 23.4 μg per filter was 101.3%. Therefore, there is no significant bias in either the sampling or analytical method. No tests of sample stability during storage were conducted.

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[13] Material Safety Data Sheet for Tricresyl Phosphate, No. 332, General Electric Company, Schenectady, N.Y., November, 1977.

[14] Material Safety Data Sheet for Tricresyl Phosphate, No. T5161, J.T. Baker Chemical Company, Phillipsburg, N.J., May 1, 1989.

METHOD REVISED BY:

Robert P. Streicher, Ph.D., NIOSH/DPSE.

d. Prepare graph of recovery vs. μg triphenyl phosphate per sample.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and recovery graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5038-1. Inject 5-μL sample aliquot using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the calibration graph, dilute, reanalyze, and apply appropriate dilution factor in the calibration.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, μg (corrected for recovery), of triphenyl phosphate found in the sample (W) and in the average media blank (B).
14. Calculate concentration (C) of triphenyl phosphate in the volume of air sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range of 1.25 to 6.99 mg/m^3 at an atmospheric temperature and pressure of 24 °C and 759 mm Hg, using a 100-L sample. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.066, with average recovery of 99.1%, representing a non-significant bias. Recovery of triphenyl phosphate from filters was 99.3% for an air sample concentration of 7.0 mg/m^3 at 1.5 L/min for 66 minutes. [1,3]. A storage stability study was not conducted.

REFERENCES:

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[2] Occupational Health Guideline for Triphenyl Phosphate, U.S. Department of Health and Human Services (NIOSH) and U.S. Department of Labor (OSHA) (1978).

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METHOD REVISED BY:

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TUNGSTEN (soluble and insoluble) 7074

W MW: 183.85 CAS: 7440-33-7 RTECS: Y07175000

METHOD: 7074, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: 1 mg/m^3 solubles; STEL 3 mg/m^3
5 mg/m^3 insolubles; STEL 10 mg/m^3
ACGIH: 1 mg/m^3 solubles, STEL 3 mg/m^3
5 mg/m^3 insolubles, STEL 10 mg/m^3

PROPERTIES: brittle metal; MP 3410 °C; valence 2,3,4,5,6

SYNONYMS: wolfram.

SAMPLING

SAMPLER: FILTER
(0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 200 L @ 1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 2 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.42 to 2.0 mg/m^3 (soluble) [1];
0.84 to 19.7 mg/m^3 (insoluble) [1]

BIAS: + 0.015

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 (soluble) [1];
0.056 (insoluble) [1]

ACCURACY: ± 12.5%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: tungsten

EXTRACTION: H_2O; 6 min, 25 °C (soluble)

ASHING: 1:1 HF:HNO_3, 10 mL; 6 h, 150 °C (insoluble)

FINAL SOLUTION: 0.05 M NaOH/2% Na_2SO_4; 25 mL

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 255.1 nm

BACKGROUND CORRECTION: none used

CALIBRATION: W in 0.05 M NaOH and 2% Na_2SO_4

RANGE: 0.1 to 0.5 mg per sample (soluble);
0.25 to 12 mg per sample (insoluble)

ESTIMATED LOD: 50 μg soluble W per sample;
125 μg insoluble W per sample [2]

PRECISION ($\bar{S}_r$): 0.029 [1]

APPLICABILITY: The working range of this method is 0.25 to 5 mg/m^3 (soluble) and 0.6 to 5 mg/m^3 (insoluble) for a 400-L air sample. This is an elemental analysis and not compound-specific. For cemented tungsten carbide samples, cobalt can be quantitatively determined from the HCl extract used to remove interferences.

INTERFERENCES: None known. Ni, Mo, V, Mn, Cr, Co and Fe do not interfere at concentrations up to 50 times the tungsten concentration [3].

OTHER METHODS: This revises P&CAM 271 [1,3]. Method 7300 (ICP-AES) is an alternate measurement method; however, the extraction and ashing procedures described in this method must be followed.

REAGENTS:

1. Nitric acid, conc.*
2. Hydrofluoric acid, conc.*
3. Hydrochloric acid, conc.*
4. Hydrochloric acid, 1% (v/v). Add 26.5 mL conc. HCl to 500 mL water; dilute to 1 L.
5. Sodium hydroxide, 0.5 M. Dissolve 20 g NaOH in 500 mL water; dilute to 1 L.
6. Sodium sulfate, 20% (w/v). Dissolve 20 g Na_2SO_4 in 80 mL water; dilute to 100 mL.
7. Calibration stock solution, 10 mg W/mL. Commercially available or dissolve 1.5985 g Na_2WO_4 (dried at 125 °C) in water; add 10 mL 0.5 M NaOH and dilute to 100 mL.
8. Water, distilled, deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head.
4. Tungsten hollow cathode lamp.
5. Two-stage regulators for N_2O and acetylene.
6. Beakers, PTFE, 100-mL (with covers).*
7. Volumetric flasks, 10-, 25- and 100-mL.*
8. Assorted volumetric pipets, as needed, with pipet bulb.*
9. Hotplate for use at 150 °C.
10. Steam bath or 100 °C hotplate.
11. Filtering apparatus (funnel, clamp, frit, holder) with 47-mm, 0.45-μm pore size cellulose ester membrane filter and collection vessel.

* Clean all labware with conc. nitric acid and rinse thoroughly with distilled water before use.

SPECIAL PRECAUTIONS: Wear protective equipment (gloves, labcoats, and safety glasses) when working with HF. Do not use HF with glass labware. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette and transfer the filter to the filtering apparatus on top of a 47-mm filter.
4. Add 3 mL deionized water to the sample filter, allow it to stand 3 min, apply vacuum to transfer the extract to the holding vessel, and repeat with an additional 3 mL water.
5. Transfer the extracts to a 10-mL volumetric flask, add 1.0 mL 20% Na_2SO_4, dilute to volume, and analyze for soluble tungsten (steps 17 through 19).
6. Digest the filters and residue in a covered PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
7. Remove the beaker cover and reduce the volume to 2 mL (150 °C). Take to dryness at 100 °C.
8. Remove from heat, cool, add 10 mL 1% HCl, and agitate manually for 5 min.
9. Filter through an additional 47-mm filter (the filtrate may be analyzed for cobalt).
10. Digest the filter and residue in a PTFE beaker with 5.0 mL conc. HNO_3 and 5.0 mL conc. HF at 150 °C.
11. Remove the beaker cover and reduce the volume to 1 mL (150 °C). If filter residue (dark, charred material) is visible, add additional HNO_3 and HF (2 mL each).
12. Take to near-dryness at 100 °C.
13. Dissolve residue in beaker with 2.5 mL 0.5 M NaOH and 2.5 mL 20% Na_2SO_4 at 100 °C (15 min).
14. Transfer to a 25-mL volumetric flask and dilute to volume.

TRIPHENYL PHOSPHATE

$(C_6H_5)_3PO_4$ MW: 326.28 CAS: 115-86-6 RTECS: TC8400000

METHOD: 5038, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 3 mg/m^3
NIOSH: 3 mg/m^3
ACGIH: 3 mg/m^3

PROPERTIES: solid; MP 50 °C; BP 245 °C @ 11 mm Hg; d 1.27 g/mL @ 60 °C; VP <0.05 kPa (<0.1 mm Hg); flash point 220 °C

SYNONYMS: phosphoric acid triphenyl ester; TPP

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 3 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: One bulk sample should be submitted to laboratory in a glass container with a Teflon-lined cap. The label should match air samples.

ACCURACY

RANGE STUDIED: 1.25 to 6.99 mg/m^3 [1] (100-L sample)

BIAS: − 1.37%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.066 [1]

ACCURACY: ± 11.24

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD IN PHOSPHORUS MODE

ANALYTE: triphenyl phosphate

EXTRACTION: 10 mL anhydrous ether, 30 min

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 250 °C
-COLUMN: 210 °C

CARRIER GAS: N_2, 50 mL/min

COLUMN: 6-ft X 1/8-in stainless steel, packed with 5% OV-101 on 100/120 mesh Supelcoport

DETECTOR: H_2, 20 mL/min
air, 150 mL/min

CALIBRATION: standard solutions of triphenyl phosphate in anhydrous ether

RANGE: 30 to 900 μg per sample

ESTIMATED LOD: 10 μg per sample [1]

PRECISION ($\hat{S}_r$): 0.051 [1]

APPLICABILITY: The working range is 0.3 to 20 mg/m^3 for a 100-L air sample. This method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions.[1] A non-polar capillary column may be used for better resolution and sensitivity.

INTERFERENCES: None identified.

OTHER METHODS: This method revises S210 [1].

REAGENTS:

1. Diethyl ether, anhydrous, reagent grade.
2. Triphenyl phosphate,* reagent grade.
3. Hydrogen, purified.
4. Compressed air, prefiltered.
5. Nitrogen, purified.
6. Calibration stock solution (10-600 μg triphenyl phosphate per 10 mL diethyl ether).

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm cellulose ester membrane filter (0.8-μm pore size) with cellulose backup pad held in a three-piece cassette filter holder supported by a cellulose backup pad.
2. Personal sampling pump @ 1 to 3 L/min, with flexible tubing.
3. Gas chromatograph equipped with a flame photometric detector, phosphorus filter, and column (p. 5038-1).
4. Electronic integrator or other suitable method for measuring peak areas.
5. Ointment jars, 2 oz., squat form with aluminum-lined screw caps.
6. Syringes, 10-μL and other convenient sizes for preparing standard solutions.
7. Pipets, 10-mL and other convenient sizes for preparing standard solutions.

SPECIAL PRECAUTIONS: Repeated exposure to triphenyl phosphate through inhalation or ingestion may cause minor changes in blood enzymes. Triphenyl phosphate also causes neurotoxic effects in animals; therefore, persons with pre-existing neuromuscular disorders may be at increased risk.[2] Handle only in a fume hood. Avoid skin contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter cassette in line.
2. Remove the cassette plugs and attach to the personal sampling pump with flexible tubing.
3. Sample 10 to 400 L or more of air at an accurately known flow rate of 1 to 3 L/min.
4. Seal the collected sample cassette firmly with plugs. Pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer cellulose membrane filter and cellulose backup pad with tweezers to an ointment jar.
6. Pipet 10.0 mL of ether into each jar. Seal the jar immediately to minimize evaporation.
7. Allow samples to stand for at least 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 10 to 900 μg TPP per sample.
   a. Add know amounts of calibration stock solution to cover the range of interest to 10.0-mL volumetric flasks and dilute to the mark with diethyl ether.
   b. Analyze working standards together with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph of peak area vs. μg of triphenyl phosphate per 10-mL sample.
9. Determine recovery for each lot of filters used for sampling in the concentration range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Spike aliquot of calibration solution onto each filter.
   b. After air-drying, extract filters in 10 mL diethyl ether (steps 5 through 7).
   c. Analyze together with working standards.

CALIBRATION AND QUALITY CONTROL:

15. Calibrate with at least six working standards over the range 0.05 to 12 mg W per sample.
    a. Add known amounts of calibration stock solution to 100-mL volumetric flasks containing 10 mL 0.5 M NaOH and 10 mL 20% Na_2SO_4; dilute to volume with distilled, deionized water.
    b. Analyze together with samples and blanks (steps 17 through 19).
    c. Prepare calibration graph (absorbance vs. solution concentration, μg/mL).
16. Analyze three quality control blind spikes and three analyst spikes to ensure that the recovery and calibration graph are in control (steps 6 through 14 and 17 through 19).

MEASUREMENT:

17. Set spectrophotometer to conditions on page 7074-1.
18. Aspirate standards and samples. Record absorbance readings.
19. If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 0.05 M NaOH/2% Na_2SO_4 solution, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

20. Determine the solution concentrations of tungsten in the sample, C_s (μg/mL), and average media blank, C_b (μg/mL), from the calibration graph.
21. Using the solution volumes, mL of the sample (V_s) and media blank (V_b), calculate the concentration of tungsten, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method is based on P&CAM 271 [3,4] and was further evaluated and ruggedized under contract [1]. Laboratory testing with spiked samples over the ranges of 0.17 to 0.8 mg per sample (soluble) and 0.34 to 7.9 mg per sample (insoluble) gave precisions ($\bar{S}_r$) of 0.079 (soluble) and 0.076 (insoluble) [1]. Both soluble and insoluble tungsten species collected on filters were stable for two weeks [1].

REFERENCES:

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[4] Hull, R. D. Analysis of Tungsten by Atomic Absorption Spectrophotometry: A Feasibility Study, NIOSH, DPSE, MRB, IMDS Technical Report (unpublished, December, 1977).

METHOD WRITTEN BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS; additional data obtained under NIOSH Contract 210-79-0060.

ca. $C_{10}H_{16}$ (e.g., pinene, dipentene, and other terpenes) MW: ca. 136 CAS: 8006-64-2 RTECS: YO8400000

METHOD: 1551, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 100 ppm
NIOSH: 100 ppm; Group III Pesticide
ACGIH: 100 ppm
(1 ppm = 5.60 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.860 to 0.875 g/mL @ 15 °C; BP 150 to 180 °C; VP 0.67 kPa (5 mm Hg; 6580 ppm) @ 20 °C; lower explosive limit 0.8% v/v in air

SYNONYMS: gumspirits, wood turpentine; oil of turpentine.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required, 1 to 10 mL

ACCURACY

RANGE STUDIED: 264 to 1107 mg/m^3 [1] (10-L samples)

BIAS: − 1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.055 [1]

ACCURACY: ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: turpentine (all components)

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 to 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 50 to 250 °C @ 8°/min

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 6-mm, 10% SP-2100 on 80/100 mesh Supelcoport or 30 m x 0.32 mm ID fused silica capillary coated with DB-1

CALIBRATION: standard solutions of bulk turpentine in CS_2

RANGE: 0.5 to 20 mg per sample

ESTIMATED LOD: 0.1 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.013 [1]

APPLICABILITY: The working range is 9 to 360 ppm (50 to 2000 mg/m^3) for a 10-L air sample. Turpentine is widely used as a solvent in paints, varnishes and lacquers.

INTERFERENCES: The chief constituents of turpentine are pinene isomers, diterpene and other $C_{10}H_{16}$ terpenes. Naphtha mixtures containing C_9-C_{11} alkanes or alkyl-substituted benzenes could cause interferences with the turpentine mixture. GC column and conditions should then be optimized for maximum resolution.

OTHER METHODS: This is Method S88 [3] in a revised format.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.8% v/v undecane, 0.1% v/v octane or other suitable internal standard.
2. Turpentine, bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. (SKC ST226-01, Supelco ORBO-32, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1551-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipet, volumetric, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
   NOTE: Retain the glass wool plug if an estimate of aerosol is needed.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 20 mg turpentine per sample.
   a. Add known amounts of the turpentine bulk sample to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of sum of peak areas of turpentine to peak area of internal standard).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amounts of the turpentine bulk sample directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg turpentine recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1551-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.
NOTE: Compare chromatograms of the air samples and the turpentine bulk sample for evidence of qualitative differences and possible interferences.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of turpentine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of turpentine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S88 [3] was issued on March 14, 1975, and validated over the range 264 to 1107 mg/m^3 at 24 °C and 766 mm Hg using 10-L air samples [1]. Turpentine oil, double rectified (Fisher Scientific Co.; BP 150 to 170 °C; d 0.868 g/mL) in a calibrated syringe drive was used to generate turpentine atmospheres in dry air. Overall precision, $\hat{S}_{rT}$, was 0.055 with average recovery of 99%, representing a non-significant bias. Desorption efficiency was 0.95 in the range 2.8 to 11.3 mg per sample. The chromatographic column used was 6 ft x 1/8 in stainless steel packed with 1.5% OV-101 on 100/120 mesh Chromosorb W. Breakthrough (5% on back section) occurred at 126 min when sampling an atmosphere containing 1107 mg/m^3 turpentine at 0.19 L/min at 0% RH.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S88, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #4121-O,P (unpublished, December 2, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S88, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S88 originally validated under NIOSH Contract CDC-99-74-45.

VALERALDEHYDE

$CH_3(CH_2)_3CH=O$ M.W.: 86.13 CAS: 110-62-3 RTECS: YV3600000

METHOD: 2536, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no standard
NIOSH: 50 ppm
ACGIH: 50 ppm
(1 ppm = 3.52 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.810 g/mL @ 20 °C; BP 103 °C; VP 6.7 kPa (50 mm Hg) @ 25 °C; vapor density (air = 1) 3.0; flash point = 12.2 °C

SYNONYMS: pentanal; amyl aldehyde.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.04 L/min

VOL-MIN: 0.5 L@ 50 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 18 per set

ACCURACY

RANGE STUDIED: 9 to 374 mg/m^3 [1] (12-L samples)

BIAS: 0.12%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: ± 14.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: valeraldehyde oxazolidine (9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane)

DESORPTION: 2 mL toluene, 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 0.5 min @ 70°C; 50 °C/min to 120°C, hold 4 min; 20°C/min to 170°C, hold 7 min

CARRIER GAS: He, 27 cm/sec linear velocity makeup flow 29 mL/min

COLUMN: capillary, 15 m x 0.32-mm, 5% phenyl, 95% methyl polysiloxane, 1-µm film (DB-5 or equivalent)

CALIBRATION: standard solutions of valeraldehyde on sorbent

RANGE: 4 to 3900 µg per sample [1]

ESTIMATED LOD: 2 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.066 @ 2 to 508 µg per sample [1]

APPLICABILITY: The working range is 0.11 to 110 ppm (0.4 to 390 mg/m^3) for a 10-L air sample. The method is also suitable for determination of furfural and glutaraldehyde in a mixture [2].

INTERFERENCES: None have been observed; an alternate capillary column, 15 m x 0.32-mm cyanopropylphenyl dimethylpolysiloxane, 1-µm film (DB-1301) can be used.

OTHER METHODS: The method of Lipari and Swarin [3] uses 2,4-dinitrophenylhydrazine for the collection of valeraldehyde.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas or equivalent). Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight. (Optional if commercial tubes are used.)
4. Valeraldehyde, * 99% purity.
5. Valeraldehyde stock solution, 40 μg/μL (see APPENDIX). Add 400 mg valeraldehyde to toluene and dilute to 10 mL.
6. Valeraldehyde oxazolidine (APPENDIX A) stock solution, 10 mg/mL. Add 0.10 g 9-butyl-1-aza-8-oxabicyclo-[4.3.0]nonane to toluene and dilute to 10 mL.
7. Hydrogen, prepurified.
8. Air, filtered, compressed.
9. Helium, purified.
10. Magnesium sulfate, anhydrous.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

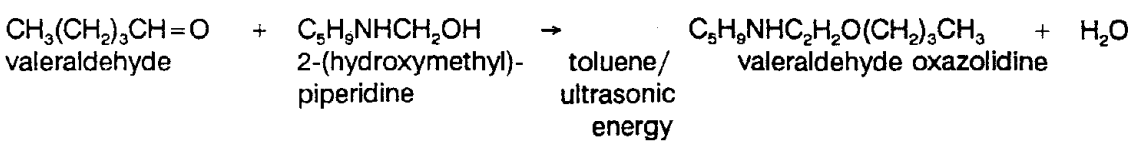
1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (front = 120 mg, back = 60 mg) (APPENDIX B). Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.1 L/min must be less than 760 Pa (5.7 mm Hg). Tubes are commercially available (Supelco Inc., ORBO 23 or equivalent).
2. Personal sampling pump, 0.01 to 0.04 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2536-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-μL (readable to 0.1 μL), 25-, and 50-μL.
10. File.
11. Beakers, 50-mL.
12. Magnetic stirrer.
13. Flasks, round-bottomed, 100-mL.
14. Soxhlet extraction apparatus.
15. Vacuum oven.
16. Distillation apparatus.

SPECIAL PRECAUTIONS: Valeraldehyde can irritate the mucous membranes [4]. It is flammable, a dangerous fire risk. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.04 L/min for a total sample size of 0.5 to 10 L.

   NOTE: Sampling rate is limited by the speed of the following reaction. Rates above 0.04 L/min may cause appreciable breakthrough owing to incomplete reaction, possibly invalidating the sample.



SAMPLE PREPARATION:

4. Score each sampler with a file in back of the back sorbent section.
5. Break sampler at score line. Remove and place back glass wool plug and back sorbent section in a vial.
6. Transfer front section with remaining glass wool plugs to a second vial.
7. Add 2.0 mL toluene to each vial. Screw cap tightly onto each vial.
8. Agitate in an ultrasonic bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

9. Identification of analytical peaks.
   a. Add known amounts of valeraldehyde oxazolidine stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with a least six working standards prepared in triplicate covering the range 2 to 3900 μg valeraldehyde per sample.
    a. Weigh 120-mg portions of unused sorbent from media blanks into vials.
    b. Add aliquots (1 to 10 μL) of valeraldehyde stock solution or dilutions thereof to the sorbent. Cap vials and allow to stand overnight at room temperature.
    c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (combined peak area vs. μg valeraldehyde).
       NOTE: Because the standard samples are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary. Check desorption efficiency in the range of interest and at least once over the entire range of the method with each lot of sorbent used. (APPENDIX C).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2536-1. Inject 1-μL sample aliquot.
    NOTE: If the amount of valeraldehyde oxazolidine in the aliquot exceeds the capacity of the column, dilute with toluene, reanalyze and apply the appropriate dilution factor in calculations. The upper limit for the column on (page 2536-1) is equivalent to ca. 260 μg valeraldehyde per sample.
13. Measure total peak area of the two analyte peaks.
    NOTE: On the recommended column, valeraldehyde oxazolidine gives two peaks, since the diastereoisomers are resolved with retention times 5.4 and 6.3 min. Retention time for 2-(hydroxymethyl)piperidine is 2.2 min for these conditions.

CALCULATIONS:

14. Determine the mass, μg, of valeraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of valeraldehyde in the air volume sampled, V (L):

$$\frac{W_f + W_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Atmospheres were generated by injection of valeraldehyde with a syringe pump into a heated block injector and flash vaporizer into a stream of air at 80% ± 5% RH flowing at a fixed rate. The generator and sampling manifold system have been described previously [5]. Concentration of valeraldehyde vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [3] or by monitoring with an AID Model 590 organic vapor monitor. Breakthrough studies of valeraldehyde at 100 ppm, conducted at 75 and 50 mL/min flow rates, gave 5% breakthrough at 170 min and 280 min, respectively.

The method was evaluated over the range of 9 to 374 mg/m^3 using 12-L samples. Desorption efficiencies from statically-spiked samples average 102.5% (89.2-126.6%) for the range 2 to 508 μg/sample. No bias with dynamically-generated samples was observed with the method when samples were collected at 40 mL/min and below. When samples were collected at ca. 60 mL/min, a negative bias of approximately 20-30% was observed. Samples were found to be stable for at least 4 weeks when stored at room temperature.

REFERENCES:

[1] Kennedy, E.R., Y.T. Gagnon, J.R. Okenfuss and A. Teass. "The Determination in Air of Selected Low-Molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography," Appl. Ind. Hyg., 3(10), 274-279 (1988).

[2] NIOSH Manual of Analytical Methods, 3rd. ed., U.S. Department of Health and Human Services (1984), Method #2531.

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[4] The Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

[5] Kennedy, E.R. and R.H. Hill, Jr. "Determination of Formaldehyde in Air as an Oxazolidine Derivative by Capillary Gas Chromatography," Anal. Chem. 54, 1739-1741 (1982).

METHOD REVISED BY:

Yvonne T. Gagnon and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX A: SYNTHESIS OF 9-BUTYL-1-AZA-8-OXABICYCLO[4.3.0]NONANE:

Place a solution of purified 2-(hydroxymethyl)piperidine (1.15 g; 10 mmol) in 20 mL of toluene in a 100-mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2-(hydroxymethyl)piperidine from the container used for weighing. Add anhydrous magnesium sulfate (2.0 g) to the flask to dry the valeraldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 0.947 g valeraldehyde (11 mmole) in 20 mL of toluene to the 2-(hydroxymethyl)piperidine solution dropwise with stirring over 1 h. (NOTE: Excess aldehyde was added to ensure complete conversion of 2-(hydroxymethyl)piperidine to oxazolidine.) Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure (1 mm Hg) by rotary evaporation. The product is a pale yellow viscous oil, ca. 90 to 95% pure by gas chromatography. Store the oxazolidine at 0 °C to prevent decomposition.

Mass spectral data for 9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane: m/e with relative intensities in parenthesis, 182 (7.0%), 152 (4.6%), 126 (100%), 110 (11.3%); 98 (37%). IR data (Vapor phase @ 280 °C) for this compound in cm^{-1} with relative intensity in parenthesis are: 2945 (s), 2874 (m), 2781 (m), 1455 (w), 1383 (w), 1339 (w), 1265 (w), 1203 (w), 1133 (m), 1075 (w), 1028 (m).

APPENDIX B: SORBENT PREPARATION (optional if commercially-prepared tubes are used):

Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C. Dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for valeraldehyde.

APPENDIX C: DESORPTION EFFICIENCY:

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10, although the DE should be determined once for each lot of sorbent used, using the following procedure:

a. Prepare and analyze a set of valeraldehyde oxazolidine standard solutions (step 9.a) and a set of working standards (step 10), including media blanks.
b. Treating the working standards as unknowns, read the mass (μg) of valeraldehyde oxazolidine found in each working standard (W), and in the average media blank (B).
c. Using the mass of valeraldehyde, μg, spiked onto the working standard (W_o) and the stoichiometric conversion factor of 2.13 between valeraldehyde and valeraldehyde oxazolidine, calculate the desorption efficiency:

$$DE = \frac{W - B}{W_o \cdot 2.13}$$

d. Prepare a graph of DE vs. μg valeraldehyde recovered per sample, (W - B)/2.13.

VANADIUM OXIDES

(1): V_2O_5 MW: (1): 181.88 CAS: (1) 1314-62-1 RTECS: (1) YW2450000 (dust)
(2): V_2O_3 (2): 149.88 (2) 1314-34-7 (1) YW2460000 (fume)
(3): NH_4VO_3 (3): 116.99 (3) 7803-55-6 (2) YW3050000
(3) YW0875000

METHOD: 7504, Issue 2 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1987
Issue 2: 15 August 1994

OSHA: C 0.5 mg/m^3 (as V) (V_2O_5 Dust);
C 0.1 mg/m^3 (as V) (V_2O_5 Fume); 1 mg/m^3 (FeV)
NIOSH: C 0.05 mg/m^3/15 min (as V_2O_5)
ACGIH: 0.05 mg/m^3 (respirable, as V_2O_5)

PROPERTIES: solids; MP 658 °C (1); MP 1967 °C (2)

SYNONYMS: (1): vanadic anhydride; vanadium pentoxide;
(2): vanadic oxide; vanadium sesquioxide; vanadium trioxide.

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm cyclone or Higgins-Dewell (HD) + 5-μm PVC membrane)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 200 L @ 0.5 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: high-volume respirable (preferred) or settled dust to identify interferences

ACCURACY

RANGE STUDIED: (1): 0.8-2.6 mg/m^3;
(2): 0.2-2.6 mg/m^3 [1]

BIAS: Table 1

OVERALL PRECISION ($\hat{S}_{rT}$): Table 1

ACCURACY: ± 26 to 62%

MEASUREMENT

METHOD: X-RAY POWDER DIFFRACTION

ANALYTE: vanadium pentoxide, vanadium trioxide, or ammonium metavanadate

SAMPLE PREPARATION: dissolve filter in tetrahydrofuran; redeposit on Ag filter

XRD: Cu target X-ray tube optimize for intensity; 1° 2θ slit graphite monochromator scintillation detector integrated intensity with background subtraction slow step scan (10 seconds/0.02° 2θ)

CALIBRATION: standard suspensions of analytes deposited on Ag filter

RANGE: 0.1 to 2 mg V per sample

ESTIMATED LOD: Table 1

PRECISION ($\hat{S}_r$): Table 1

APPLICABILITY: The working range is 0.2 to 4 mg/m^3 (as V) for a 500-L air sample. The method will determine V_2O_5, V_2O_3, and NH_4VO_3 separately on the same sample.

INTERFERENCES: α-Quartz (likely to be found in mineral samples) interferes (Table 1) but alternative diffraction lines are available. Most other compounds likely to be in the sample do not interfere [1].

OTHER METHODS: This replaces P&CAM 364 [2]. Methods S391 (Vanadiaum by graphite atomizer AAS) and 7300 (Elements by ICP-AES) determine total V.

REAGENTS:

1. V_2O_5, V_2O_3 or NH_4VO_3 (≥99%). Grind in freezer mill. Sieve through 10-μm sieve in isopropanol (for V_2O_3 or NH_4VO_3) or acetonitrile (for V_2O_5). Dry at 110 °C for one hour. Store in desiccator.
2. Tetrahydrofuran (THF), reagent grade.*
3. Isopropanol, reagent grade.
4. Acetonitrile, reagent grade.
5. Glue or tape for securing silver filters to XRD holders.
6. Desiccant.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
      NOTE: Test PVC filter for THF digestion (see Step 4).
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone, and coupler together rigidly so that air enters only at the cyclone inlet.
2. Bulk sampler: PVC membrane filter, 37-mm, 5-μm pore size in two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and bulk sampler, 3 L/min.
4. Filters, silver membrane, 25-mm diameter, 0.45-μm pore size (Osmonics, Inc., Nuclepore, Poretics, or equivalent).
5. X-ray powder diffractometer with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard. Source: Gem Dugout, State College, PA, 16801) for data normalization.
7. Filtration apparatus and side arm vacuum flask, with 25-mm filter holders.
8. Sieve, 10-μm, for wet-sieving.
9. Centrifuge tubes, wide-mouth, 40-mL.
10. Ultrasonic bath or probe.
11. Analytical balance (0.01 mg).
12. Magnetic stirrer with thermally-insulated top.
13. Bottles, reagent, 1-L, with ground glass stoppers.
14. Drying oven.
15. Polyethylene wash bottle.
16. Desiccator.
17. Pipets, TD, 2- to 25-mL.

SPECIAL PRECAUTIONS: THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with a nylon cyclone or 2.2 ± 5% L/min with an HD cyclone for a total sample size of 200 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to more than 90 °C from vertical may deposit over-sized material from the cyclone body onto the filter.
3. Obtain an area high-volume bulk sample in the vicinity of the personal sampling area.

SAMPLE PREPARATION:

4. Place sample filter in a centrifuge tube. Add 10 mL THF. Place centrifuge tube in ultrasonic bath for 10 min.
   NOTE: The filter should dissolve almost instantaneously.
5. Mount a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL THF onto the filter. Pour the sample suspension from the centrifuge tube into the funnel. Rinse centrifuge tube twice with 5-mL portions of THF, adding rinses to the funnel, and apply vacuum.
6. Control filtration rate to keep liquid level near top of funnel during filtering. Do not wash the walls or add THF to the funnel when the liquid level is lower than 4 cm above the filter. Leave vacuum on after filtration for sufficient time to dry the filter. Transfer filter with forceps to sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

7. Select six silver membrane filters as media blanks, randomly from the same box of filters to be used for depositing the samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL THF through the filter. Remove, let dry and mount on XRD holders.
   NOTE: These will be used to test for sample self-absorption.
8. Prepare standard suspensions.
   a. Weigh 10- and 50-mg portions of the dry analytes to the nearest 0.01 mg. Quantitatively transfer to 1-L glass-stoppered bottles. Add 1.00 L acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3).
   b. Disperse the powder in the liquid using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
9. Prepare a series of standard filters over the range 0.05 to 2 mg V per sample.
   a. Mount a filter on the filtration apparatus. Wet the filter with ca. 3 mL of acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3).
   b. Turn off the stirrer and shake the bottle vigorously by hand. Immediately remove the lid and withdraw an aliquot (2 to 25 mL) from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot.
   c. Transfer the aliquot from the pipet to the funnel. Keep the tip of the pipet near the surface but not submerged in the suspension. Rinse the pipet with ca. 5 mL of acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3), draining the rinse into the funnel. Repeat the rinse three more times.
   d. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down sides of funnel after deposit is in place (to avoid rearranging the material on the filter).
   e. Transfer the filter to the XRD sample holder.

10. Perform step scans on the standards and reference specimen using the same conditions as for samples. Use steps 12 and 13 to determine normalized intensity, $\hat{I}_x^\circ$, for each peak measured. Use exactly the same normalization factor, N, as for samples (step 13).
11. Prepare calibration graph ($\hat{I}_x^\circ$ vs. mg of each standard). Determine slope, m (counts/μg).
    NOTE 1: The intercept with the $\hat{I}_x^\circ$ axis should be ca. zero. A large negative intercept indicates an error in determining background (e.g., incorrectly measuring the baseline, or interference by another phase at the angle of background measurement). A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.
    NOTE 2: Poor repeatability at a given level indicates problems in the sample preparation technique and new standards should be made. Eliminate curvature with absorption corrections based on the mass absorption coefficient of the analyte (step 15, or from Tables 2 through 4).

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (broad 2θ range) of high-volume sample to determine the presence of interferences.
    NOTE: If quantitative analysis is to be done on the bulk sample, wet-sieve it first through a 10-μm sieve.
13. Mount the filter (sample, standard, or blank) in the XRD instrument and perform the following:
    a. Determine net intensity, I_r°, of the reference specimen before filter is scanned. Select a convenient scale factor, N, which is approximately equivalent to the net count for the reference specimen peak; use this for all analyses.
    b. Step-scan the most intense, interference-free diffraction peak of each compound to be determined, integrating the counts.
       NOTE: Useful analytical lines for the analytes are given in Table 1. Use strongest line of the analyte which does not have a matrix interference. Avoid lines in the proximity of Ag (JCPDS #4-0783 [3]) and AgCl (JCPDS #31-1238 [4]) (the latter often exists on the surface of silver filters).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain total (average) background.
    d. Calculate net intensity, I_x, (different between peak integrated count and total background count).
    e. Calculate and record the normalized intensity for the analyte peak on each sample and standard:

$$\hat{I}_x = \left(\frac{I_x}{I_r^\circ}\right) \times N.$$

       For each media blank, determine the net count for the analyte diffraction peak. Calculate the average normalized intensity, $\hat{I}_b$, for the 6 media blanks.
    f. Determine net count, I_{Ag}, of an interference-free silver peak on the filter following the same procedure. Scan times should be shorter for the silver peak (e.g., about 5% of scan times for analyte peaks) and should be consistent throughout the method. For each media blank, determine the net count for the silver peak. Calculate the average value, $\hat{I}_{Ag}^\circ$, for the 6 media blanks.
       NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently. In this case, the net intensities of the analyte, blank, and silver peaks (I_x, I_b, and I_{Ag}) should be normalized to the most recently measured reference intensity.

14. Scan each field blank over the same 2θ range used for the analyte and silver peaks. The analyte peak should be absent. The normalized intensity of the silver peak of the field blanks should match that of the media blanks.
NOTE: These analyses serve only to verify that contamination of the filters has not occurred.

CALCULATIONS:

15. Calculate absorption correction factors (Tables 2, 3, and 4) [5]:

$$f(T) = \frac{-R \ln T}{1 - T^R}$$

where: $R = (\sin \theta_{Ag})/(\sin \theta_x)$ and
$T = \hat{I}_{Ag}/\hat{I}^{\circ}_{Ag}$ = transmittance of sample.

16. Calculate concentration, C, of analyte in air volume sampled, V (L):

$$C = \frac{([\hat{I}_x \cdot f(T)] - \hat{I}_b)}{m \cdot V}, \text{ mg/m}^3.$$

where: $\hat{I}_x$ = normalized intensity of sample peak
$\hat{I}_b$ = normalized intensity of blank
m = slope of calibration graph, counts/μg

EVALUATION OF METHOD:

VANADIUM PENTOXIDE: The V_2O_5 method was evaluated [1] with both spiked and generated samples of V_2O_5. With the spiked samples, using the 31.05° line and loadings of 433 to 699 μg/filter, the overall $\hat{S}_{rT}$ was 8.3% with an average bias of -7.3%. Five sets of generated samples, ranging from 184 to 2400 μg V_2O_5 per filter, gave an average bias of 10.12% with a pooled $\bar{S}_r$ of 6.9%. The generated samples used an aerosol which had been sized with a cyclone with characteristics similar to the 10-mm nylon cylone; however, individual 10-mm nylon cyclones on the cassettes were not used.

VANADIUM TRIOXIDE: The method was evaluated [1] with both spiked and generated samples of V_2O_3. With the spiked samples, and the 24.39° line and loadings of 107 to 321 μg per filter, the overall $\bar{S}_r$ was 8.2% with an average bias of 12.2%. Five sets of generated samples, from atmospheres of 0.24 to 2.57 mg V_2O_3/m^3, gave an average bias of -10.1% with a pooled $\bar{S}_r$ of 13.4% (24.39° line). As above, the samples were generated by using an aerosol, which had been sized by means of a cyclone with characteristics similar to the 10-mm nylon cylone; however, individual 10-mm nylon cyclones on the cassettes were not used.

AMMONIUM METAVANADATE: The method was evaluated [1] with spiked NH_4VO_3 samples over the range of 109 to 277 μg NH_4VO_3 per filter, and with samples generated as described above, with atmospheres of 0.037 to 0.435 mg/m^3 of NH_4VO_3. The 18.10 °2 θ line provided an overall $\hat{S}_{rT}$ of 26.3%, with a bias of -10.2% over the generation range. The stability of the compound is critical and analysis should occur within two weeks of sampling, unless refrigeration storage is employed. Sampling is quantitative using the two-filter technique described.

For the analytes, biases of spiked samples were determined by assuming the volume of suspension as "true." Biases of generated samples were determined by assuming that the concentration obtained from the ICP-AES analysis of monitor AAWP filters was the "true" concentration.

Instrumental imprecision increases with smaller depositions. For low loading levels, higher counting times will increase precision, as should sample spinning. The stated lower limit of quantitation of ca. 100 μg per analyte when the recommended analytical lines were used is an estimate based on numerous spiked and generated sample experiments.

REFERENCES:

[1] T. Carsey, "Quantitation of Vanadium Oxides in Airborne Dusts by X-Ray Diffraction," Anal. Chem., 57: 2125-2130 (1985).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 8 (unpublished, 1982).
[3] Powder Diffraction File Search Manual, International Centre for Diffraction Data (JCPDS), Swarthmore, PA, 19081, p. 809 (1981).
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[5] M. Abell, D. Dollberg, J. Crable, "Quantitative Analysis of Dust Samples from Occupational Environments Using Computer-Automated X-ray Diffraction," in Advances in X-Ray Analysis, Vol. 24, Plenum, p. 37 (1981).
[6] E. Bertin: Principles and Practice of X-ray Spectrometric Analysis, 2nd Ed., Plenum, New York, p. 471 (1975).
[7] Criteria for a Recommended Standard...Occupational Exposure to Vanadium, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-222 (1977).

METHOD REVISED BY:

Charles Lorberau, NIOSH/DPSE.

Table 1. Characteristics of analytical lines.

d-space (A)	Relative Intensity[1]	Peak 2θ[1]	Scan Min 2θ	Scan Max 2θ	Detection Limit[2] (μg)	Calibration Slope (ct/μg)	Precision[3] (% $\hat{S}_{rT}$)	Bias[4] (%)	Comments
					Vanadium Pentoxide (PDF # 9-0387)				
4.38	100	20.27	19.4	20.9	4	205.0	11.5	-28.9	α-Quartz interf. 20.85 °2θ
4.09	35	21.73	20.9	22.4	13	57.1	-	-	α-Quartz interf. 20.85 °2θ
3.40	90	26.21	25.5	26.6	10	54.2	11.3	-22.3	α-Quartz interf. 26.69 °2θ
2.88	65	31.05	30.3	31.4	9	73.0	8.3	10.1	good
2.185	17	41.32	40.5	41.6	28	24.9	-	-	weak; V_2O_3 interf. 41.42 °2θ
					Vanadium Trioxide (PDF # 26-278)				
3.65	60	24.39	24.75	23.5	6	75.1	14.7	-10.1	good
2.70	80	33.18	33.5	32.5	5	78.3	16.0	0.0	AgCl interf. 32.32 °2θ
2.47	60	36.37	36.8	35.7	9	70.6	15.6	14.2	α-Quartz interf. 36.53 °2θ
2.18	20	41.42	41.7	40.6	62	11.7	-	-	weak; V_2O_5 interf. 41.32 °2θ
1.83	25	49.83	50.4	49.3	21	30.2	-	-	weak
1.69	100	54.28	54.5	53.3	5	91.2	20.7	-10.1	good
1.43	30	65.25[5]							
					Ammonium Metavanadate (PDF # 9-411)				
5.88	50	15.07	14.3	15.4	7	133.8	24.0	11.4	good
4.90	75	18.10	17.7	18.2	7	101.4	26.3	-10.2	good
4.14	95	21.46	21.0	21.8	10	49.8	-	13.2	weak; V_2O_5 interf. 21.73 °2θ
3.77	40	23.60	23.1	23.9	18	38.5	-	-	weak; V_2O_5 interf. 41.32 °2θ
3.164	100	28.21[6]			50.3	-	-		AgCl interf. at 27.88 °2θ
2.912	60	30.74	30.1	30.9	21	33.9	-	-	weak
2.628	45	34.12	33.5	34.4	20	36.0	-	-	weak

[1] From Reference [7], p. 979 (g = 1.5418A)°.
[2] Reference [6].
[3] $\hat{S}_{rT} = (GRSD^2 + 0.1667 \cdot SRSD^2 + .05^2)^{1/2}$, where GRSD is the generated-sample pooled relative standard deviation, and SRSD is the spiked-sample pooled relative standard deviation. This is the estimated relative standard deviation for the total (sampling plus measurement) air-monitoring method.
[4] From generated samples.
[5] Not evaluated because of an Ag interference at 64.48 °2θ.
[6] Not evaluated because of an AgCl interference at 27.88 °2θ.

Table 2. Matrix absorption correction factors for vanadium pentoxide/silver peaks by degrees two-theta.

V_2O_5	20.27°	26.13°	31.00°		20.27°	26.13°	31.00°
Silver	38.12°	38.12°	38.12°		38.12°	38.12°	38.12°
T	(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000	0.74	1.3053	1.2332	1.1952
0.99	1.0094	1.0073	1.0062	0.73	1.3203	1.2445	1.2046
0.98	1.0189	1.0147	1.0124	0.72	1.3356	1.2560	1.2141
0.97	1.0285	1.0222	1.0187	0.71	1.3512	1.2677	1.2238
0.96	1.0384	1.0298	1.0251	0.70	1.3672	1.2796	1.2337
0.95	1.0483	1.0375	1.0317	0.69	1.3835	1.2918	1.2438
0.94	1.0585	1.0454	1.0383	0.68	1.4002	1.3043	1.2541
0.93	1.0688	1.0533	1.0450	0.67	1.4172	1.3170	1.2646
0.92	1.0794	1.0614	1.0518	0.66	1.4346	1.3300	1.2753
0.91	1.0901	1.0697	1.0587	0.65	1.4524	1.3432	1.2862
0.90	1.1009	1.0780	1.0658	0.64	1.4706	1.3567	1.2973
0.89	1.1120	1.0865	1.0729	0.63	1.4892	1.3706	1.3087
0.88	1.1233	1.0952	1.0801	0.62	1.5083	1.3847	1.3203
0.87	1.1348	1.1040	1.0875	0.61	1.5278	1.3992	1.3322
0.86	1.1465	1.1129	1.0950	0.60	1.5478	1.4139	1.3444
0.85	1.1584	1.1220	1.1026	0.59	1.5682	1.4291	1.3568
0.84	1.1705	1.1312	1.1103	0.58	1.5892	1.4445	1.3695
0.83	1.1828	1.1406	1.1182	0.57	1.6107	1.4604	1.3825
0.82	1.1954	1.1502	1.1261	0.56	1.6327	1.4766	1.3957
0.81	1.2082	1.1599	1.1343	0.55	1.6553	1.4932	1.4094
0.80	1.2213	1.1698	1.1425	0.54	1.6784	1.5102	1.4233
0.79	1.2346	1.1799	1.1509	0.53	1.7022	1.5277	1.4376
0.78	1.2482	1.1902	1.1595	0.52	1.7266	1.5456	1.4522
0.77	1.2620	1.2006	1.1682	0.51	1.7516	1.5640	1.4672
0.76	1.2762	1.2113	1.1770	0.50	1.7774	1.5828	1.4826
0.75	1.2906	1.2221	1.1860	0.49	1.8039	1.6022	1.4984

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

Table 3. Matrix absorption correction factors for vanadium trioxide/silver peaks by degrees two-theta.

V_2O_3	24.39°	33.18°	36.37°	54.28		24.39°	33.18°	36.37°	54.28°
Silver	38.15°	38.15°	38.15°	38.15°		38.15°	38.15°	38.15°	38.15°
T	f(T)	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)	f(T)
1.00	1.00000	1.00000	1.00000	1.00000	0.74	1.25097	1.18219	1.16591	1.11173
0.99	1.00779	1.00576	1.00527	1.00360	0.73	1.26315	1.19089	1.17379	1.11696
0.98	1.01571	1.01161	1.01061	1.00725	0.72	1.27558	1.19975	1.18182	1.12228
0.97	1.02375	1.01753	1.01603	1.01095	0.73	1.28825	1.20877	1.19000	1.12769
0.96	1.03191	1.02354	1.02152	1.01469	0.70	1.30119	1.21797	1.19832	1.13320
0.95	1.04021	1.02964	1.02709	1.01849	0.69	1.31439	1.22734	1.20681	1.13880
0.94	1.04863	1.03583	1.03274	1.02233	0.68	1.32786	1.23689	1.21546	1.14450
0.93	1.05719	1.04211	1.03847	1.02622	0.67	1.34162	1.24663	1.22427	1.15030
0.92	1.06589	1.04848	1.04429	1.03016	0.66	1.35567	1.25657	1.23326	1 15621
0.91	1.07474	1.05494	1.05019	1.03416	0.65	1.37002	1.26670	1.24242	1.16223
0.90	1.08372	1.06151	1.05617	1.03822	0.64	1.38469	1.27705	1.25177	1.16837
0.89	1.09286	1.06817	1.06225	1.04232	0.63	1.39968	1.28761	1.26131	1.17462
0.88	1.10215	1.07494	1.06842	1.04649	0.62	1.41500	1.29839	1.27105	1.18099
0.87	1.11160	1.08181	1.07468	1.05071	0.61	1.43068	1.30941	1.28100	1.18749
0.86	1.12122	1.08879	1.08104	1.05500	0.60	1.44672	1.32066	1.29116	1.19411
0.85	1.13099	1.09589	1.08749	1.05934	0.59	1.46313	1.33216	1.30153	1.20088
0.84	1.14094	1.10309	1.09405	1.06375	0.58	1.47993	1.34392	1.31214	1.20778
0.83	1.15107	1.11042	1.10072	1.06823	0.57	1.49713	1.35595	1.32298	1.21483
0.82	1.16137	1.11786	1.10749	1.07277	0.56	1.51475	1.36825	1.33408	1.22203
0.81	1.17186	1.12543	1.11437	1.07738	0.55	1.53281	1.38084	1.34542	1.22939
0.80	1.18255	1.13313	1.12137	1.08206	0.54	1.55133	1.39374	1.35704	1.23691
0.79	1.19342	1.14096	1.12848	1.08681	0.53	1.57031	1.40695	1.36893	1.24460
0.78	1.20450	1.14892	1.13571	1.09164	0.52	1.58979	1.42048	1.38111	1.25246
0.77	1.21579	1.15702	1.14306	1.09654	0.51	1.60978	1.43435	1.39359	1.26051
0.76	1.22729	1.16526	1.15055	1.10152	0.50	1.63030	1.44858	1.40639	1.26875
0.75	1.23902	1.17365	1.15816	1.10659	0.49	1.65139	1.46318	1.41952	1.27719

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

Table 4. Matrix absorption correction factors for ammonium metavanadate/silver peaks by degrees two-theta.

NH_4VO_3 Silver	15.07° 38.15°	18.10° 38.15°	21.46° 38.15°	23.60 38.15°		15.07° 38.15°	18.10° 38.15°	21.46° 38.15°	23.60° 38.15°
T	f(T)	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000	1.0000	0.74	1.0000	1.0000	1.0000	1.0000
0.99	1.0126	1.0105	1.0088	1.0081	0.73	1.0126	1.0105	1.0088	1.0081
0.98	1.0254	1.0211	1.0178	1.0162	0.72	1.0254	1.0211	1.0178	1.0162
0.97	1.0384	1.032	1.0270	1.0245	0.71	1.0384	1.0320	1.0270	1.0245
0.96	1.0517	1.043	1.0362	1.0330	0.70	1.0517	1.0430	1.0362	1.0330
0.95	1.0653	1.0542	1.0457	1.0415	0.69	1.0653	1.0542	1.0457	1.0415
0.94	1.0791	1.0656	1.0553	1.0503	0.68	1.0791	1.0656	1.0553	1.0503
0.93	1.0932	1.0773	1.0650	1.0591	0.67	1.0932	1.0773	1.0650	1.0591
0.92	1.1075	1.0891	1.0749	1.0681	0.66	1.1075	1.0891	1.0749	1.0681
0.91	1.1221	1.1011	1.0850	1.0773	0.65	1.1221	1.1011	1.0850	1.0773
0.90	1.1371	1.1134	1.0953	1.0866	0.64	1.1371	1.1134	1.0953	1.0866
0.89	1.1523	1.1259	1.1057	1.0960	0.63	1.1523	1.1259	1.1057	1.0960
0.88	1.1678	1.1386	1.1164	1.1056	0.62	1.1678	1.1386	1.1164	1.1056
0.87	1.1836	1.1516	1.1272	1.1154	0.61	1.1836	1.1516	1.1272	1.1154
0.86	1.1997	1.1648	1.1382	1.1254	0.60	1.1997	1.1648	1.1382	1.1254
0.85	1.2162	1.1783	1.1494	1.1355	0.59	1.2162	1.1783	1.1494	1.1355
0.84	1.2330	1.1920	1.1608	1.1458	0.58	1.2330	1.1920	1.1608	1.1458
0.83	1.2501	1.2060	1.1724	1.1563	0.57	1.2501	1.2060	1.1724	1.1563
0.82	1.2676	1.2202	1.1842	1.1669	0.56	1.2676	1.2202	1.1842	1.1669
0.81	1.2855	1.2348	1.1963	1.1778	0.55	1.2855	1.2348	1.1963	1.1778
0.80	1.3038	1.2496	1.2086	1.1889	0.54	1.3038	1.2496	1.2086	1.1889
0.79	1.3224	1.2647	1.2211	1.2002	0.53	1.3224	1.2647	1.2211	1.2002
0.78	1.3414	1.2801	1.2338	1.2116	0.52	1.3414	1.2801	1.2338	1.2116
0.77	1.3609	1.2959	1.2468	1.2233	0.51	1.3609	1.2959	1.2468	1.2233
0.76	1.3807	1.3120	1.2601	1.2353	0.50	1.3807	1.3120	1.2601	1.2353
0.75	1.4474	1.3284	1.2736	1.2474	0.49	1.4010	1.3284	1.2736	1.2474

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

VINYL ACETATE

$CH_3CO_2CHCH_2$ MW: 86.09 CAS: 108-05-4 RTECS: AK0875000

METHOD: 1453, Issue 1 **EVALUATION: UNRATED** **Issue 1: 15 August 1994**

OSHA : no PEL
NIOSH: C 4 ppm/15 min
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 3.52 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 72.7 °C; d 0.934 g/mL @ 20 °C; VP 11.1 kPa (83 mm Hg, 1.2%) @ 20 °C; vapor density (air = 1) 3.0

SYNONYMS: acetic acid, vinyl ester; acetic acid, ethenyl ester; Vinyl A monomer; ethenyl ethanoate; 1-acetoxyethylene; ethenyl acetate; vinyl acetate monomer; vinyl ethanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (carbon molecular sieve; 160 mg/80 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 0.75 L @ 10 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: at least 14 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7.8 to 29.6 mg/m^3 [1] (24-L samples)

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

wNALYTE: vinyl acetate

DESORPTION: 1.0 mL 95% (v/v) methylene chloride/methanol

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C

COLUMN: 0.2% Carbowax 1500 on Carbopack C, 6 ft x 2-mm ID glass

CALIBRATION: standard solutions of vinyl acetate in 95% methylene chloride/methanol

RANGE: 0.03 to 8.7 mg per sample [1]

ESTIMATED LOD: 1.0 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.007 [1]

APPLICABILITY: The working range is 0.9 to 170 ppm (3 to 600 mg/m^3) for a 10-L air sample. The method is sensitive enough for ceiling measurements. Vinyl acetate was analyzed under Sequence 6599 with a 30 m x 0.32-mm, 1.0-µm DB-5 fused silica capillary column, 40°C isothermal [2].

INTERFERENCES: Vinyl acetate that is not stabilized or has been depleted of inhibitor can polymerize. Any substance collected with the vinyl acetate that is capable of reacting with it is a potential interference. Acids, bases, free radical initiators, etc., are capable of reacting with vinyl acetate during and after air sampling.

OTHER METHODS: This method is adapted from OSHA Method No. 51 [1] and replaces NIOSH method P&CAM 278 [3].

REAGENTS:

1. Vinyl acetate, practical grade, inhibited with 275-325 ppm diphenylamine.
2. Methanol, distilled in glass
3. Methylene chloride*, distilled in glass.
4. Eluent, 95% (v/v) methylene chloride/methanol.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.
8. Calibration stock solution, 74.7 mg/mL. Add 2 mL vinyl acetate into 25-mL volumetric flask and dilute to volume with methanol.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of carbon molecular sieve, Carboxen-564 (front = 160 mg, back = 80 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 25 mm/Hg. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with a FID detector, recorder, integrator and column (page 1453-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL and other sizes as needed.

SPECIAL PRECAUTIONS: Vinyl acetate can irritate the eyes, nose, and throat. Methylene chloride is an irritant, can be desorbed through the skin, and is a suspect carcinogen [4]. Prepare samples in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.2 L/min for a total sample size of 0.75 to 24 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section along with the glass wool plug in a separate vial from the back sorbent section of the sampler. Discard the foam plugs.
6. Add 1.0 mL of 95% (v/v) methylene chloride/methanol to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add 2 mL vinyl acetate to methanol in a 25-mL volumetric flask and dilute to the mark. This is the stock calibration solution. Use serial dilutions as needed to obtain the desired concentration range.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (area vs. μg/mL).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount (2 to 20 μL) of a standard mixture of vinyl acetate directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg vinyl acetate recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1453-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of vinyl acetate found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of vinyl acetate in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated by the Organic Methods Development Branch, OSHA Technical Center, Salt Lake City, UT, over the range 187-710 μg per sample. The recovery from samples stored 14 days at 5 °C remained above 90% for the same levels. The pooled coefficient of variation obtained from replicate determinations of analytical standards in this range was 0.0073. Breakthrough studies at 70% RH, sampling an atmosphere of 150 mg/m^3 at 0.19 L/min, indicated a tube capacity of approximately 9 mg of vinyl acetate.

REFERENCES:

[1] OSHA Analytical Methods Manual, USDOL/OSHA Method No. 51, U.S. Occupational Safety and Health Administration, OSHA Analytical Laboratory, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1988).
[2] DataChem Report, MRSB Sequence #6599 (unpublished, September 1989).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., Vol. 4, P&CAM 278, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] NIOSH Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 90-117 (1990), available as GPO Stock #1990-751-238 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE.

VINYL BROMIDE

$CH_2=CHBr$ MW: 106.95 CAS: 593-60-2 RTECS: KU8400000

METHOD: 1009, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA: 1 ppm; C 5 ppm
NIOSH: suspect carcinogen; lowest feasible conc. (0.2 ppm LOQ)
ACGIH: 5 ppm; suspect carcinogen
(1 ppm = 4.37 mg/m^3 @ NTP)

PROPERTIES: d 1.493 g/mL @ 20 °C; BP 15.8 °C; MP −137.8 °C; VP 141 kPa (1054 mm Hg) @ 20 °C; explosive range 9 to 15% v/v in air

SYNONYMS: bromoethene; bromoethylene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 1 ppm
-MAX: 10 L

SHIPMENT: no special precautions

SAMPLE STABILITY: at least 14 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	1.32 to 56.5 mg/m^3 [1] (6-L samples)
BIAS:	0.021 [2]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.090 (1.3 to 6.4 mg/m^3) [1]; 0.063 (6.4 to 56 mg/m^3)
ACCURACY:	± 17.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl bromide

DESORPTION: 15 mL ethanol, 30 min ultrasonic agitation

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 140 °C
-DETECTOR: 240 °C
-PROGRAM: 3 min @ 50 °C, 40 °C/min to 225 °C, 5 min hold

CARRIER GAS: N_2, 25 mL/min

COLUMN: nickel, 6 m x 2-mm ID, 10% FFAP on 80/100 mesh Chromosorb W AW DMCS

CALIBRATION: vinyl bromide in ethanol

RANGE: 8 to 355 µg per sample

ESTIMATED LOD: 3 µg per sample

PRECISION ($\bar{S}_r$): 0.040 [1]

APPLICABILITY: The working range is 0.3 to 33 ppm (1.3 to 145 mg/m^3) for a 6-L air sample.

INTERFERENCES: Presence of other volatile compounds may interfere with collection of vinyl bromide or reduce capacity of sorbent tube. Under stated chromatographic conditions, ethylene, acetylene, and ethylene dibromide are separated from vinyl bromide; bromine is not separated.

OTHER METHODS: This is Method P&CAM 349 [1] in a revised format. OSHA Method 08 uses a smaller (100 mg/50 mg coconut charcoal) sorbent tube and desorption by CS_2, recommends a 5-L sample, and was evaluated for a 1-ppm target level.

REAGENTS:

1. Ethanol, absolute.*
2. Vinyl bromide (liquid), ≥ 98% purity.*
3. Calibration stock solution, ca. 30 μg/μL.
   a. Accurately weigh ca. 5 mL ethanol in a stoppered 10-mL volumetric flask.
   b. Chill (0 °C) the flask, vinyl bromide and a 1-mL gas-tight syringe.
   c. Transfer 0.2 mL vinyl bromide to the volumetric flask with the gas-tight syringe.
   d. Allow flask to return to room temperature. Reweigh flask to determine mass of vinyl bromide transferred.
   e. Fill flask to mark with ethanol and calculate solution concentration.
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, with flame-sealed ends containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal; (front = 400 mg; back = 200 mg) separated by a urethane foam plug. A silyated glass wool plug precedes the front section and a urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less 3.4 kPa. Tubes are commercially available (Supelco ORBO-32; SKC ST 226-09).
2. Personal sampling pumps, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Ultrasonic bath.
4. Gas chromatograph, FID, integrator and column (page 1009-1).
5. Vials, glass, 25-mL, crimp seals or caps with FTFE-lined silicone rubber septa.
6. Pipet, 15-mL, with pipet bulb.
7. Syringes, 10-μL, readable to 0.1 μL; 1-mL, gas-tight, with valve.
8. Balance, readable to 1 mg.
9. Flasks, volumetric, 2-, 5-, 10- and 25-mL.
10. File, triangular.
11. Ice.

SPECIAL PRECAUTIONS: Ethanol (flash point = 12 °C) is a fire hazard. Vinyl bromide is suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately know flow rate between 0.01 and 0.2 L/min for at total sample size of 2 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and front sorbent section in one vial. Place the back sorbent section and foam plugs into another vial.
6. Add 15.0 mL ethanol to each vial. Attach crimp cap to each vial.
7. Place vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 750 μg vinyl bromide per sample.
   a. Add known amounts of calibration stock solution to ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. μg vinyl bromide per 15 mL).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg vinyl bromide recovered per sample.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1009-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Under given conditions, retention time is about 3.0 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethanol, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of vinyl bromide found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front ((B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of vinyl bromide in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Analytical precision was determined by analyzing spiked sampling media. Average desorption efficiency was 0.910. Breakthrough volume was 10 L for a concentration of 130 mg/m^3 at 40 °C and >80% RH. Overall precision, bias, and storage stability were determined by sampling and analyzing generated atmospheres. Generated concentrations were independently verified. Reference [2] provides more specific information.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 349, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

[2] Spafford, R. B. and H. K. Dillon. Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide, NIOSH Contract No. 210-79-0100, Southern Research Institute, Birmingham, AL, available from NTIS (PB 83-133447), Springfield, VA (1981).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0100.

VINYL CHLORIDE

$CH_2=CHCl$ MW: 62.50 CAS: 75-01-4 RTECS: KU9625000

METHOD: 1007, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1 ppm; C 5 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 5 ppm; carcinogen
(1 ppm = 2.56 mg/m³ @ NTP)

PROPERTIES: BP −14 °C; vapor density 2.2 (air = 1); lower explosive limit = 4% v/v in air

SYNONYMS: chloroethylene; chloroethane.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [1]

BIAS: − 6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [1]

ACCURACY: ± 17.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 2 to 200 µg per sample [1]

ESTIMATED LOD: 0.04 µg per sample [1]

PRECISION ($\bar{S}_r$): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [2].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
3. Calibration stock solutions 0.26 mg/mL.
   a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 and add the washings to the flask.
   d. Dilute to the mark with CS_2.
4. Helium, purified.
5. Hydrogen, purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two tandem glass tubes, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: A pair of two-section (100 mg/50 mg) tubes may be used. (SKC ST226-01, or equivalent).
2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
4. File.
5. Bent wire for removing plugs from sampling tube.
6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
7. Volumetric flasks, 10-mL, with polyethylene stoppers.
8. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
9. Air sampling bags, Tedlar, 10-L.
10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
11. Syringe, 10-μL, with 0.1-μL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

5. Add 1.0 mL CS_2 to an empty vial. Loosely cap the vial.
6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.
7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate with at least six working standards covering the range 0.2 to 200 μg per sample.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
      NOTE: Working standards can be stored at -20 °C for at least three days.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graphs of peak area vs. quantity (μg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
10. Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m^3.
    b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m^3)	Volume Sampled (L)	Quantity of Vinyl Chloride (μg)
2.6	0.8	2
	2.2	6
21	0.8	17
	2.2	46
52	2.5	130

    Obtain three samples at each level.
    c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
    d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples to verify concentration.
    e. Prepare a graph of DE vs. μg of vinyl chloride recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set the gas chromatograph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE) of vinyl chloride found in the sample front (W_f) and back (W_b) tubes, and in the average media blank (B).
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - 2B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was evaluated with single 150-mg coconut shell charcoal tubes (100-mg front beds and 50-mg back) [1]. Atmospheres were generated at four concentrations between 1 and 64 mg/m^3. Recoveries, based on atmosphere concentrations calculated from the volumes of vinyl chloride and dilution air, averaged 94% with a pooled relative standard deviation ($\hat{S}_{rT}$) of 0.06. Samples at the 3-μg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal, challenged at 100 mL/min with vinyl chloride in air at 16 mg/m^3 and a relative humidity of 70%, was 4.6 L [5].

REFERENCES:

[1] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. Anal. Chem., 48,.1395-1398 (1976).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
[3] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment 1993-94, ACGIH, Cincinnati, OH (1993).
[4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
[5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

METHOD WRITTEN BY:

A. W. Teass, Ph.D., NIOSH/DBBS.

VINYLIDENE CHLORIDE

$CH_2=CCl_2$ MW: 96.94 CAS: 75-35-4 RTECS: KV9275000

METHOD: 1015, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: lowest feasible; carcinogen
ACGIH: 5 ppm; STEL 20 ppm; carcinogen
(1 ppm = 3.96 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.213 g/mL @ 20 °C;
BP 31.7 °C; MP −122.5 °C; flammable

SYNONYMS: 1,1-dichloroethene; 1,1-dichloroethylene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2.5 L @ 1 ppm
-MAX: 7 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C
21 days @ 5 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7.6 to 10 mg/m^3 [2]

BIAS: − 0.05

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069

ACCURACY: ± 18.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinylidene chloride

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 200 °C
-COLUMN: 65 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: silanized glass, 3 m x 6-mm OD packed with Durapak OPN 100/120 mesh or equivalent

CALIBRATION: standard solutions of vinylidene chloride in CS_2

RANGE: 10 to 100 µg per sample

ESTIMATED LOD: 7 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.048 @ 12 to 85 µg per sample [2]

APPLICABILITY: The working range is 0.5 to 5 ppm (2 to 20 mg/m^3) for a 5-L air sample. The capacity of charcoal for vinylidene chloride decreased rapidly with increasing relative humidity and was also found to be a function of concentration.

INTERFERENCES: The GC column will not separate vinyl chloride and carbon disulfide. Other GC packings that separate vinyl chloride and CS_2 may not separate vinylidene chloride and CS_2. If determination of both of these monomers is to be performed, a capillary column such as a 105 meter Rtx® 502.2 would be required.

OTHER METHODS: The revises P&CAM 266 [1].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. Vinylidene chloride, 99%.
3. Cyclohexane.
4. Calibration stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in CS_2 to make 10 mL solution. Prepare in duplicate.
5. DE stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in cyclohexane to make 10 mL solution. Prepare in duplicate.
6. Nitrogen or helium, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1015-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, volumetric, 10- to 100-μL, and 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Vinylidene chloride is a suspect carcinogen [3]. Carbon disulfide and vinylidene chloride are toxic and severe fire and explosion hazards (flash point = −30 °C for CS_2 and −10 °C for vinylidene chloride). Work with both compounds only in a hood. Vinylidene chloride polymerizes above 0 °C, especially in the presence of oxygen or catalysts; explosive reaction products may result [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2.5 to 7 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Refrigerated shipment will decrease migration of vinylidene chloride to back sorbent section.

SAMPLE PREPARATION:

5. Allow samples to equilibrate to room temperature before uncapping. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL CS_2 to each vial. Cap vial immediately.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark. Prepare working standards in the range 10 to 100 μg vinylidene chloride/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or peak height vs. μg vinylidene chloride).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 10 μL) of DE stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. μg vinylidene chloride recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1015-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If response is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of vinylidene chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of vinylidene chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method P&CAM 266 was issued on November 21, 1977 [1]. The method was tested with sample loadings between 13 and 85 μg vinylidene chloride per charcoal tube [2]. The samples were collected from atmospheres containing vinylidene chloride in the range 7.6 to 10.0 mg/m^3 and having relative humidity in the range 10 to 95%. The pooled relative standard deviation of the measurement was 4.8% for the analysis of 36 samples over the range 12 to 85 μg vinylidene chloride per sample. Desorption efficiency was determined to be 80% for a loading of 7 μg vinylidene chloride at a vinylidene chloride concentration of 10 mg/m^3 and high relative humidity; the breakthrough volume was 7.3 L when sampling at 0.2 L/min from this atmosphere. At 87% relative humidity, the breakthrough volume was 10% of the breakthrough volume at 10% relative humidity.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 266, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[2] Foerst, D. "A Sampling and Analytical Method for Vinylidene Chloride in Air," Am. Ind. Hyg. Assoc. J., 40: 888-893 (1979).

[3] NIOSH/OSHA Current Intelligence Bulletin 28, Vinyl Halides Carcinogenicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-102 (1978).

[4] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE.

VINYLTOLUENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

WARFARIN

$C_{19}H_{16}O_4$ MW: 308.33 CAS: 81-81-2 RTECS: GN4550000

METHOD: 5002, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 0.1 mg/m^3
NIOSH: 0.1 mg/m^3; Group I Pesticide
ACGIH: 0.1 mg/m^3; STEL 0.3 mg/m^3

PROPERTIES: solid, MP 161 °C; VP not available

SYNONYMS: 3-(*α*-acetonylbenzyl)-4-hydroxycoumarin.

SAMPLING

SAMPLER:	FILTER (1-μm PTFE membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	200 L @ 0.1 mg/m^3
-MAX:	1000 L
SHIPMENT:	routine
SAMPLE STABILITY:	93% recovery after 7 days @ 25 °C [1]
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	desirable; 1 to 5 g

ACCURACY

RANGE STUDIED:	0.054 to 0.24 mg/m^3 [1] (408-L samples)
BIAS:	none identified [1]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.056 [1]
ACCURACY:	± 11.0%

MEASUREMENT

TECHNIQUE:	HPLC, UV DETECTION
ANALYTE:	Warfarin
EXTRACTION:	5 mL methanol; swirl
INJECTION VOLUME:	20 μL
MOBILE PHASE:	30% 0.0025 N phosphoric acid and 70% methanol, isocratic, 1.5 mL/min, ambient temperature
COLUMN:	C_{18} reverse phase, 10-μm packing, 25 to 30 cm
DETECTOR:	UV absorption @ 280 nm
CALIBRATION:	standard solutions of Warfarin in methanol
RANGE:	20 to 200 μg per sample
ESTIMATED LOD:	2.5 μg per sample
PRECISION ($\hat{S}_r$):	0.016 [1]

APPLICABILITY: The working range is 0.05 to 0.5 mg/m^3 for a 400-L air sample.

INTERFERENCES: No interferences have been studied.

OTHER METHODS: This is P&CAM 313 [2] in a new format. Analytical methods for Warfarin in some rodenticides [3] and in drugs [4] are available; these are spectrophotometric methods for bulk materials.

REAGENTS:

1. Warfarin, 99%.*
2. Methanol, HPLC grade.*
3. Water, HPLC grade.
4. Phosphoric acid, 85%.*
5. Calibration stock solution, 2 mg/mL.* Dissolve 20.0 mg Warfarin in 10 mL methanol.
6. Mobile phase component, 0.0025 N phosphoric acid. Dissolve 0.06 mL 85% phosphoric acid in 1 L water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter, 1-μm pore size, and cellulose backup pad in two-piece filter holder held together with tape or shrinkable band.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with 20 to 50-μL injection loop; 25 to 30 cm, 10-μm C_{18} column; UV absorption detector at 280 nm; and integrator.
4. Jars, squat form, 60-mL, ointment, with PTFE film gaskets and screw caps.
5. Tweezers.
6. Pipet, 5-mL, and pipet bulb.
7. Syringes, microliter.
8. Volumetric flasks, 10-mL and 1-L.

SPECIAL PRECAUTIONS: Methanol is flammable and toxic. Use in fume hood and away from ignition sources.

Warfarin is toxic and can be absorbed through the skin.

Phosphoric acid is corrosive. Use gloves, goggles and other appropriate equipment to prevent eye contact and repeated or prolonged skin contact. Wash skin with water and change clothes if contact occurs.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately know flow rate between 1 and 4 L/min for a sample size of 200 to 1000 L. Do not exceed a total loading of 2 mg on the filter.

SAMPLE PREPARATION:

3. Transfer filter with tweezers to jar.
4. Add 5.0 mL methanol. Cap the jar. Swirl to wet filter thoroughly.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards covering the range 4 to 120 μg Warfarin per sample.
   a. Add aliquots (2 to 60 μL) of calibration stock solution to 5 mL methanol in ointment jars.
   b. Analyze the working standards together with the samples and blanks (steps 7 and 8). NOTE: Duplicate injections should differ by no more than 3% in peak area.
   c. Prepare a calibration graph (peak area vs. μg Warfarin).
6. Determine recovery at least once in the calibration range for each lot of filters. Prepare three filters at each of five levels plus three media blanks.
   a. Inject known volumes of calibration stock solution onto blank filters with a microliter syringe. Include media blanks.

b. Allow the filters to air dry overnight.
c. Analyze the filters (steps 3, 4, 6 and 7).
d. Prepare a graph of recovery vs. μg of Warfarin recovered.

MEASUREMENT:

7. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5002-1.
8. Make duplicate injections of each sample and working standard. Measure peak area.

CALCULATIONS:

9. Read the mass, μg (corrected for recovery) corresponding to the sample peak area of the sample (W) and average media blank (B) from the calibration graph.
10. Calculate the concentration, C (mg/m^3), of Warfarin in the volume of air sampled, V (L):

$$C = \frac{W - B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method P&CAM 313 was issued on April 13, 1979 [2]. Lab testing was done with spiked samples and atmospheres dynamically generated by Wright dust feeder from commercial formulation; no adequate independent method was used for verification [1,5]. Storage stability was 93.5% for 60-μg samples stored seven days at ambient conditions. Collection efficiency = 100% for 408-L samples at 0.24 mg/m^3; no evidence of vapor in Tenax backup. Precision was as given on page 5002-1.

REFERENCES:

[1] Backup Data Report, P&CAM 313, prepared under NIOSH Contract 210-76-0123 (unpublished, April, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 313, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] Horwitz, W., Ed. Official Methods for Analysis of the AOAC, 13th ed., p. 85 (1980).
[4] Ibid, 628.
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; P&CAM 313 developed under NIOSH Contract 210-76-0123.

XYLENE

See HYDROCARBONS, AROMATIC (Method 1501) for procedure

2,4-XYLIDINE

See AMINES, AROMATIC (Method 2002) for procedure

YTTRIUM

See ELEMENTS (Method 7300) for procedure

ZINC and compounds, as Zn

Zn MW: 65.37 (Zn); 83.17 (ZnO) CAS: 7440-66-6 (Zn), 1314-13-2 (ZnO) RTECS: ZG8600000 (Zn), ZH4810000 (ZnO)

METHOD: 7030, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3 (ZnO fume & resp. fraction); 10 mg/m^3 (ZnO dust)
NIOSH: 5 mg/m^3 (ZnO); 15 mg/m^3/15 min (ZnO dust); STEL 10 mg/m^3 (ZnO Fume)
ACGIH: 5 mg/m^3, STEL 10 mg/m^3 (ZnO fume) 10 mg/m^3 (ZnO dust)

PROPERTIES: metal; valence 2; MP 419 °C (Zn)

SYNONYMS: vary depending upon the compound.

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not measured
OVERALL PRECISION ($\hat{S}_{rT}$):	not measured
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	ATOMIC ABSORPTION, FLAME
ANALYTE:	zinc
ASHING:	conc. HNO_3, 6 mL; 140 °C
FINAL SOLUTION:	1% HNO_3, 100 mL
FLAME:	air-acetylene, oxidizing
WAVELENGTH:	213.9 nm
BACKGROUND CORRECTION:	D_2 or H_2 lamp, if needed
CALIBRATION:	Zn^{2+} in 10% HNO_3
RANGE:	10 to 100 μg per sample [1]
ESTIMATED LOD:	3 μg per sample [2]
PRECISION ($\bar{S}_r$):	0.03 [1]

APPLICABILITY: The working range is 1 to 10 mg/m^3 for a 10-L sample. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: None known.

OTHER METHODS: This method is a revision and replacement of P&CAM 173 for Zinc [1,3]. Method 7300 (plasma emission) is an alternate analytical method. Method 7502 (X-ray diffraction) is specific for ZnO.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Add 10 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 μg/mL Zn. Commercial standard or dissolve 1.00 g Zn metal in minimum volume of (1+1) HCl; dilute to 1 L with 1% (v/v) HNO_3.
4. Air, filtered.
5. Acetylene.
6. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with air-acetylene burner head and zinc hollow cathode lamp or electrodeless discharge lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, With watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Micropipets, 1 to 100 μL.*
8. Hotplate, surface temperature 140 °C.

* Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 2 to 400 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add additional acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 1% HNO_3.
7. Place the beakers on the hotplate and allow to go to near dryness (ca. 0.5 mL liquid remaining).
8. Rinse walls of beaker with 10 mL 10% HNO_3. Reheat 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 100-mL volumetric flask and dilute to volume with distilled or deionized water.

   NOTE: Dilute to a smaller volume, e.g., 10 mL, if required for sensitivity of analysis for other metals in the sample.

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts, covering the range 0 to 100 μg Zn per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 1% HNO_3.
11. Analyze the working standards together with the samples and blanks (steps 16 and 17).
12. Prepare a calibration graph of absorbance vs. solution concentration (μg/mL).
13. Aspirate a standard for every 10 samples to check instrument drift.
14. Check recoveries with at least one spiked media blank per 10 samples.
15. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

16. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7030-1.
    NOTE: Non-atomic absorption may require the use of D_2 or H_2 continuum background correction in some samples.
17. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 1% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. Using the measured absorbances, calculate the corresponding concentrations (μg/mL) of zinc in the sample, C_s, and average media blank, C_b, from the calibration graph.
19. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of zinc in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Estimated LOD was 3 μg Zn per sample [2]. Since only the analytical procedure was studied, bias, overall precision, and accuracy were not determined.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2] User check, UBTL, NIOSH Seq.# 3990-P (unpublished, November 29, 1983).
[3] Criteria for a Recommended Standard...Occupational Exposure to Zinc Oxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-104 (1976).

METHOD WRITTEN BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS.

ZINC OXIDE

ZnO MW: 81.38 CAS: 1314-13-2 RTECS: ZH4810000

METHOD: 7502, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3 (fume); 15 mg/m^3 (dust)
NIOSH: 5 mg/m^3; C 15 mg/m^3/15 min (dust); 5 mg/m^3; STEL 10 mg/m^3 (fume)
ACGIH: 5 mg/m^3; STEL 10 mg/m^3 (fume) 10 mg/m^3 (dust)

PROPERTIES: solid; d 5.61 g/cm^3 @ 25 °C; MP 1975 °C

SYNONYMS: China white; zinc white; zincite.

SAMPLING

SAMPLER: FILTER (0.8-µm PVC membrane, 25-mm diameter, in open-face cassette)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: high-volume air sample required

ACCURACY

RANGE STUDIED: 0.1 to 11 mg/m^3 [1,2] (180-L samples)

BIAS: 2.7% [2,3,4]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [2]

ACCURACY: ± 21.6%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: crystalline zinc oxide; direct analysis on filter

XRD: Cu target X-ray tube. Optimize for intensity; 1° slit, Graphite monochromator; scintillation detector. Slow step scan, 0.02°/10 sec, integrated intensity with background subtraction

CALIBRATION: suspensions of ZnO in 2-propanol

RANGE: 50 to 2000 µg per sample

ESTIMATED LOD: 5 µg per sample

PRECISION ($\hat{S}_r$): 0.15 @ 1 mg/m^3; 0.05 for greater than 2 mg/m^3

APPLICABILITY: The working range is 0.25 to 10 mg/m^3 for a 200-L air sample. The method does not distinguish zinc oxide fume from zinc oxide dust.

INTERFERENCES: Major interferences include Fe_2O_3, Zn, $Zn(NH_3)_2Cl_2$, $(NH_4)_3ZnCl_5$, $(NH_4)_2ZnCl_4$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$; these are resolved by using alternate analyte peaks. Particle size affects intensity measurements.

OTHER METHODS: This method combines and replaces Methods P&CAM 222 [1] and S316 [5]. The criteria document contains an elemental analysis for zinc [6].

REAGENTS:

1. Zinc oxide, ACS reagent grade. Average particle size between 0.5 μm and 10 μm.
2. 2-Propanol.
3. Desiccant.
4. Glue or tape for securing filters to XRD holders.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) or PVC-acrylonitrile membrane filters, 25-mm diameter, 0.8-μm pore size; three-piece filter cassette.
   NOTE: An extension cowl on the filter cassette is desirable to produce a more uniform deposit and to prevent contamination of the open-face filter during sampling.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High-volume sampling pump, 10 L/min.
4. X-ray powder diffractometer equipped with copper target X-ray tube and scintillation detector.
5. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
6. Filtration apparatus and side arm vacuum flask with 25-mm filter holders.
7. Analytical balance (0.01 mg); magnetic stirrer; ultrasonic bath or probe; volumetric pipettes and flasks; desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: none.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample open-face at 1 to 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.
3. Take a high-volume (4000 L) air sample using a clean sampler and high-volume sampling pump in the same area as the personal sample(s) for qualitative identification.

SAMPLE PREPARATION:

4. Mount field samples and blanks on XRD sample holders using appropriate methods for securing the sample to the XRD holder.

CALIBRATION AND QUALITY CONTROL:

5. Prepare two suspensions of ZnO in 2-propanol by weighing 10 mg and 50 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer to a 1-L glass-stoppered bottle using 1 L 2-propanol.
6. Suspend the powder in 2-propanol by using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.

7. Prepare a series of standard filters using the 10 and 50 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range (or sample range if known). Standards at 20, 30, 50 100, 200 and 500 μg are usually sufficient.
8. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet. Transfer the aliquot from the pipet to the filter funnel, keeping the tip of the pipet near the surface of the liquid but not submerged.
9. Rinse the pipet with several mL of 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
10. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place to avoid disturbing it. Transfer the filter to the XRD sample mount.
11. Perform step scans on the standards using the same diffraction peaks and instrumental conditions as for samples (step 16). The resulting intensities for standards, I_x°, are normalized in the following procedure.
12. Determine the net count, I_r, of the reference specimen before or after each unknown, standard or blank is scanned. Use a diffraction peak of high intensity that can be measured rapidly but reproducibly (less than 1% S_r). Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak. This factor never changes and should be used for all measurements made on a particular diffractometer.

    Calculate and record the normalized intensity, $\hat{I}_x^\circ$, for the analyte or silver peaks on each sample, field blank, media blank and standard:

$$\hat{I}_x^\circ = \frac{I_x^\circ}{I_r} \cdot N.$$

    NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently. In this case, the net intensities of the analyte, I_x, should be normalized to the most recently measured reference intensity.
13. Prepare a calibration graph ($\hat{I}_x^\circ$ vs. μg analyte).
    NOTE: Poor reproducibility at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable. Curvature can be eliminated with absorption corrections based on the mass absorption coefficient of the analyte [7,8,9].
14. Determine the initial slope, m, of the linear portion of the calibration graph in counts/μg. The intercept, b, of the line with the $\hat{I}_x^\circ$ axis should be approximately zero.
    NOTE: A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

MEASUREMENT:

15. Obtain a qualitative X-ray diffraction scan (broad 2-theta range) of the high-volume respirable sample to determine the presence of ZnO and any matrix interference. The expected diffraction peaks are as follows:

ZnO Peak (2-Theta Degrees)		
Primary	Secondary	Tertiary
36.26	31.75	34.44

16. Analyze the sample filters by step-scanning the most intense interference-free diffraction peak of zinc oxide and determine the integrated intensity. Measure the background on each side of the peak for one half the time used for peak scanning and add the counts from each side for a total (average) background. Determine the 2-theta position of the background for each sample. The net count or intensity, I_x, is the difference between the peak integrated count and the total background count. The net intensity is normalized as in step 12 to obtain $\hat{I}_x$.
17. Scan each field blank over the same 2-theta range used for the analyte. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent.

CALCULATIONS:

18. The concentration of ZnO in the air sample is:

$$C = \frac{(\hat{I}_x - b)}{m \cdot V}, \text{ mg/m}^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration curve (I_x^o vs. W)
m = initial slope of calibration graph (counts/μg)
V = air volume sampled (L).

In heavily-loaded samples, particularly those rich in heavy elements, X-ray absorption may cause reduced intensities and underestimation of ZnO. If this is suspected, an absorption correction can be made [8]. The collection filters and blanks are mounted on a smooth metal plate (substrate) for XRD quantitation. The substrate should have a non-interfering diffraction peak which is measured at the same time as the ZnO peak. By measuring the substrate peak on both samples and blanks, an absorption correction like that in the silica method (Method 7500) can be made. The absorption correction factor must be calculated for each sample from the formula in Method 7500 which takes into account the diffraction angles for the particular substrate chosen. Altree-Williams used a silver filter under the collection filter [7].

EVALUATION OF METHOD:

In a comparison of this method with atomic absorption spectrophotometry [3,4], zinc was determined on 15 Gelman DM-800 filters containing added zinc oxide in the range 250 to 1000 μg. The average percent difference for the 15 pairs was 2.7%. Method S316 was validated with generated samples in the range of 2.4 to 9.9 mg/m^3 [2,5,10]. A pooled $\hat{S}_{rT}$ of 0.088 was found for 18 samples of 180 L collected from the aerosol.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 222, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Zinc Oxide Fume, S316, Backup Data Report, NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB 275-834 from National Technical Information Service, Springfield, VA 22161.
[3] Haartz, J. C., M. L. Bolyard and M. T. Abell. Quantitation of Zinc Chloride and Zinc Oxide in Airborne Samples, paper presented at the American Industrial Hygiene Conference, Minneapolis, MN (June, 1975).
[4] Dollberg, D. D., M. T. Abell and B. A. Lange. Occupational Health Analytical Chemistry: Quantitation Using X-Ray Powder Diffraction, ACS Symposium Series, 120, 43 (1980).
[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, S316, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1979).
[6] Criteria for a Recommended Standard...Occupational Exposure to Zinc Oxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-104 (1975).
[7] Altree-Williams, S., J. Lee and N. V. Mezin. Quantitative X-ray Diffraction on Respirable Dust Collected on Nuclepore Filters, Annals of Occup. Hyg., 20, 109 (1977).
[8] Leroux, J. and C. Powers. Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters, Occup. Health Rev., 21, 26 (1970).
[9] Williams, D. D. Direct Quantitative Diffractometric Analysis, Anal. Chem., 31, 1841 (1959).
[10] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD WRITTEN BY:

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ZIRCONIUM

See ELEMENTS (Method 7300)

ELEMENTS IN BLOOD AND TISSUE (Method 8005)

VOLUME

cm^3	liters	m^3	in^3	ft^3	oz (fl, U.S.)
1	0.001	0.000001	0.061024	0.000035315	0.033814
1000	1	0.001	61.024	0.035315	33.814
1000000	1000	1	61024.	35.315	33814.
16.387	0.016387	0.000016387	1	0.0005787	0.55411
28317	28.317	0.028317	1728.	1	957.51
29.574	0.029574	0.000029574	1.8047	0.0010444	1

PRESSURE

atm	mm Hg, 0 °C	in. water, 20 °C	lb/in^2	kg/cm^2	kPa
1	760.	407.51	14.696	1.0333	101.33
0.0013158	1	0.53620	0.019337	0.0013595	0.13332
0.0024539	1.8650	1	0.036062	0.0025354	0.24864
0.068046	51.715	27.730	1	0.070307	6.8947
0.96784	735.56	394.41	1.4223	1	98.066
0.0098692	7.5006	4.0219	0.14504	0.010197	1

CONCENTRATION IN AIR

Gas or Vapor

parts per million	% by volume	mg/m^3
1	0.0001	$M.W./V_m$
10000	1	$M.W.\cdot 10^4/V_m$
$V_m/M.W.$	$V_m/M.W.\cdot 10^4$	1

where V_m, the volume of 1 mole of gas, is:

V_m (L) = 62.36 (t, °C + 273.15)/(P, mm Hg)

V_m as a function of t and P

	p, mm Hg			
	640	680	720	760
40	30.51	28.72	27.12	25.70
30	29.54	27.80	26.26	24.87
25	29.05	27.34	25.82	24.46
t, °C 20	28.56	26.88	25.39	24.05
10	27.59	25.97	24.52	23.23
0	26.62	25.05	23.66	22.41

Aerosol

mg/m^3	particles per cm^3	MPPCF
1	S/1000	S/35310
1000/S	1	0.02832
35310/S	35.31	1

where S, specific mass in particles/μg, is:

$S = 1/[(4\pi/3)(D_s/2)^3\ d\cdot 10^6]$

where: D_s = Stokes diam., μm
d = particle density, g/cm^3

EXAMPLES (assumes monodisperse aerosol):

Aerosol	D_s, μm	d, g/cm^3	S, p/μg
Steel	10	7.5	250
Quartz	10	2.65	720
Fe_2O_3	5	5.2	2900
Quartz	5	2.65	5800
Quartz	2	2.65	$9\cdot 10^4$
PbO fume	1	9.5	$2\cdot 10^5$
PbO fume	0.2	9.5	$2.5\cdot 10^7$

APPENDIX B. Air Concentration Calculations for Comparison to OSHA Standards

OSHA Permissible Exposure Limits (PEL) are set on the basis of mass of toxic substance per unit volume of air at ambient conditions. Therefore, the OSHA PEL in mg/m^3 is absolutely fixed and not subject to corrections for temperature and pressure. This constraint implies that volume concentration of gases in parts per million (ppm) must be with reference to some defined temperature and pressure; these are NTP (25 °C and 760 mm Hg) in the OSHA PEL limit.

The following formulae, therefore, must be used in calculations comparing analytical results to OSHA PEL. Each of the methods in this Manual uses a similar calculation.

Physical Form of Substance Sampled	Unit of Air Concentration	Formula for Direct Comparison With OSHA PEL Table
Gas	ppm	$C_v = \frac{m \cdot 10^3}{V} \cdot \frac{24.46}{MW}$
Gas	mg/m3	$C = \frac{m \cdot 10^3}{V}$
Aerosol	mg/m^3	$C = \frac{m \cdot 10^3}{V}$

where: m = actual mass of substance, in mg, found on the sampling device
V = air volume, L, taken at the sampling site, ambient temperature and pressure
24.46 = the volume (L) of 1 mole of gas at 25 °C and 760 mm Hg
C_v = air concentration, ppm by volume, at 25 °C and 760 mm Hg
C = air concentration, mg/m^3
MW = molecular weight, grams/mole

Example: A personal sampling pump is calibrated at 25 °C and 630 mm Hg, and then used to sample air at 20 °C and 660 mm Hg for 60 min at a flow rate of 1.00 L/min. The analytical lab reports 0.188 mg of allyl chloride (MW 76.5) in the sample. What is the air concentration relative to the OSHA PEL?

NOTE: If the sampling pump uses a rotometer for flow rate indication, the calibrated flow rate must be corrected for the actual air pressure and temperature during sampling. (See formula on p. 26.) In this example the pump does not use a rotameter, so the calibrated flow rate is used.

Solution: Concentration of allyl chloride, for comparison with the OSHA PEL, is:

$$C_v = \frac{0.188 \cdot 1000}{60} \cdot \frac{24.46}{76.5} = 1.0 \text{ ppm}$$

or

$$C = \frac{0.182 \cdot 1000}{60} = 3.13 \text{ mg/m}^3$$

These values indicate that the concentration of allyl chloride is at the OSHA PEL.

IV. GLOSSARY OF ABBREVIATIONS, DEFINITIONS, AND SYMBOLS

AAS	Atomic absorption spectrophotometry.
Acceptable range (biological)	The range of values of a biological monitoring analyte that would be expected in workers with exposure to the environmental chemical in the workplace at or below Federal Standard or TLV-recommended levels. These ranges are often method-specific.
Accuracy	The degree of agreement between a measured value and the accepted reference value. In this manual, accuracy is calculated from the absolute mean bias of the method plus the overall precision, $\hat{S}_{r,T}$, at the 95% confidence level. For an individual measurement, it includes the combination of precision and bias (see Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 and NIOSH Research Report, Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, USDHHS Publ. (NIOSH) 80-133).
ACGIH	American Conference of Governmental Industrial Hygienists, 1330 Kemper Meadow Drive, Suite 600, Cincinnati, OH 45240, telephone: (513)-742-2020. See TLV.
Ashing	The decomposition, prior to analysis, of organic matrix constituents of the sample and sampler. The most common ashing techniques are solvent, acid, or alkali dissolution; alkaline fusion; and oxidation using either low-temperature oxygen plasma or muffle furnace.
ASV	Anodic stripping voltammetry.
B	Media blank result for a single-section sampler (e.g., membrane filter).
B_b	Media blank result for back section of a sampler.
B_f	Media blank result for front section of a sampler.
Bias	Difference between the average measured mass or concentration and reference mass or concentration expressed as a fraction of reference mass or concentration.
Bioaerosol	Suspension of microorganisms in air.
Biological monitoring	The measurements of the absorption of an environmental chemical in the worker by analysis of a biological specimen for the chemical agent, its metabolites or some specific effect on the worker.
Blank	See Field blank, Media blank, and Reagent blank.

BP	Boiling point, °C.
Breakthrough	Elution of substance being sampled from the exit end of a sorbent bed during the process of sampling air.
C	1. Concentration of gaseous, liquid, or solid substance in air, mg/m^3; 2. Acceptable ceiling concentration (for a specified maximum time of exposure) when applied to personal permissible exposure limits.
Calibration graph	Plot of analytical response vs. known mass or concentration of analyte.
CAS #	Chemical Abstracts Service Registry Number.
CE	Collection efficiency, expressed as a decimal fraction.
49 CFR 171-177	Title 49 (Transportation), Code of Federal Regulations. U. S. regulations governing shipment of hazardous materials.
conc.	Concentrated.
Control (biological)	A value or group of values of a biological monitoring parameter collected from workers with little or no occupational exposure to the specific chemical.
C_v	Concentration of gaseous substance in air, parts per million (V/V). In this manual, C_v is referred to NTP such that $C_v = C \times 24.46/M.W.$
CV	See S_r.
d	Density, g/cm^3.
DE	Desorption efficiency; fraction of known quantity of analyte recovered from spiked solid sorbent media blank. DE may be a function of loading, and should be determined by the chemist for each lot of solid sorbent used for sampling, in the concentration range of interest. Plot (mass recovered minus average media blank)/mass added vs. (mass recovered minus average media blank).
Detection limit	See LOD.
DNE	Do not exceed.
D_s	Stokes diameter.
ECD	Electron capture detector.
EPA	U.S. Environmental Protection Agency.
est	Estimated.

f	Fibers.
FID	Hydrogen-air flame ionization detector.
Field blank	A sampler handled exactly the same as the field samples, except no air is drawn through it. Used to estimate contamination in preparation for sampling, shipment and storage prior to measurement, but not actually subtracted from sample readings (see media blank).
FPD	Flame photometric detector.
FTIR	Fourier transform infrared spectroscopy.
GC	Gas chromatography.
GPO	U.S. Government Printing Office, Washington, DC 20402.
Hemolysis	Rupture of red blood cells due to improper collection and handling of whole blood.
HGAAS	Heated graphite furnace atomic absorption spectrophotometry.
HPLC	High performance liquid chromatography.
IC	Ion chromatography; ion-exchange chromatography.
ICP-AES	Inductively coupled plasma - atomic emission spectrometry, also called ICP.
Interference equivalent	Mass or concentration of interfering substance which gives the same measurement reading as unit mass or concentration of substance being measured.
IR	Infrared.
LAQL	Lowest analytically quantifiable level; see LOQ.
LC	Liquid chromatography.
LOD	Limit of detection (detection limit); smallest amount of analyte which can be distinguished from background. A good estimate for unbiased analyses, with media blanks not distinguishable from background, is three times the standard error of the calibration graph for low concentrations, divided by the slope (instrument reading per unit mass or per unit concentration of analyte).
LOQ	Limit of quantitation; mass of analyte equal to 10 times the standard error of the calibration graph divided by the slope; approximately the mass of analyte for which relative standard deviation, $\bar{S}_r$, equals 0.10.

LTA	Low temperature (oxygen plasma) ashing.
MCEF	Mixed cellulose ester membrane filter.
Measurement range	Range of substance, in mass per sample, from the LOQ (or from 10 times the LOD, if LOQ is not known) to an upper limit characteristic of the analytical method, e.g., the limit of linearity or the mass at which precision of the method starts to become worse than $\bar{S}_r = 0.1$.
Media blank	An unexposed sampler, not taken to the field or shipped, used for background correction of sample readings or for recovery studies.
Metabolite	A substance produced directly by a biotransformation of a chemical. For example, phenol in urine is a metabolite of benzene and is representative of benzene absorption in the worker.
MP	Melting point, °C.
mppcf	Million particles per cubic foot.
MS	Mass spectrometry.
M.W.	Molecular weight.
NIOSH	National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, Public Health Service, U. S. Department of Health and Human Services.
Normal range (biological)	The range of values of a biological monitoring analyte that would be expected in workers without exposure to the environmental chemical in the workplace. Normal ranges are often method-specific.
NTIS	National Technical Information Service, Springfield, VA 22161.
NTP	Normal temperature and pressure, 25 °C (298 K) and 760 mm Hg (101.33 kPa), at which the molar volume of an ideal gas is 24.46 L.
OSHA	Occupational Safety and Health Administration, U. S. Department of Labor.
P	1 Peak (maximum permissible instantaneous) concentration; 2 pressure.
PAH	Polynuclear aromatic hydrocarbons; PNAH.
P_c	Pressure, kPa, at which sampling pump was calibrated.
PCM	Phase contrast microscopy.

PEL	OSHPEL; OSHA permissible exposure limit, expressed as ppm or mg/m^3 of substance in air.
PID	Photoionization detector.
Plasma, blood	The clear supernatant from whole blood collected with anticoagulants. Blood is collected, mixed with the anticoagulant and centrifuged to separate the plasma from red blood cells. Plasma contains all clotting factors.
PLM	Polarized light microscopy.
Pool (biological)	A combination of biological specimens (i.e., urine or serum) from many workers that is used to prepare small aliquots to be run with each batch of analyses. The analyte must be stable in the biological matrix and under the storage conditions used. Aliquots of these pools are analyzed with each batch of samples and the data are used to develop quality control charts.
Precision	The repeatability or reproducibility of individual measurements expressed as standard deviation, S, or relative standard deviation, S, (q.v.). See Accuracy.
Proficiency testing	Any interlaboratory testing program where stable specimens are sent to participating laboratories for analysis. Results from all participating laboratories are compared, pooled, and tabulated by the testing program operator with the purpose of improving laboratory performance.
P_s	Pressure, kPa, at which air sample was taken.
PTFE	Polytetrafluoroethylene; polyperfluoroethylene; tetrafluoroethene homopolymer; Teflon.
PVC	Polyvinyl chloride.
Q	Sampling flow rate, L/min.
Reagent blank	Reagent(s), without analyte or sampling media added, which are analyzed to determine their contribution to the total blank reading.
Recovery, R	Fraction recovered (see DE); previously associated with Analytical Method Recovery (AMR), a term which is no longer used.
Relative standard deviation	See S_r and Precision.

Respirable dust	Dust deposited in the non-ciliated portions of the lungs. Percent deposition is a function of the particle's aerodynamic diameter. Different definitions for the deposition of respirable dust have been given by the ACGIH (see reference under TLV), the British Medical Research Council and other groups. Respirable dust is measured by a sampler whose collection efficiency is equivalent to one of these definitions [see International Standards Organization, TC146, "Size Definitions for Particle Sampling," Amer. Ind. Hyg. Assoc. J. 42(5), A64-A68 (1981)].
R_f	In thin-layer chromatography, the ratio of distance travelled by the analyte from point of application to that of the solvent front.
RF	Radio frequency.
Rotameter calibration correction	See V, and Appendix B (page A-2) for an example.
RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH).
Ruggedness test	Partial or complete analysis of variance using experiments in which operational parameters of a sampling and measurement method are varied within a small range to determine their effect on overall variance (see Youden, W. J. and E. H. Steiner, Statistical Manual of the AOAC, Association of Official Analytical Chemists, Arlington, VA, 1975).
S	1. Estimate of the standard deviation; 2. Specific mass, particles/mg.
S_b	Estimate of the standard deviation of media blank.
S_r	Estimate of the relative standard deviation, equal to S divided by the mean of a series of measurements. A measure of precision. Previously called CV (coefficient of variation).
$\bar{S}_r$	Pooled relative standard deviation. Formerly $\hat{C}V$.
$\hat{S}_{rT}$	Estimate of overall precision including pump error. Formerly $\hat{C}V_T$.
Screening test (biological)	An easily performed method, often relatively non-specific, to assess worker exposure to a class of compounds by use of biological monitoring.
SEM	Scanning electron microscopy.
Sensitivity	Change in measurement signal per unit change in analyte mass (e.g., slope of calibration graph).
Serum	The clear supernatant from whole blood collected without anticoagulants, allowed to clot (30 minutes) and centifuged to separate serum from the clotted blood. Serum does not contain clotting factors.

Solvent flush technique	Recommended manual gas chromatographic injection technique: 1. Flush syringe several times with solvent; 2. Draw into 10-μL syringe, in order: 3 μL solvent, 0.2 μL air, 5 μL sample, 1.2 μL air; and 3. Inject entire contents of syringe into GC.
Spike	A known mass of analyte added to a sampler for the purpose of determining recovery (analyst spikes), or for quality control (blind spikes). Also see DE.
sp.gr.	Specific gravity, relative to water at the same temperature.
Spot sample (urine)	Urine sample collected at a specified time.
STEL	Short-Term (15-min) Exposure Limit.
t	1. Temperature, °C; 2. time, min.
T_c	Temperature, kelvins (K), at which sampling pump was calibrated.
TEM	Transmission electron microscopy.
TLC	Thin-layer chromatography.
TLV	Threshold limit value, listed in 1993-1994 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Indices (American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1993).
t_r	Retention time, min.
T_s	Temperature, kelvins (K), at which air sample was taken.
TWA	Time-weighted average.
User check	An evaluation of a written procedure for clarity and accuracy in which an independent laboratory analyzes a small number of spiked samples following the procedure exactly.
UV	Ultraviolet.
V	Volume of air sample, in L, as taken at the sampling site, corrected if necessary for rotameter calibration at a different temperature and pressure: $V = (\text{flow rate})(\text{time})(P_c\ T_s/P_s\ T_c)^{0.5}$ (see Appendix II for an example).

Validated method	A method which meets or exceeds certain sampling and measurement performance criteria; for example, the criteria given in Chapter E, "Development and Evaluation of Methods."
V_m	Volume of 1 mole of ideal gas at the specified temperature and pressure (e.g., 24.45 L at 25 °C and 1 atm).
VOL-MAX	Maximum recommended air sample volume, L, based on sampler capacity or other limitation, @ OSHA PEL.
VOL-MIN	Minimum recommended air sample volume, L, based on an atmosphere at the OSHA PEL concentration and collecting a mass of substance which is equal to the LOQ. See also Working range.
VP	Vapor pressure.
W	Mass of analyte found on an exposed single-section sampler (e.g., membrane filter).
W_b	Mass of analyte found on the back section of an exposed sampler.
W_f	Mass of analyte found on the front section of an exposed sampler.
Working range	Range of air concentrations, in ppm or mg/m^3 at specified air sample volume, extending from the LOQ to a maximum determined by sampler capacity or measurement considerations.
XRD	X-ray diffraction.
XRF	X-ray fluorescence.

V. A. INDEX OF FOURTH EDITION METHOD NUMBERS

0500 PARTICULATES NOT OTHERWISE REGULATED, TOTAL (Grav)
0600 PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE (Grav)

1000 ALLYL CHLORIDE (GC)
1001 METHYL CHLORIDE (GC)
1002 CHLOROPRENE (GC)
1003 HYDROCARBONS, HALOGENATED (GC)
- benzyl chloride
- bromoform
- carbon tetrachloride
- chlorobenzene
- chlorobromomethane
- chloroform
- o-dichlorobenzene
- p-dichlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethylene
- ethylene dichloride
- hexachloroethane
- methylchloroform
- tetrachloroethylene
- 1,1,2-trichloroethane
- 1,2,3-trichloropropane

1004 DICHLOROETHYL ETHER (GC)
1005 METHYLENE CHLORIDE (GC)
1006 FLUOROTRICHLOROMETHANE(GC)
1007 VINYL CHLORIDE (GC)
1008 ETHYLENE DIBROMIDE (GC)
1009 VINYL BROMIDE (GC)
1010 EPICHLOROHYDRIN (GC)
1011 ETHYL BROMIDE (GC)
1012 DIFLUORODIBROMOMETHANE(GC)
1013 PROPYLENE DICHLORIDE (GC)
1014 METHYL IODIDE (GC)
1015 VINYLIDENE CHLORIDE (GC)
1016 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE (GC)
1017 BROMOTRIFLUOROMETHANE (GC)
1018 DICHLORODIFLUOROMETHANE & 1,2-DICHLOROTETRAFLUOROETHANE (GC)
1019 1,1,2,2-TETRACHLOROETHANE (GC)
1020 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE (GC)
1022 TRICHLOROETHYLENE (GC)
1024 1,3-BUTADIENE (GC)
1300 KETONES I (GC)
- acetone
- cyclohexanone
- diisobutyl ketone
- 2-hexanone
- methyl isobutyl ketone
- 2-pentanone

1301 KETONES II (GC)
- camphor
- ethyl butyl ketone
- mesityl oxide
- 5-methyl-3-heptanone
- methyl-(n-amyl)-ketone

1400 ALCOHOLS I (GC)
- tert-butyl alcohol
- isopropyl alcohol
- ethanol

1401 ALCOHOLS II (GC)
- n-butyl alcohol
- sec-butyl alcohol
- isobutyl alcohol
- n-propyl alcohol

1402 ALCOHOLS III (GC)
- allyl alcohol
- cyclohexanol
- isoamyl alcohol
- diacetone alcohol
- methyl isobutyl carbinol

1403 ALCOHOLS IV (GC)
- 2-butoxyethanol
- 2-ethoxyethanol
- 2-methoxyethanol

1404 METHYLCYCLOHEXANOL (GC)
1450 ESTERS I (GC)
- n-amyl acetate
- sec-amyl acetate
- n-butyl acetate
- sec-butyl aetate
- tert-butyl acetate
- 2-ethoxyethyl acetate
- ethyl acrylate
- isoamyl acetate
- isobutyl acetate
- methyl isoamyl acetate
- n-propyl acetate

1451 METHYL CELLOSOLVE ACETATE (GC)
1452 ETHYL FORMATE (GC)
1453 VINYL ACETATE (GC)
1454 ISOPROPYL ACETATE (GC)
1457 ETHYL ACETATE (GC)
1458 METHYL ACETATE (GC)
1459 METHYL ACRYLATE (GC)
1500 HYDROCARBONS, BP 36-126°C (GC)
- benzene
- cyclohexane

cyclohexene
n-heptane
n-hexane
methylcyclohexane
n-octane
n-pentane
toluene

1501 HYDROCARBONS, AROMATIC (GC)
benzene
p-tert-butyl toluene
cumene
ethylbenzene
α-methylstyrene
naphthlene
styrene
toluene
vinyl toluene
xylene
1550 NAPHTHAS (GC)
Coal tar naphtha
Kerosene
Mineral spirits
Petroleum ether
Petroleum naphtha
Rubber solvent
Stoddard solvent
1551 TURPENTINE (GC)
1600 CARBON DISULFIDE (GC)
1601 1,1-DICHLORO-1-NITROETHANE (GC)
1602 DIOXANE (GC)
1603 ACETIC ACID (GC)
1604 ACRYLONITRILE (GC)
1606 ACETONITRILE (GC)
1608 GLYCIDOL (GC)
1609 TETRAHYDROFURAN (GC)
1610 ETHYL ETHER (GC)
1611 METHYLAL (GC)
1612 PROPYLENE OXIDE (GC)
1613 PYRIDINE (GC)
1614 ETHYLENE OXIDE (GC)
1615 METHYL tert-BUTYL ETHER (MTBE)(GC)
1616 n-BUTYL GLYCIDYL ETHER (GC)
1617 PHENYL ETHER (GC)
1618 ISOPROPYL ETHER (GC)
1619 PHENYL GLYCIDYL ETHER (GC)
1620 ISOPROPYL GLYCIDYL ETHER (GC)

2000 METHANOL (GC)
2002 AMINES, AROMATIC (GC)
aniline
N,N-dimethyl aniline
N,N-dimethyl-p-toluidine
o-toluidine
2,4-xylidine
2003 1,1,2,2-TETRABROMOETHANE(GC)
2004 DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE (GC)
2005 NITROBENZENES (GC)
4-chloronitrobenzene
nitrobenzene
nitrotoluene
2007 AMINOETHANOL COMPOUNDS I (GC)
2-aminoethanol
2-dibutylaminoethanol
2-diethylaminoethanol
2008 CHLOROACETIC ACID (IC)
2010 AMINES, ALIPHATIC (GC)
diethylamine
dimethylamine
2011 FORMIC ACID (IC)
2012 n-BUTYLAMINE (GC)
2013 PHENYL ETHER & DIPHENYL (GC)
2014 p-CHLOROPHENOL (HPLC)
2500 METHYL ETHYL KETONE (GC)
2501 ACROLEIN (GC)
2504 TETRAETHYL PYROPHOSPHATE (TEPP)(GC)
2505 FURFURYL ALCOHOL (GC)
2506 ACETONE CYANOHYDRIN (GC)
2507 NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE (GC)
2508 ISOPHORONE (GC)
2510 1-OCTANETHIOL (GC)
2513 ETHYLENE CHLOROHYDRIN (GC)
2514 ANISIDINE (HPLC)
2515 DIAZOMETHANE (GC)
2516 DICHLOROFLUOROMETHANE (GC)
2517 PENTACHLOROETHANE (GC)
2518 HEXACHLORO-1,3-CYCLOPENTADIENE (GC)
2519 ETHYL CHLORIDE (GC)
2521 METHYL CYCLOHEXANONE (GC)
2522 NITROSAMINES (GC)
N-nitrosodimethylamine
N-nitrodiethylamine
N-nitrosodipropylamine
N-nitrosodibutylamine
N-nitrosomorpholine
N-nitrosopiperidine
N-nitrosopyrrolidine
2523 1,3-CYCLOPENTADIENE (GC)
2524 DIMETHYL SULFATE (GC)
2526 NITROETHANE (GC)
2527 NITROMETHANE (GC)
2528 2-NITROPROPANE (GC)
2529 FURFURAL (GC)
2530 DIPHENYL (GC)
2532 GLUTARALDEHYDE (HPLC)
2533 TETRAETHYL LEAD, as Pb (GC)

2534 TETRAMETHYL LEAD, as Pb (GC)
2535 TOLUENE-2,4-DIISOCYANATE (HPLC)
2536 VALERALDEHYDE (GC)
2537 METHYL METHACRYLATE (GC)
2538 ACETALDEHYDE (GC)
2539 ALDEHYDES, SCREENING (GC)
2540 ETHYLENEDIAMINE, DIETHYLENETRIAMINE, and TRIETHYLENETETRAMINE (HPLC)
2541 FORMALDEHYDE by GC
2542 MERCAPTANS, METHYL, ETHYL, n-BUTYL (GC)
2543 HEXACHLOROBUTADIENE (GC/ECD)
2544 NICOTINE (GC/NPD)
2545 ALLYL GLYCIDIL ETHER (GC)
2546 CRESOLS and PHENOL (GC)

3500 FORMALDEHYDE (chromotropic acid)(VIS)
3503 HYDRAZINE (VIS)
3505 TETRAMETHYL THIOUREA (VIS)
3506 ACETIC ANHYDRIDE (VIS)
3507 ACETALDEHYDE (HPLC)
3508 METHYL ETHYL KETONE PEROXIDE (VIS)
3509 AMINOETHANOL COMPOUNDS II (IC)
monoethanolamine (MEA)
diethanolamine (DEA)
triethanolamine (TEA)
3510 MONOMETHYLHYDRAZINE (VIS)
3511 n-METHYLANILINE (GC)
3512 MALEIC ANHYDRIDE (HPLC)
3513 TETRANITROMETHANE (GC/NPD)
3514 ETHYLENIMINE (HPLC)
3515 1,1-DIMETHYLHYDRAZINE (VIS)
3516 CROTONALDEHYDE (POL)
3518 PHENYLHYDRAZINE (VIS)
3700 BENZENE (portable GC)
3701 TRICHLOROETHYLENE (portable GC)
3702 ETHYLENE OXIDE (portable GC)
3703 METHYLENE CHLORIDE (portable GC)

4000 TOLUENE, passive (GC)

5000 CARBON BLACK (Grav)
5001 2,4-D AND 2,4,5-T (HPLC)
5002 WARFARIN (HPLC)
5003 PARAQUAT (HPLC)
5004 HYDROQUINONE (HPLC)
5005 THIRAM (HPLC)
5006 CARBARYL (SEVIN) (VIS)
5007 ROTENONE (HPLC)
5008 PYRETHRUM (HPLC)
5009 BENZOYL PEROXIDE (HPLC)
5010 BROMOXYNIL and BROMOXYNIL OCTANOATE (HPLC)
5011 ETHYLENE THIOUREA (VIS)
5012 EPN (GC)
5013 DYES, BENZIDINE, *o*-ANISIDINE, and *o*-TOLIDINE (HPLC)
5014 CHLORINATED TERPHENYL (GC)
5016 STRYCHNINE (HPLC)
5017 DIBUTYL PHOSPHATE (GC)
5018 2,4,7-TRINITROFLUOREN-9-ONE (HPLC)
5019 AZELAIC ACID (GC)
5020 DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE (GC)
5021 *o*-TERPHENYL (GC)
5022 ARSENIC, ORGANO- (IC/HGAAS)
p-aminophenyl arsonic acid
dimethyl arsenic acid
methylarsonic acid
5025 CHLORINATED DIPHENYL ETHER (GC)
5026 OIL MIST, MINERAL (IR)
5027 RIBAVARIN (HPLC)
5029 4,4'-METHYLENEDIANILINE (MDA)(HPLC)
5030 CYANURIC ACID (HPLC)
5031 ASPARTAME (HPLC)
5032 PENTAMIDINE ISETHIONATE (HPLC)
5033 *p*-NITROANILINE (HPLC)
5034 TRIBUTYL PHOSPHATE (GC)
5035 SUPER ABSORBENT POLYMER (ICP)
5036 TRIMELLITIC ANHYDRIDE (GC)
5037 TRIORTHOCRESYL PHOSPHATE (GC)
5038 TRIPHENYL PHOSPHATE (GC)
5039 CHLORINATED CAMPHENE (GC)
5502 ALDRIN & LINDANE (GC)
5503 POLYCHLOROBIPHENYLS (GC)
5504 ORGANOTIN COMPOUNDS, as Sn (HPLC/GFAAS)
bibutyltin bis(isooctyl mercaptoacetate)
tetrabutyltin
tributyltin chloride
tricyclohexyltin hydroxide
5506 POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)
acenaphthene
acephthalene
anthracene
benz[a]anthracene
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[ghi]perylene
benzo[a]pyrene
benzo[e]pyrene
chrysene
dibenz[a,h]anthracene
fluoranthene
fluorene
indo[1,2,3-cd]pyrene
naphthalene
phenanthrene
pyrene

5508 KEPONE (GC/ECD)
5509 BENZIDINE and 3,3'-DICHLOROBENZIDINE (HPLC)
5510 CHLORDANE (GC)
5512 PENTACHLOROPHENOL (HPLC)
5514 DEMETON (GC)
5515 POLYNUCLEAR AROMATIC HYDROCARBONS (GC)
acenaphthene
acephthalene
anthracene
benz[a]anthracene
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[ghi]perylene
benzo[a]pyrene
benzo[e]pyrene
chrysene
dibenz[a,h]anthracene
fluoranthene
fluorene
indo[1,2,3-cd]pyrene
naphthalene
phenanthrene
pyrene

5516 TOLUENEDIAMINES (HPLC)
5517 POLYCHLOROBENZENES (GC)
pentachlorobenzene
1,2,4,5-tetrachlorobenzene
1,2,4-trichlorobenzene
5518 NAPHTHYLAMINES (GC)
5519 ENDRIN (GC)
5521 ISOCYANATES (HPLC)
5600 ORGANOPHOSPHOROUS PESTICIDES (GC/FPD)
5700 FORMALDEHYDE ON DUST/FIBERS (HPLC)

6001 ARSINE (HGAAS)
6002 PHOSPHINE (UV/VIS)
6004 SUFUR DIOXIDE/SULFATE (IC)
6005 IODINE (IC)
6006 DIBORANE (PES)
6007 NICKEL CARBONYL (GFAAS)
6008 STIBINE (VIS)
6009 MERCURY (Hopcalite)(cold vapor AAS)
6010 HYDROGEN CYANIDE (VIS)
6011 CHLORINE and BROMINE (IC)
6012 SULFURYL FLUORIDE (GC)
6013 HYDROGEN SULFIDE (IC)
6014 NITRIC OXIDE/NITROGEN DIOXIDE (VIS)
6015 AMMONIA (VIS)
6402 PHOSPHORUS TRICHLORIDE (VIS)
6600 NITROUS OXIDE (portable IR)
6601 OXYGEN (EC sensor)
6602 SULFUR HEXAFLUORIDE (portable GC)
6603 CARBON DIOXIDE (portable GC)

7013 ALUMINUM (FAAS)
7020 CALCIUM (FAAS)
7024 CHROMIUM (FAAS)
7027 COBALT (FAAS)
7029 COPPER (FUME/DUST) (FAAS)
7030 ZINC (ICP)
7048 CADMIUM (FAAS)
7056 BARIUM, soluble (FAAS)
7074 TUNGSTEN, sol/insol (FAAS)
7082 LEAD (FAAS)
7101 VANADIUM, sol/insol (ICP)
7102 BERYLLIUM (HGAAS)
7105 LEAD (HGAAS)
7300 ELEMENTS (ICP)
7400 ASBESTOS and other FIBERS by PCM
7401 ALKALINE DUST (titration)
7402 ASBESTOS by TEM
7500 SILICA (XRD)
7501 SILICA, AMORPHOUS (XRD)
7502 ZINC OXIDE (XRD)
7504 VANADIUM OXIDES (XRD)
7505 LEAD SULFIDE (XRD)
7506 BORON CARBIDE (XRD)
7600 CHROMIUM HEXAVALENT (VIS)
7601 SILICA (VIS)
7602 SILICA (IR)
7603 SILICA IN COAL MINE DUST, (IR)
7604 CHROMIUM HEXAVALENT (IC)
7900 ARSENIC (HYDRIDE AAS)
7901 ARSENIC TRIOXIDE (HGAAS)
7902 FLUORIDES by ISE
7903 ACIDS,INORGANIC (IC)
7904 CYANIDES (ISE)
7905 PHOSPHORUS (GC)
7906 FLUORIDES by IC

8001 PENTACHLOROPHENOL in blood
8002 METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood
8003 LEAD in blood and urine
8004 POLYCHLORINATED BIPHENYLS in serum
8005 ELEMENTS in blood or tissue (ICP)
8300 HIPPURIC ACID in urine (VIS)
8301 HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC)
8302 MBOCA in urine
8303 PENTACHLOROPHENOL in urine
8305 PHENOL & *p*-CRESOL in urine
8306 BENZIDINE in urine (GC)
8308 FLUORIDE in urine
8310 METALS in urine (ICP)

9000 ASBESTOS, CHRYSOTILE by XRD
9002 ASBESTOS (bulk) by PLM
9100 LEAD in surface wipe samples

V. B. INDEX OF SECOND EDITION METHOD NUMBERS

(The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols. 1 through 7).
CRDT = Criteria Document
SDS = Sampling Data Sheet from NIOSH Publication 77-159
NRNR = Not revised and not recommended for use
NRIU = Not revised because of infrequent usage by NIOSH; the 2nd Ed. method is recommended for use at present.

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	102	1	Lead in blood (Dithizone)	LEAD [7082]; LEAD [7105]; LEAD IN BLOOD OR URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	106	1	Silica (colorimetric)	SILICA, CRYSTALLINE [7601]
	107	1	Antimony in urine	NRIU
	108	1	Nitrogen oxides	NITRIC OXIDE and NITROGEN DIOXIDE [6014]
	109	1	Silica (XRD)	SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)	SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide	NRNR (obsolete instrument)
	113	1	Carbon monoxide in blood	NRIU
	114	1	Fluoride in urine	FLUORIDE IN URINE [8308]
	115	1	Hydrogen chloride	ACIDS, INORGANIC [7903]
	116	1	Cyanide	CYANIDES [7904]
	117	1	Hydrogen fluoride	ACIDS, INORGANIC [7903]
	118	1	Acrolein	ACROLEIN [2501]
	121	1	Beryllium	BERYLLIUM [7102]; ELEMENTS by ICP [7300]
	124	1	Selenium in urine	NRIU
	125	1	Formaldehyde	FORMALDEHYDE [2541, 3500, 3501]
	126	1	Hydrogen sulfide	see HYDROGEN SULFIDE [6013]
	127	1	Acetone	KETONES I [1300]
	127	1	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; BENZENE [3700]; HYDROCARBONS, AROMATIC [1501]
	127	1	2-Butanone	METHYL ETHYL KETONE [2500]
	127	1	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	p-Dioxane	DIOXANE [1602]
	127	1	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methylene chloride	METHYLENE CHLORIDE [1005]
	127	1	Styrene	HYDROCARBONS, AROMATIC [1501]
	127	1	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1300]
	127	1	Toluene	HYDROCARBONS, BP 35-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
	127	1	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1300]
	127	1	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
	127	1	Xylene	HYDROCARBONS, AROMATIC [1501]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	139	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	139	1	Arsenic in urine	NRIU
	140	1	Arsenic in urine	NRIU
	141	1	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]
	142	1	MDI	NRNR; see ISOCYANATES [5521]
	145	1	Mercury in urine	NRIU
	146	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	152	1	Chromium	CHROMIUM [7024]; ELEMENTS by ICP [7300]
	153	1	Ozone	NRIU
	154	1	Ozone	NRIU
	158	1	Parathion	ORGANOPHOSPHORUS PESTICIDES [5600]
	159	1	Oil mist	OIL MIST, MINERAL [5026]
	160	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	163	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	165	1	Mercury in urine	NRIU
	167	1	Mercury in blood	NRIU
	168	1	Aniline	AMINES, AROMATIC [2002]
	168	1	o-Toluidine	AMINES, AROMATIC [2002]
	168	1	2,4-Xylidine	AMINES, AROMATIC [2002]
	168	1	Dimethylaniline	AMINES, AROMATIC [2002]
	169	1	Chromic acid	CHROMIUM, HEXAVALENT [7600, 7604]
	173	1,5	Aluminum	ALUMINUM [7013]; ELEMENTS by ICP [7300]
	173	1	Antimony	NRIU
	173	1,5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	173	1,5	Barium	NRIU
	173	1,5	Beryllium	BERYLLIUM [7102]; ELEMENTS by ICP [7300]
	173	1,5	Bismuth	NRIU
	173	1,5	Cadmium	CADMIUM [7048]; ELEMENTS by ICP [7300]
	173	1,5	Calcium	CALCIUM [7020]; ELEMENTS by ICP [7300]
	173	1,5	Chromium	CHROMIUM [7024]; ELEMENTS by ICP [7300]
	173	1,5	Cobalt	COBALT [7027]; ELEMENTS by ICP [7300]
	173	1,5	Copper	COPPER [7029]; ELEMENTS by ICP [7300]
	173	1,5	Indium	NRIU
	173	1,5	Iron	ELEMENTS by ICP [7300]
	173	1,5	Lead	LEAD [7082, 7105]; ELEMENTS by ICP [7300]
	173	1,5	Lithium	ELEMENTS by ICP [7300]
	173	1,5	Magnesium	ELEMENTS by ICP [7300]
	173	1,5	Manganese	ELEMENTS by ICP [7300]
	173	1,5	Molybdenum	ELEMENTS by ICP [7300]
	173	1,5	Nickel	ELEMENTS by ICP [7300]
	173	1,5	Palladium	NRIU
	173	1,5	Potassium	NRIU
	173	1,5	Rubidium	NRIU
	173	1,5	Silicon	NRIU
	173	1,5	Silver	ELEMENTS by ICP [7300]
	173	1,5	Sodium	ELEMENTS by ICP [7300]
	173	1,5	Strontium	NRIU
	173	1,5	Tellurium	ELEMENTS by ICP [7300]
	173	1,5	Thallium	ELEMENTS by ICP [7300]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	173	1,5	Vanadium	ELEMENTS by ICP [7300]
	173	1,5	Zinc	ZINC [7030]; ELEMENTS by ICP [7300]
	175	5	Mercury	NRIU; see MERCURY [6009]
	176	1	Tin	NRIU
	177	1	Gallium	NRIU
	178	1	Vinyl chloride	VINYL CHLORIDE [1007]
	179	1	Carbon disulfide	CARBON DISULFIDE [1600]
	180	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	181	1	Selenium	ELEMENTS by ICP [7300]
	182	1	Chromium	CHROMIUM [7024]; CHROMIUM HEXAVALENT [7600, 7604]; ELEMENTS by ICP [7300]
	183	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	184	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	186	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	187	1	Sulfuric acid	ACIDS, INORGANIC [7903]
	188	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	189	1	Antimony	NRIU
	190	1	Indium	NRIU
	191	1	Cadmium	CADMIUM [7048]; ELEMENTS by ICP [7300]
	191	1	Lead	LEAD [7082, 7105]; ELEMENTS by ICP [7300]
	192	1	Arsenic in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	193	1	Antimony in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	194	1	Indium in blood	NRIU
	195	1	Lead in blood	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	196	1	Arsenic in urine	NRIU
	197	1	Antimony in urine	NRIU
	198	1	Gallium in urine	NRIU
	199	1	Indium in urine	NRIU
	200	1	Lead in urine	LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	201	1	Methyl chloride	METHYL CHLORIDE [1001]
	202	1	Acrylonitrile	NRIU; see ACRYLONITRILE [1604]
	203	1	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
	204	1	Sulfur dioxide	NRIU; see SULFUR DIOXIDE [6004]
	205	1	Ammonia	NRIU; see AMMONIA [6015]
	206	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	208	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005] METALS IN URINE [8310]
	209	1	Chlorine	NRNR; see CHLORINE AND BROMINE [6011]
	211	1	Acrolein	ACROLEIN [2501]
	212	1	Fluorides	ACIDS, INORGANIC [7903]
	213	1	bis-(Chloromethyl)ether	NRIU

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	214	1	Lead in air or blood	LEAD [7082, 7105]; ELEMENTS BY ICP [7300]; LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	215	1	Phosphate in urine	NRIU
	216	1	Phosphoric acid	ACIDS, INORGANIC [7903]
	217	1	Benzene solubles	NRNR; see OSHA METHOD 58, COAL TAR PITCH VOLATILES
	219	1	Phosgene	NRIU
	220	1	Chloromethyl methyl ether	NRIU
	221	1	Aliphatic amines	AMINES, ALIPHATIC [2010]
	222	1	Zinc oxide	ZINC OXIDE [7502]
	223	1	Cadmium in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	224	1	Cadmium in urine	METALS IN URINE [8310]
	225	1	Kepone	KEPONE [5508]
	226	1	2,6-Di-t-butyl-p-cresol	NRIU
	227	1	Polymethylsiloxane	NRIU
	228	1	Thiram	THIRAM [5005]
	230	1	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	231	1	Nitrogen oxides	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
	232	1	Formic acid	NRIU; see FORMIC ACID [2011]
	234	1	Dyes, benzidine, o-tolidine	DYES [5013]
	235	1	Formaldehyde	NRIU; see FORMALDEHYDE [2541, 3500]
	236	1	MOCA	NRIU
	237	1	Tissue preparation	ELEMENTS IN BLOOD OR TISSUE [8005]
	239	1	Asbestos	ASBESTOS AND OTHER FIBERS BY PCM [7400]; ASBESTOS FIBERS BY TEM [7402]
	241	1	Sodium hydroxide	ALKALINE DUSTS [7401]
	242	1	Phosphorus	PHOSPHORUS [7905]
	243	1	Benzidine	BENZIDINE AND 3,3'-DICHLOROBENZIDINE [5509]
	244	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	245	1	Asbestos (chrysotile, bulk)	ASBESTOS,CHRYSOTILE BY XRD [9000]; ASBESTOS (bulk) BY PLM [9002]
	246	1	3,3'-Dichlorobenzidine	BENZIDINE and 3,3'-DICHLOROBENZIDINE [5509
	247	1	Methanol	METHANOL [2000]
	248	1	1,1-Dimethyl hydrazine	NRNR; see 1,1-DIMETHYLHYDRAZINE [3515]
	248	1	Hydrazine	HYDRAZINE [3503]
	248	1	Methyl hydrazine	NRNR; see MONOMETHYLHYDRAZINE [3510]
	248	1	Phenyl hydrazine	NRNR; see PHENYLHYDRAZINE [3518]
	250	4	Zirconium oxide	NRIU; see ELEMENTS [7300]
	251	1	Benzo(a)pyrene	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	252	1	Dimethylnitrosamine	NITROSAMINES [2522]
	253	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	255	1	Thiophene	NRIU
	256	1	Azelaic acid	AZELAIC ACID [5019]
	257	1	Phosphorus	PHOSPHORUS [7905]
	259	1,5	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
	260	4	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
	261	4	Antimony	NRIU

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	262	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]; METALS IN URINE [8310]
	263	4	Hexamethylenetetramine	NRIU
	264	4	Naphthylamines	NAPHTHYLAMINES [5518]
	265	4	Arsine	ARSINE [6001]
	266	4	Vinylidene chloride	VINYLIDENE CHLORIDE [1015]
	267	5	Sulfuric acid	NRNR; see ACIDS, INORGANIC [7903]
	268	5	Sulfur dioxide, sulfates, sulfites	SULFUR DIOXIDE [6004]
	269	4	4-Aminobiphenyl	NRIU
	270	4	Aminoethanol compounds	AMINOETHANOL COMPOUNDS I [2007]; AMINOETHANOL COMPOUNDS II [3509]
	271	4	Tungsten	TUNGSTEN [7074]
	272	4	2-Nitropropane	2-NITROPROPANE [2528]
	273	4	4-Nitrobiphenyl	NRIU
	276	4	Ethylenediamine	ETHYLENEDIAMINE, DIETHYLENETRIAMINE & TRIETHYLENETETRAMINE [2540]
	277	4	Methylamine	NRIU
	278	4	Vinyl acetate	VINYL ACETATE [1453]
	279	4	Beryllium in tissue	ELEMENTS IN BLOOD OR TISSUE [8005]
	280	4	N,N-Dimethyl-p-toluidine	AMINES, AROMATIC [2002]
	281	4	Ethylene thiourea	ETHYLENE THIOUREA [5011]
	282	4	Tetramethyl thiourea	TETRAMETHYL THIOUREA [3505]
	283	4	Oil mist	OIL MIST, MINERAL [5026]
	284	4	4-Dimethylaminoazobenzene	NRIU
	285	5	Crotonaldehyde	CROTONALDEHYDE [3516]
	286	5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
	288	5	Beryllium	BERYLLIUM [7102]; ELEMENTS BY ICP [7300]
	290	5	Vanadium	ELEMENTS BY ICP [7300]
	291	5	a-Chloroacetophenone	NRIU
	294	5	Cyclopentadiene	1,3-CYCLOPENTADIENE [2523]
	295	5	Dichlorovos	NRIU
	296	6	Hydrogen sulfide	NRIU, see HYDROGEN SULFIDE [6013]
	297	5	Dibutyl phosphate	DIBUTYL PHOSPHATE [5017]
	298	5,7	Nickel	ELEMENTS BY ICP [7300]
	299	5	Dimethylnitrosamine	NITROSAMINES [2522]
	300	5	Ethylenimine (aziridine)	ETHYLENIMINE [3514]
	301	5	Dimethyl sulfate	DIMETHYL SULFATE [2524]
	302	5	Maleic anhydride	MALEIC ANHYDRIDE [3512]
	303	5	Styrene oxide	NRIU
	304	5	OCBM	NRIU
	305	5	Phosphorus trichloride	PHOSPHORUS TRICHLORIDE [6402]
	307	5	Hexachlorobutadiene	HEXACHLOROBUTADIENE [2543]
	308	5	Hexachlorocyclopentadiene	HEXACHLORO-1,3-CYCLOPENTADIENE [2518]
	309	5	Chrysotile asbestos (bulk)	ASBESTOS, CHRYSOTILE BY XRD [9000]
	310	5	Hydrogen chloride	ACIDS, INORGANIC [7903]
	313	6	Warfarin	WARFARIN [5002]
	314	5	Trichloroisocyanuric acid	NRIU
	315	5	Benzidine in urine	BENZIDINE IN URINE [8306]
	316	6	Silica, amorphous	SILICA, AMORPHOUS [7501]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	317	6	Diethylcarbamoyl chloride	NRIU
	318	6	Formaldehyde	FORMALDEHYDE [2541, 3500]
	319	6	Chromium (VI)	CHROMIUM, HEXAVALENT [7600, 7604]
	320	6	Arsenic, organo-	ARSENIC, ORGANO- [5022]
	321	6	1,2-Dichloroproane	1,2-DICHLOROPROPANE [1013]
	322	6	Trimellitic anhydride	TRIMELLITIC ANHYDRIDE [5036]
	323	6	Titanium diboride	NRIU
	324	6	Boron carbide	BORON CARBIDE [7506]
	325	6	Benzidine, o-anisidine, and o-tolidine dyes	DYES [5013]
	326	6	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]; ISOCYANATES [5521]
	327	6	Hippuric acid in urine	HIPPURIC ACID IN URINE [8300]
	328	6	ALAD in blood	NRNR; see LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	329	6	PCB in blood	POLYCHLORINATED BIPHENYLS IN SERUM [8004]
	330	6	Phenol and Cresol in urine	PHENOL and p-CRESOL IN URINE [8305]
	331	6	Methyl ethyl ketone peroxide	METHYL ETHYL KETONE PEROXIDE [3508]
	332	6	Chloroacetic acid	CHLOROACETIC ACID [2008]
	333	6	Bisphenol A	NRIU
	335	6	Pentachloroethane	PENTACHLOROETHANE [2517]
	336	6	Tetraethyl pyrophosphate	TETRAETHYL PYROPHOSPHATE [2504]
	337	7	p-Chlorophenol	p-CHLOROPHENOL [2014]
	338	7	Ethylene glycol	NRNR
	339	7	Inorganic acids	ACIDS, INORGANIC [7903]
	340	7	Acetone cyanohydrin	ACETONE CYANOHYDRIN [2506]
	341	7	Diborane	DIBORANE [6006]
	342	7	MOCA in urine	MBOCA IN URINE [8302]
	343	7	Polychlorobenzenes	POLYCHLOROBENZENES [5517]
	344	7	Nickel carbonyl	NICKEL CARBONYL [6007]
	345	7	Welding and brazing fume	NRIU; see ELEMENTS BY ICP [7300]
	346	7	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
	347	7	MDI	NRNR; see ISOCYANATES [5521]
	348	7	2,4,7-Trinitro-9-fluorenone	2,4,7-TRINITROFLUOREN-9-ONE [5018]
	349	7	Vinyl bromide	VINYL BROMIDE [1009]
	350	7	Lead sulfide	LEAD SULFIDE [7505]
	351	7	Elements by ICP	ELEMENTS BY ICP [7300]
	354	7	Formaldehyde	FORMALDEHYDE [2541, 3500]
	355	--	Talc, respirable	NRIU
	357	--	n-Octanethiol	1-OCTANETHIOL [2510]
	358	--	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	359	--	Benzidine in urine	BENZIDINE IN URINE [8306]
	360	--	Hippuric Acid in urine	HIPPURIC ACID IN URINE [8300]; HIPPURIC and METHYL HIPPURIC ACIDS IN URINE [8301]
	361	--	2-Butanone, ethanol, and toluene in blood	METHYL ETHYL KETONE, ETHANOL, AND TOLUENE IN BLOOD [8002]
	362	--	Pentachlorophenol in blood	PENTACHLOROPHENOL IN BLOOD [8001]
	363	--	Polychlorinated terphenyls	CHLORINATED TERPHENYL [5014]
	364	--	Vanadium oxides	VANADIUM OXIDES [7504]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	365	--	2-Butanone	METHYL ETHYL KETONE [2500]
	368	--	Tin, organo-	ORGANOTIN COMPOUNDS [5504]
	374	--	Acrolein	ACROLEIN [2501]
	S1	2	Acetone	KETONES I [1300]
	S2	2	Antimony	NRIU
	S3	2	2-Butanone	METHYL ETHYL KETONE [2500]
	S4	2	Hydrogen sulfide	NRIU; see HYDROGEN SULFIDE [6013]
	S5	2	Manganese	ELEMENTS BY ICP [7300]
	S7	5	p-Nitroaniline	p-NITROANILINE [5033]
	S8	2	Ozone	NRIU
	S10	2	Camphor	KETONES II [1301]
	S11	5	Chloroacetaldehyde	CHLOROACETALDEHYDE [2015]
	S12	2	Mesityl oxide	KETONES II [1301]
	S13	2	5-Methyl-3-heptanone	KETONES II [1301]
	S15	2	Methyl (n-amyl) ketone	KETONES II [1301]
	S16	2	Ethyl butyl ketone	KETONES II [1301]
	S17	5	Furfural	FURFURAL [2529]
	S18	2	Hexone (MIBK)	KETONES I [1300]
	S19	2	Cyclohexanone	KETONES I [1300]
	S20	2	2-Pentanone	KETONES I [1300]
	S22	2	p-tert-Butyltoluene	HYDROCARBONS, AROMATIC [1501]
	S23	2	Cumene	HYDROCARBONS, AROMATIC [1501]
	S24	4	Diphenyl	DIPHENYL [2530]
	S25	2	Vinyl toluene	HYDROCARBONS, AROMATIC [1501]
	S26	2	a-Methyl styrene	HYDROCARBONS, AROMATIC [1501]
	S27	2	Terphenyl	o-TERPHENYL [1521]
	S28	2	Cyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
	S29	2	Ethylbenzene	HYDROCARBONS, AROMATIC [1501]
	S30	2	Styrene	HYDROCARBONS, AROMATIC [1501]
	S31	2	sec-Amyl acetate	ESTERS I [1450]
	S32	2	tert-Butyl acetate	ESTERS I [1450]
	S33	2	Dibutyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
	S35	2	Ethyl acrylate	ESTERS I [1450]
	S36	2	Ethyl formate	ETHYL FORMATE [1452]
	S37	2	Methyl isoamyl acetate	ESTERS I [1450]
	S38	2	Methyl acrylate	METHYL ACRYLATE [1459]
	S39	2	Methyl cellosolve acetate	METHYL CELLOSOLVE ACETATE [1451]
	S40	2	Di-2-ethylhexyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
	S41	2	2-Ethoxyethyl acetate	ESTERS I [1450]
	S42	2	Methyl acetate	METHYL ACETATE [1458]
	S43	6	Methyl methacrylate	METHYL METHACRYLATE [2537]
	S44	2	Isobutyl acetate	ESTERS I [1450]
	S45	2	Isoamyl acetate	ESTERS I [1450]
	S46	2	sec-Butyl acetate	ESTERS I [1450]
	S47	2	n-Butyl acetate	ESTERS I [1450]
	S48	2	n-Propyl acetate	ESTERS I [1450]
	S49	2	Ethyl acetate	ETHYL ACETATE [1457]
	S50	2	Isopropyl acetate	ISOPROPYL ACETATE [1454]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S51	2	n-Amyl acetate	ESTERS I [1450]
S52	2	Allyl alcohol	ALCOHOLS III [1402]
S53	2	sec-Butyl alcohol	ALCOHOLS II [1401]
S54	2	Cyclohexanol	ALCOHOLS III [1402]
S55	2	Diacetone alcohol	ALCOHOLS III [1402]
S56	2	Ethanol	ALCOHOLS I [1400]
S57	2	Hydroquinone	HYDROQUINONE [5004]
S58	2	Isoamyl alcohol	ALCOHOLS III [1402]
S59	2	Methanol	METHANOL [2000]
S60	2	Methyl isobutyl carbinol	ALCOHOLS III [1402]
S62	2	n-Propyl alcohol	ALCOHOLS II [1401]
S63	2	tert-Butyl alcohol	ALCOHOLS I [1400]
S64	2	Isobutyl alcohol	ALCOHOLS II [1401]
S65	2	Isopropyl alcohol	ALCOHOLS I [1400]
S66	2	n-Butyl alcohol	ALCOHOLS II [1401]
S67	2	Chlorinated camphene	CHLORINATED CAMPHENE [5039]
S69	2	Dipropylene glycol methyl ether	NRIU
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	PHENYL ETHER [1617]
S73	2	Phenyl ether-biphenyl mixture	PHENYL ETHER-DIPHENYL MIXTURE [2013]
S74	2	Phenyl glycidyl ether	PHENYL GLYCIDYL ETHER [1619]
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	ISOPROPYL GLYCIDYL ETHER [1620]
S78	2	Tetrahydrofuran	TETRAHYDROFURAN [1609]
S79	2	2-Methoxyethanol	ALCOHOLS IV [1403]
S80	2	Ethyl ether	ETHYL ETHER [1610]
S81	2	n-Butyl glycidyl ether	n-BUTYL GLYCIDYL ETHER [1616]
S82	2	Cyclohexene	HYDROCARBONS, BP 36-126 °C [1500]
S84	5	Methyl acetylene (propyne)	NRIU
S85	6	Methyl acetylene/propadiene	NRIU
S86	2	Naphtha, coal tar	NAPHTHAS [1550]
S87	2	Propane	NRIU
S88	2	Turpentine	TURPENTINE [1551]
S89	2	Heptane	HYDROCARBONS, BP 36-126 °C [1500]
S90	2	Hexane	HYDROCARBONS, BP 36-126 °C [1500]
S91	2	Butadiene	1,3-BUTADIENE [1024]
S92	2	Ketene	NRIU
S93	2	LPG	NRIU
S94	2	Methylcyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S95	2	Propylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S96	2	Pentachloronaphthalene	NRIU
S97	2	Octachloronaphthalene	NRIU
S98	2	Methyl iodide	METHYL IODIDE [1014]
S99	4	Methyl chloride	METHYL CHLORIDE [1001]
S100	2	Hexachloronaphthalene	NRIU
S101	2	Hexachloroethane	HYDROCARBONS, HALOGENATED [1003]
S102	2	Fluorotrichloromethane	FLUOROTRICHLOROMETHANE [1006]
S103	2	Ethylene chlorohydrin	ETHYLENE CHLOROHYDRIN [2513]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S104	2	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
S105	4	Ethyl chloride	ETHYL CHLORIDE [2519]
S106	2	Ethyl bromide	ETHYL BROMIDE [1011]
S107	2	Dibromodifluoromethane	DIFLUORODIBROMOMETHANE [1012]
S108	2	Dichlorotetrafluoroethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]
S109	2	Dichlorofluoromethane	DICHLOROFLUOROMETHANE [2516]
S110	2	1,2-Dichloroethylene	HALOGENATED HYDROCARBONS [1003]
S111	2	Dichlorodifluoromethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLORO-TETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]
S112	2	Chloroprene	CHLOROPRENE [1002]
S113	2	Chlorobromomethane	HYDROCARBONS, HALOGENATED [1003]
S114	2	Bromoform	HYDROCARBONS, HALOGENATED [1003]
S115	2	Benzyl chloride	HYDROCARBONS, HALOGENATED [1003]
S116	2	Allyl chloride	ALLYL CHLORIDE [1000]
S117	2	Acetylene tetrabromide	1,1,2,2-TETRABROMOETHANE [2003]
S118	2	Epichlorohydrin	EPICHLOROHYDRIN [1010]
S119	2	Chlorinated diphenyl oxide	CHLORINATED DIPHENYL ETHER [5025]
S120	4	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S121	2	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S122	2	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S123	2	1,1-Dichloroethane	HYDROCARBONS, HALOGENATED [1003]
S124	2	1,1,2,2-Tetrachloroethane	1,1,2,2-TETRACHLOROETHANE [1019]
S125	2	Trifluorobromomethane	TRIFLUOROBROMOMETHANE [1017]
S126	2	1,2,3-Trichloropropane	HYDROCARBONS, HALOGENATED [1003]
S128	2	Trichloronaphthalene	NRIU
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE [1020]
S130	2	Tetrachloronaphthalene	NRIU
S131	2	1,1,1,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S132	2	1,1,2,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S133	2	Chlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S134	2	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1003]
S135	3	o-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S137	3	Diazomethane	DIAZOMETHANE [2515]
S138	4	n-Butylamine	n-BUTYLAMINE [2012]; AMINES, ALIPHATIC [2010]
S139	3	Diethylamine	AMINES, ALIPHATIC [2010]
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS I [2007]; AMINOETHANOL COMPOUNDS II [3509]
S141	4	Diisopropylamine	NRIU; see AMINES, ALIPHATIC [2010]
S142	3	Dimethylamine	AMINES, ALIPHATIC [2010]
S143	3	1,1-Dimethyl hydrazine	1,1-DIMETHYLHYDRAZINE [3515]
S144	3	Ethylamine	NRIU
S146	3	N-Ethyl morpholine	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S147	3	Isopropylamine	NRIU
S148	6	Methylamine	NRIU
S149	3	Methyl hydrazine	MONOMETHYLHYDRAZINE [3510]
S150	3	Morpholine	NRIU
S152	3	Triethylamine	NRIU
S153	3	Monomethylaniline	MONOMETHYLANILINE [3511]
S155	3	Tetramethylsuccinonitrile	NRIU
S156	3	Acrylonitrile	ACRYLONITRILE [1604]
S158	4	2-Aminopyridine	NRIU
S160	3	Phenyl hydrazine	PHENYLHYDRAZINE [3518]
S161	3	Pyridine	PYRIDINE [1613]
S162	3	2,4-Xylidine	AMINES, AROMATIC [2002]
S163	5	Anisidine (o and p-)	ANISIDINE [2514]
S164	3	Dimethylaniline	AMINES, AROMATIC [2002]
S165	3	Acetonitrile	ACETONITRILE [1606]
S166	5	Dinitro-o-cresol	NRIU
S167	3	Cresol	CRESOLS AND PHENOL [2546]
S168	3	o-Toluidine	AMINES, AROMATIC [2002]
S169	4	Acetic acid	ACETIC ACID [1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE [3506]
S173	5	Formic acid	FORMIC ACID [2011]
S174	3	Sulfuric acid	ACIDS, INORGANIC [7903]
S175	3	Hydrogen bromide	ACIDS, INORGANIC [7903]
S176	3	Hydrogen fluoride	FLUORIDES [7902, 7906]; ACIDS, INORGANIC [7903]
S178	3	2-Hexanone	KETONES I [1300]
S179	3	Phthalic anhydride	NRIU
S181	4	Quinone	NRIU
S182	5	Silver	ELEMENTS BY ICP [7300]
S183	3	Tin	NRIU
S185	3	Zirconium	ELEMENTS BY ICP [7300]
S186	3	Copper	COPPER [7029]; ELEMENTS BY ICP [7300]
S187	3	Tellurium hexafluoride	NRIU
S188	3	Rhodium, fume and dust	NRIU
S189	3	Rhodium, soluble	NRIU
S190	3,7	Selenium	ELEMENTS BY ICP [7300]
S191	3,7	Platinum	ELEMENTS BY ICP [7300]
S193	3	Molybdenum	ELEMENTS BY ICP [7300]
S194	5	Hafnium	NRIU
S198	3	Barium	BARIUM [7056]
S199	4	Mercury	NRIU; see MERCURY [6009]
S200	3	Yttrium	ELEMENTS BY ICP [7300]
S201	5	Tantalum	NRIU
S203	4	Cobalt	COBALT [7027]; ELEMENTS BY ICP [7300]
S204	3,7	Tellurium	ELEMENTS BY ICP [7300]
S205	3	Calcium	CALCIUM [7020]; ELEMENTS BY ICP [7300]
S206	3	Nickel	ELEMENTS BY ICP [7300]
S208	3	Tributyl phosphate	TRIBUTYL PHOSPHATE [5034]
S209	3	Triorthocresyl phosphate	TRIORTHOCRESYL PHOSPHATE [5037]
S210	3	Triphenyl phosphate	TRIPHENYL PHOSPHATE [5038]
S211	5	1-Chloro-1-nitropropane	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	NRIU
S215	4	Dinitrotoluene	NRIU
S216	3	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
S217	3	Nitrobenzene	NITROBENZENES [2005]
S218	3	p-Nitrochlorobenzene	NITROBENZENES [2005]
S219	4,6	Nitroethane	NITROETHANE [2526]
S220	6	Nitromethane	NITROMETHANE [2527]
S223	3	Nitrotoluene	NITROBENZENES [2005]
S224	3	Tetranitromethane	NRIU
S225	3	Tetryl	NRIU
S227	3	n-Propyl nitrate	NRIU
S228	4	Picric acid	NRIU
S229	3	Arsine	ARSINE [6001]
S237	3	Hydrazine	HYDRAZINE [3503]
S243	4	Stibine	STIBINE [6008]
S244	5	Sulfur hexafluoride	NRIU
S245	6	Sulfuryl fluoride	SULFURYL FLUORIDE [6012]
S246	3	Hydrogen chloride	ACIDS, INORGANIC [7903]
S248	3	Carbon disulfide	CARBON DISULFIDE [1600]
S249	3	Carbon dioxide	CARBON DIOXIDE [6603]
S250	3	Cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S253	4	Benzoyl peroxide	BENZOYL PEROXIDE [5009]
S254	3	Dimethylacetamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S255	3	Dimethylformamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S256	5	Thiram	THIRAM [5005]
S257	5	Phosphorus pentachloride	NRIU
S262	3	Carbon black	CARBON BLACK [5000]
S264	3	Ethyl silicate	NRIU
S272	3	Oil mist	OIL MIST, MINERAL [5026]
S273	3	Carbaryl (Sevin)	CARBARYL [5006]
S274	3	DDT	NRIU
S275	3	Aldrin	ALDRIN and LINDANE [5502]
S276	5	ANTU	NRIU
S278	6	Chlordane	CHLORDANE [5510]
S279	5	2,4-D	2,4-D and 2,4,5-T [5001]
S280	6	Demeton	DEMETON [5514]
S281	3	p-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S283	3	Dieldrin	NRIU
S284	6	Endrin	ENDRIN [5519]
S285	3	EPN	EPN [5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE [1607, 3702]
S287	5	Heptachlor	NRIU
S288	4	Hydrogen cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S290	3	Lindane	ALDRIN and LINDANE [5502]
S291	5	Methyl formate	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]; POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
S293	3	Nicotine	NICOTINE [2544]
S294	5	Paraquat	PARAQUAT [5003]
S295	3	Parathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S296	6	Mevinphos (Phosdrin)	ORGANOPHOSPHORUS PESTICIDES [5600]
S297	4	Pentachlorophenol	PENTACHLOROPHENOL [5512]
S298	6	Pyrethrum	PYRETHRUM [5008]
S299	6	Ronnel	ORGANOPHOSPHORUS PESTICIDES [5600]
S300	5	Rotenone	ROTENONE [5007]
S301	5	Sodium fluoroacetate	NRIU
S302	5	Strychnine	STRYCHNINE [5016]
S303	5	2,4,5-T	2,4-D and 2,4,5-T [5001]
S306	3	Thallium	ELEMENTS BY ICP [7300]
S308	4	Sulfur dioxide	SULFUR DIOXIDE [6004]
S309	3	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
S310	3	Aniline	AMINES, AROMATIC [2002]
S311	3	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; BENZENE [3700]
S312	3	Cadmium	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S313	3	Cadmium fume	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S314	3	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
S315	3	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
S316	4	Zinc oxide	ZINC OXIDE [7502]
S317	3	Chromium, hexavalent	CHROMIUM, HEXAVALENT [7600, 7604]
S318	3	Xylene	HYDROCARBONS, AROMATIC [1501]
S319	4	Nitric acid	ACIDS, INORGANIC [7903]
S320	4	Nitrogen dioxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
S321	4	Nitric oxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
S323	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S327	4	Formaldehyde (Girard T)	NRNR; see FORMALDEHYDE [2542, 3500]
S328	3	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
S329	3	Methylene chloride	METHYLENE CHLORIDE [1005]
S330	3	Phenol	CRESOLS AND PHENOL [2546]
S332	5	Phosphine	PHOSPHINE [6002]
S333	3	Phosphoric acid	ACIDS, INORGANIC [7903]
S334	3	Phosphorus	PHOSPHORUS [7905]
S335	3	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]
S336	3	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
S339	3	Beryllium	BERYLLIUM [7102]; ELEMENTS BY ICP [7300]
S340	4	Carbon monoxide	NRNR (obsolete instrument)
S341	3,7	Lead	LEAD [7082]; ELEMENTS BY ICP [7300]
S342	6	Mercury, organo	NRIU
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
S345	5	Acetaldehyde	ACETALDEHYDE [3507]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S346	4	Allyl glycidyl ether	ALLYL GLYCIDYL ETHER [2545]
S347	5	Ammonia	see AMMONIA BY VIS [6015]
S348	5	Ammonium sulfamate	NRIU
S349	3	Boron oxide	PARTICULATES NOT OTHERWISE REGULATED, TOTAL [0500]
S350	4	n-Butyl mercaptan	MERCAPTANS, METHYL, ETHYL, and n-BUTYL [2542]
S351	3	Chloroform	HYDROCARBONS, HALOGENATED [1003]
S352	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S354	4	Copper fume	COPPER [7029]; ELEMENTS BY ICP [7300]
S356	5	Crag herbicide I	NRIU
S357	3	sym-Dichloroethyl ether	DICHLOROETHYL ETHER [1004]
S358	3	Diisobutyl ketone	KETONES I [1300]
S360	3	Dioxane	DIOXANE [1602]
S361	5	2-Ethoxyethanol	ALCOHOLS IV [1403]
S365	4	Furfuryl alcohol	FURFURYL ALCOHOL [2505]
S366	4	Iron oxide fume	ELEMENTS BY ICP [7300]
S367	3	Isophorone	ISOPHORONE [2508]
S368	3	Isopropyl ether	ISOPROPYL ETHER [1618]
S369	3	Magnesium oxide fume	ELEMENTS BY ICP [7300]
S370	3	Malathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S371	4	Methoxychlor	NRIU
S372	3	Methyl bromide	NRNR
S374	4	Methylcyclohexanol	METHYL CYCOHEXANOL [1404]
S375	4	Methylcyclohexanone	METHYL CYCLOHEXANONE [2521]
S376	3	Molybdenum	ELEMENTS BY ICP [7300]
S378	3	Octane	HYDROCARBONS, BP 36-126 °C [1500]
S379	3	Pentane	HYDROCARBONS, BP 36-126 °C [1500]
S380	3	Naphtha, petroleum	NAPHTHAS [1550]
S381	4	Sodium hydroxide	ALKALINE DUSTS [7401]
S382	3	Stoddard solvent	NAPHTHAS [1550]
S383	4	Tetraethyl lead	TETRAETHYL LEAD [2533]
S384	4	Tetramethyl lead	TETRAMETHYL LEAD [2534]
S385	3	Titanium dioxide	NRIU
S388	4	Vanadium	ELEMENTS BY ICP [7300]
S391	3	Vanadium	ELEMENTS BY ICP [7300]
CRDT	--	Fibrous glass	CARBON BLACK [5000]; ASBESTOS AND OTHER FIBERS [7400]
CRDT	--	Nitrous oxide	NITROUS OXIDE [6600]
CRDT	--	Organotins	ORGANOTIN COMPOUNDS [5504]
SDS29	--	Nuisance dust, respirable	PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE [0600]

Example: The references to method title and number are listed in the following manner:

ACETIC ACID, 1603	(Method Title)
Ethanoic acid, see ACETIC ACID, 1603	(Synonym)
Glacial acetic acid, see ACETIC ACID, 1603	(Synonym)
Methane carboxylic acid, see ACETIC ACID, 1603	(Synonym)
CAS #64-19-7, see ACETIC ACID, 1603	(Chemical Abstracts Registry Number)

Acenaphthene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Acenaphthylene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
ACETALDEHYDE, 2538 (GC), 3507 (HPLC), see ALDEHYDES, SCREENING, 2539
ACETIC ACID, 1603
Acetic acid anhydride, see ACETIC ANHYDRIDE, 3506
Acetic acid ethyl ester, see ETHYL ACETATE, 1457
Acetic acid butyl ester, see ESTERS I, 1450
Acetic acid 1,1-dimethylethyl ester, see ESTERS I, 1450
Acetic acid ethylene glycol monoethyl ether ester, see ESTERS I, 1450
Acetic acid isobutyl ester, see ESTERS I, 1450
Acetic acid 3-methyl-1-butanol ester, see ESTERS I, 1450
Acetic acid methyl ester, see METHYL ACETATE, 1458
Acetic acid 4-methyl-2-pentanol ester, see ESTERS I, 1450
Acetic acid 1-methyl propyl ester, see ESTERS I, 1450
Acetic acid 1-pentanol ester, see ESTERS I, 1450
Acetic acid 2-pentanol ester, see ESTERS I, 1450
Acetic acid n-propyl ester, see ESTERS I, 1450
Acetic acid vinyl ester, see VINYL ACETATE, 1453
Acetic aldehyde, see ACETALDEHYDE (GC), 2538; 3507 (HPLC)
ACETIC ANHYDRIDE, 3506
Acetone, see KETONES I, 1300
ACETONE CYANOHYDRIN, 2506
ACETONITRILE, 1606
3-(a-Acetonylbenzyl)-4-hydroxycoumarin, see WARFARIN, 5002
Acetyl oxide, see ACETIC ANHYDRIDE, 3506
Acetylene black, see CARBON BLACK, 5000
Acetylene dichloride, see HYDROCARBONS, HALOGENATED, 1003
Acetylene tetrabromide, see 1,1,2,2-TETRABROMOETHANE, 2003
Acetylene tetrachloride, see 1,1,2,2-TETRACHLOROETHANE, 1019
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2,6-Diaminotoluene, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
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DIAZOMETHANE, 2515
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1,1-DIMETHYLHYDRAZINE, 3515
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Dimethylarsenic acid, see ARSENIC, ORGANO-, 5022
1,3-Dimethyl butyl acetate, see ESTERS I, 1450
Dimethylbenzene, see HYDROCARBONS, AROMATIC, 1501
N,N-Dimethylbenzeneamine, see AMINES, AROMATIC, 2002
1,1'-Dimethyl-4,4'-bipyridinium bis methyl sulfate, see PARAQUAT, 5003
1,1'-Dimethyl-4,4'-bipyridinium dichloride, see PARAQUAT, 5003
1,1-Dimethylethyl ether, see METHYL tert-BUTYL ETHER, 1615
Dimethylene oxide, see ETHYLENE OXIDE, 1607; ETHYLENE OXIDE (portable GC), 3702
Dimethylenimine, see ETHYLENIMINE, P&CAM 300
Dimethylformamide, see DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE, 2004
N,N-Dimethylformamide, see DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE, 2004
2,6-Dimethyl-4-heptanone, see KETONES I, 1300
N,N-Dimethylhydrazine see 1,1-DIMETHYLHYDRAZINE, 3515
Dimethyl 2-methoxycarbonyl-l-methylethenyl phosphate, see ORGANOPHOSPHORUS PESTICIDES, 5600
Dimethylnitromethane, see 2-NITROPROPANE, 2528
DIMETHYL SULFATE, 2524
N,N-Dimethyl-p-toluidine, see AMINES, AROMATIC, 2002
Dimethyl trichlorophenyl phosphate, see ORGANOPHOSPHORUS PESTICIDES, 5600
Dioctyl phthalate, see DI(2-ETHYLHEXYL) PHTHALATE, 5020
Dioxan, see DIOXANE, 1602
DIOXANE, 1602
p-Dioxane, see DIOXANE, 1602
DIPHENYL, 2530
o-Diphenyl benzene, see o-TERPHENYL, 5021
Diphenyl Ether, see PHENYL ETHER, 1617
Diphenyl Oxide, see PHENYL ETHER, 1617
Diphenyl oxide-diphenyl mixture, see, PHENYL ETHER - DIPHENYL MIXTURE, 2013
Diphosphoric acid tetraethyl ester, see TETRAETHYL PYROPHOSPHATE, 2504
Direct Azurine G, see DYES, 5013
Disulfoton, see ORGANOPHOSPHORUS PESTICIDES, 5600
Dithiocarbonic anhydride, see CARBON DISULFIDE, 1600
DMF, see DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE, 2004
DOP, see DI(2-ETHYLHEXYL) PHTHALATE, 5020
Dowco-213, see ORGANOTIN COMPOUNDS, 5504
Dowtherm A, see PHENYLETHER-DIPHENYL MIXTURE, 2013
Drawing oil, see OIL MIST, MINERAL, 5026
Dust, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
DYES, BENZIDINE, o-ANISIDINE, and o-TOLIDINE, 5013

EDB, see ETHYLENE DIBROMIDE, 1008
EGDN, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
ELEMENTS by ICP, 7300
ELEMENTS in blood or tissue, 8005
Emery, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
ENDRIN, 5519
Engine oil, see OIL MIST, MINERAL, 5026
EPICHLOROHYDRIN, 1010
EPN, 5012
1,2-Epoxyethane, see ETHYLENE OXIDE, 1614; ETHYLENE OXIDE (portable GC), 3702
1,2-Epoxypropane, see PROPYLENE OXIDE, 1612
2,3-Epoxy-1-propanol, see GLYCIDOL, 1608
1,2-Epoxy-3-phenoxy propane, see PHENYL GLYCIDYL ETHER, 1619
2,3-Epoxypropyl butyl ether, see n-BUTYL GLYCIDYL ETHER, 1616
1,2-Epoxy-3-isopropoxypropane, see ISOPROPYL GLYCIDYL ETHER, 1620
2,3-Epoxypropyl phenyl ether, see PHENYL GLYCIDYL ETHER, 1619
Epoxypropyl alcohol, see GLYCIDOL, 1608
ESTERS I, 1450

Ethanethiol, see MERCAPTANS, Methyl, Ethyl, and n-Butyl, 2542
Ethanal, see ACETALDEHYDE (GC), 2538; ALDEHYDES, SCREENING, 2539; ACETALDEHYDE (HPLC), 3507
Ethanoic acid, see ACETIC ACID, 1603
Ethanol, see ALCOHOLS I, 1400
Ethanol in blood, see METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
Ethanolamine, see AMINOETHANOL COMPOUNDS I, 2007; AMINOETHANOL COMPOUNDS II, 3509
Ethanolamine compounds, see AMINOETHANOL COMPOUNDS I, 2007; AMINOETHANOL COMPOUNDS II, 3509
Ether, see ETHYL ETHER, 1610
Ethion, see ORGANOPHOSPHORUS PESTICIDES, 5600
Ethoprop, see ORGANOPHOSPHORUS PESTICIDES, 5600
2-Ethoxyethanol, see ALCOHOLS IV, 1403
2-Ethoxyethyl acetate, see ESTERS I, 1450
ETHYL ACETATE, 1457
Ethyl acrylate, see ESTERS I, 1450
Ethyl alcohol, see ALCOHOLS I, 1400; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
Ethyl amyl ketone, see KETONES II, 1301
ETHYL BROMIDE, 1011
Ethyl butyl ketone, see KETONES II, 1301
ETHYL CHLORIDE, 2519
ETHYL ETHER, 1610
ETHYL FORMATE, 1452
Ethyl methanoate, see ETHYL FORMATE, 1452
Ethylbenzene, see HYDROCARBONS, AROMATIC, 1501
ETHYLENE CHLOROHYDRIN, 2513
ETHYLENEDIAMINE (EDA), see ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE, 2540
ETHYLENIMINE, 3514
Ethyleneimine, see ETHYLENIMINE, 3514
ETHYLENE DIBROMIDE, 1008
Ethylene dichloride, see HYDROCARBONS, HALOGENATED, 1003
Ethylene dinitrate, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
Ethylene glycol dinitrate, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
Ethylene glycol monomethyl ester acetate, see METHYL CELLOSOLVE ACETATE, 1451
ETHYLENE OXIDE, 1614; ETHYLENE OXIDE (portable GC), 3702
ETHYLENE THIOUREA, 5011
Ethylidene chloride, see HYDROCARBONS, HALOGENATED, 1003
Ethyl mercaptan, see MERCAPTANS, Methyl, Ethyl, and n-Butyl, 2542
Etrolene, see ORGANOPHOSPHORUS PESTICIDES, 5600
ETU, see ETHYLENE THIOUREA, 5011

Fast red GG, see p-NITROANILINE, 5033
Fenamiphos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Fenchlorphos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Ferroactinolite, see ASBESTOS (bulk) by PLM, 9002; ASBESTOS FIBERS by TEM, 7402; ASBESTOS and OTHER FIBERS by PCM, 7400
Fibers, see ASBESTOS and OTHER FIBERS by PCM, 7400
Fibrous glass, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; ASBESTOS and OTHER FIBERS by PCM, 7400
Fluoranthene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Fluorene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
FLUORIDE in urine, 8308
FLUORIDES by ISE, 7902; 7906 (IC)
FLUOROTRICHLOROMETHANE, 1006
Fonofos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Formal, see METHYLAL, 1611
FORMALDEHYDE (2-HMP), 2541; see ALDEHYDES, SCREENING, 2539
FORMALDEHYDE (chromotropic acid); 3500, see ALDEHYDES, SCREENING, 2539
FORMALDEHYDE ON DUST, 5700
FORMIC ACID, 2011

Formic acid ethyl ester, see ETHYL FORMATE, 1452
Formonitrile, see CYANIDES, 7904
Free crystalline silica, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); QUARTZ in coal mine dust, 7603
Freon, also see Refrigerants
Freon 11, see FLUOROTRICHLOROMETHANE, 1006
Freon 12, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE, 1018
Freon 12B2, see DIFLUORODIBROMOMETHANE, 1012
Freon 13B1, see TRIFLUOROBROMOMETHANE, 1017
Freon 21, see DICHLOROFLUOROMETHANE, 2516
Freon 113, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Freon TF, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Fumed amorphous silica, see SILICA, AMORPHOUS, 7501
2-Furaldehyde, see FURFURAL, 2529
2-Furancarboxaldehyde, see FURFURAL, 2529
2,5-Furandione, see MALEIC ANHYDRIDE, 3512
FURFURAL, 2529; see ALDEHYDES SCREENING, 2539
FURFURYL ALCOHOL, 2505
2-Furyl carbinol, see FURFURYL ALCOHOL, 2505
2-Furylmethanol, see FURFURYL ALCOHOL, 2505
Furnace black, see CARBON BLACK, 5000
Fused amorphous silica, see SILICA, AMORPHOUS, 7501

Galena, see LEAD SULFIDE, 7505
Glacial acetic acid, see ACETIC ACID, 1603
GLUTARALDEHYDE, 2532
Glycerin mist, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Glycerol trichlorohydrin, see HYDROCARBONS, HALOGENATED, 1003
Glycide, see GLYCIDOL, 1608
GLYCIDOL, 1608
Glycol, see ETHYLENE CHLOROHYDRIN, 2513
Graphite (synthetic), see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Gumspirits, see TURPENTINE, 1551
Gypsum, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600

Halon 112, see DICHLOROFLUOROMETHANE, 2516
Halon 1011, see HYDROCARBONS, HALOGENATED, 1003
HCN, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904
HDI, see ISOCYANATES, 5521
Heat-treating oils, see OIL MIST, MINERAL, 5026
Heptanal, see ALDEHYDES, SCREENING, 2539
Hepatic gas, see HYDROGEN SULFIDE 6013
n-Heptane, see HYDROCARBONS, BP 36-126 °C, 1500
1,7-Heptanedicarboxylic acid, see AZELAIC ACID, 5019
2-Heptanone, see KETONES II, 1301
3-Heptanone, see KETONES II, 1301
HEXACHLOROBUTADIENE, 2543
q-Hexachlorocyclohexane, see ALDRIN and LINDANE, 5502
HEXACHLORO-1,3-CYCLOPENTADIENE, 2518
Hexachloroethane, see HYDROCARBONS, HALOGENATED, 1003
Hexadrin, see ENDRIN, 5519
Hexahydrobenzene, see HYDROCARBONS, BP 36-126 °C, 1500
Hexahydrocresol, see METHYLCYCLOHEXANOL, 1404
Hexahydromethylphenol, see METHYLCYCLOHEXANOL, 1404
Hexalin, see ALCOHOLS III, 1402
Hexamethylene, see HYDROCARBONS, BP 36-126 °C, 1500
Hexamethylenediisocyanate (HDI), see ISOCYANATES, 5521

Hexanal, see ALDEHYDES SCREENING, 2539
n-Hexane, see HYDROCARBONS, BP 36-126 °C, 1500
2-Hexanone, see KETONES I, 1300
Hexone, see KETONES I, 1300
sec-Hexyl acetate, see ESTERS I, 1450
HF, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
HIPPURIC ACID in urine (VIS), 8300
HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC), 8301
Hi-sil, see SILICA, AMORPHOUS, 7501
Hydrated amorphous silica, see SILICA, AMORPHOUS, 7501
Hydrated lime, see CALCIUM, 7020
Hydraulic oils, see OIL MIST, MINERAL, 5026
HYDRAZINE, 3503
Hydrazinobenzene, see PHENYL ETHER, 3518
Hydrobromic acid, see ACIDS, INORGANIC, 7903
HYDROCARBONS, AROMATIC, 1501
HYDROCARBONS, BP 36-126 °C, 1500
HYDROCARBONS, HALOGENATED, 1003
Hydrochloric acid, see ACIDS, INORGANIC, 7903
Hydrocyanic acid, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904
Hydrofluoric acid, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
Hydrogen bromide, see ACIDS, INORGANIC, 7903
Hydrogen carboxylic acid, see FORMIC ACID, 2011
Hydrogen chloride, see ACIDS, INORGANIC, 7903
HYDROGEN CYANIDE, 6010; see CYANIDES, 7904
Hydrogen fluoride, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
HYDROGEN SULFIDE, 6013
Hydroquinol, see HYDROQUINONE, 5004
HYDROQUINONE, 5004
Hydrosulfuric acid, see HYDROGEN SULFIDE, 6013
4-Hyroxychlorobenzene, see p-CHLOROPHENOL, 2014
Hydroxydimethylarsine oxide, see ARSENIC, ORGANO-, 5022
2-Hydroxyethylamine, see AMINOETHANOL COMPOUNDS I, 2007
Hydroxymethyl ethylene oxide, see GLYCIDOL, 1608
2-(Hydroxymethyl) furan, see FURFURYL ALCOHOL, 2505
2-(Hydroxymethyl)oxiran, see GLYCIDOL, 1608
4-Hydroxy-4-methyl-2-pentanone, see ALCOHOLS III, 1402
2-Hydroxy-2-methylpropanenitrile, see ACETONE CYANOHYDRIN, 2506
3-Hydroxypropylene oxide, see GLYCIDOL, 1608
2-Hydroxytriethylamine, see AMINOETHANOL COMPOUNDS I, 2007
Hyponitrous acid anhydride, see NITROUS OXIDE, 6600

ICN 1229, see RIBAVIRIN, 5027
IGE, see ISOPROPYL GLYCIDYL ETHER, 6020
2-Imidazolidinethione, see ETHYLENE THIOUREA, 5011
2,2'-Iminodiethanol, see AMINOETHANOL COMPOUNDS II, 3509
Indeno[1,2,3-cd]pyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
IODINE, 6005
Iron, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Iodomethane, see METHYL IODIDE, 1014
Isoamyl acetate, see ESTERS I, 1450
Isoamyl alcohol, see ALCOHOLS III, 1402
Isobutyl acetate, see ESTERS I, 1450
Isobutyl alcohol, see ALCOHOLS II, 1401
Isobutyraldehyde, see ALDEHYDES, SCREENING, 2539
ISOCYANATES, 5521; see 2,4-TOLUENEDIISOCYANATE, 2535
Isocyanuric acid, see CYANURIC ACID, 5030
ISOPHORONE, 2508

Isopropenylbenzene, see HYDROCARBONS, AROMATIC, 1501
ISOPROPYL ACETATE, 1454
Isopropyl alcohol, see ALCOHOLS I, 1400
ISOPROPYL ETHER, 1618
Isopropyl epoxypropyl ether, see ISOPROPYL GLYCIDYL ETHER, 1620
ISOPROPYL GLYCIDYL ETHER, 1620
Isopropylbenzene, see HYDROCARBONS, AROMATIC, 1501
Isovaleraldehyde, see ALDEHYDES, SCREEENING, 2539

Jasmolin I, II, see PYRETHRUM, 5008

Kaolin, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
KEPONE, 5508
Kerosene, see NAPHTHAS, 1550
Kerosine, see NAPHTHAS, 1550
KETONES I, 1300
KETONES II, 1301

Lamp black, see CARBON BLACK, 5000
Lanthanum, see ELEMENTS in blood or tissue, 8005
Lanthanum in blood, see ELEMENTS in blood or tissue, 8005
Lanthanum in tissue, see ELEMENTS in blood or tissue, 8005
Laughing gas, see NITROUS OXIDE, 6600
LEAD, 7082 (FAAS); 7105 (GFAAS); also see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; LEAD in blood and urine, 8003; METALS in urine, 8310
Lead Oxide, see LEAD, 7082 (FAAS), 7105 (GFAAS)
LEAD SULFIDE, 7505
Lead tetraethyl, see TETRAETHYL LEAD (as Pb), 2533
Lead tetramethyl, see TETRAMETHYL LEAD (as Pb), 2534
Lepargylic acid, see AZELAIC ACID, 5019
Limestone, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
Lindane, see ALDRIN and LINDANE, 5502
Lithium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005
Lithium hydroxide, see ALKALINE DUSTS, 7401
Lye, see ALKALINE DUSTS, 7401

Machine oil, see OIL MIST, MINERAL, 5026
Magnesite, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
Magnesium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005
Malathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
MALEIC ANHYDRIDE, 3512
Manganese, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Marble, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
MBK, see KETONES I, 1300
MBOCA in urine, 8302
MDA, see 4,4'-METHYLENEDIANILINE, 5029
MDI, see, ISOCYANATES, 5521
MEA, see AMINOETHANOL COMPOUNDS II, 3509
MEK, see METHYL ETHYL KETONE, 2500
MEK in blood, see 2-BUTANONE, ETHANOL, and TOLUENE in blood, 8002
Mendrin, see ENDRIN, 5519
MERCAPTANS, Methyl, Ethyl, and n-Butyl, 2542
1-Mercaptooctane, see 1-OCTANETHIOL, 2510
MERCURY, 6009
Mesityl oxide, see KETONES II, 1301

Metals in air, see ELEMENTS by ICP, 7300; or individual metals
METALS in urine (ICP), 8310
Meta-phosphoric acid, see ACIDS, INORGANIC, 7903
Methacrylic acid methyl ester, see METHYL METHACRYLATE, 2537
Methamidophos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Methanal, see FORMALDEHYDE (2-HMP), 2502; (chromotropic acid), 3500; ALDEHYDES, SCREENING, 2539
Methanearsonic acid, see ARSENIC, ORGANO-, 5022
Methane carboxylic acid, see ACETIC ACID, 1603
Methanoic acid, see FORMIC ACID, 2011
METHANOL, 2000
2-Methoxy-2-methyl propane, see METHYL tert-BUTYL ETHER, 1615
2-Methoxyacetate, see METHYL CELLOSOLVE ACETATE, 1451
2-Methoxybenzenamine, see ANISIDINE, 2514
4-Methoxybenzeneamine, see ANISIDINE, 2514
2-Methoxyethanol, see ALCOHOLS IV, 1403
METHYLAL, 1611
METHYL ACETATE, 1458
METHYL ACRYLATE, 1459
Methyl alcohol, see METHANOL, 2000
Methyl-(n-amyl)-ketone, see KETONES II, 1301
Methylarsonic acid, see ARSENIC, ORGANO-, 5022
Methylbenzene, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126 °C, 1500; TOLUENE, 4000; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
4-Methyl-1,3-benzenediamine, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
2-Methyl-1,3-benzenediamine, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
3-Methyl-1-butanol, see ALCOHOLS III, 1402
Methyl n-butyl ketone, see KETONES I, 1300
Methyl cellosolve, see ALCOHOLS IV, 1403
METHYL CELLOSOLVE ACETATE, 1451
METHYL CHLORIDE, 1001
Methyl ethanoate, see METHYL ACETATE, 1458
Methylchloroform, see HYDROCARBONS, HALOGENATED, 1003
Methyl cyanide, see ACETONITRILE, 1606
Methylcyclohexane, see HYDROCARBONS, BP 36-126 °C, 1500
METHYLCYCLOHEXANOL, 1404
METHYLCYCLOHEXANONE, 2521
2-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
3-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
4-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
4,4'-Methylenebis(2-chloroaniline) in urine, see MBOCA in urine, 8302
METHYLENE CHLORIDE, 1005
4,4'-METHYLENEDIANILINE, 5029
4,4'-Methylenediphenyldiisocyanate (MDI), see ISOCYANATES, 5521
(1-Methylethenyl)-benzene, see HYDROCARBONS, AROMATIC, 1501
METHYL ETHYL KETONE, 2500; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
METHYL ETHYL KETONE PEROXIDE, 3508
5-Methyl-3-heptanone, see KETONES II, 1301
Methyl hippuric acid in urine, see HIPPURIC and METHYL HIPPURIC ACIDS in urine, 8301
METHYL IODIDE, 1014
Methyl isoamyl acetate, see ESTERS I, 1450
Methyl isobutyl acetate, see ISOPROPYL ACETATE, 1454
Methyl isobutyl carbinol, see ALCOHOLS III, 1402
Methyl isobutyl ketone, see KETONES I, 1300
2-Methyllactonitrile, see ACETONE CYANOHYDRIN, 2506
METHYL METHACRYLATE, 2537
Methyl parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
m-Methylnitrobenzene, see NITROBENZENES, 2005
o-Methylnitrobenzene, see NITROBENZENES, 2005

p-Methylnitrobenzene, see NITROBENZENES, 2005
Methyloxirane, see PROPYLENE OXIDE, 1612
4-Methyl-2-pentanol, see ALCOHOLS III, 1402
4-Methyl-2-pentanone, see KETONES I, 1300
4-Methyl-3-penten-2-one, see KETONES II, 1301
2-Methylphenol, see CRESOLS and PHENOL, 2546
3-Methylphenol, see CRESOLS and PHENOL, 2546
4-Methylphenol, see CRESOLS and PHENOL, 2546; PHENOL and p-CRESOL in urine, 8305
2-Methyl-1-propanol, see ALCOHOLS II, 1401
Methyl hydrazine, see MONOMETHYL HYDRAZINE, 3510
Methyl propenoate, see METHYL ACRYLATE, 1459
2-Methyl-2-propanol, see ALCOHOLS I, 1400
Methyl propyl ketone, see KETONES I, 1300
METHYL tert-BUTYL ETHER, 1615
Methylstyrene, see HYDROCARBONS, AROMATIC, 1501
a-Methylstyrene, see HYDROCARBONS, AROMATIC, 1501
Methylvinylbenzene, see HYDROCARBONS, AROMATIC, 1501
Methyl viologen, see PARAQUAT, 5003
Mevinphos, see ORGANOPHOSPHORUS PESTICIDES, 5600
MIBC, see ALCOHOLS III, 1402
MIBK, see KETONES I, 1300
Mineral oil mist, see OIL MIST, MINERAL, 5026
Mineral spirits, see NAPHTHAS, 1550
Mineral wool fiber, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; ASBESTOS and OTHER FIBERS by PCM, 7400
MOCA in urine, see MBOCA in urine, 8302
Molybdenum, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Monochloroacetic acid, see CHLOROACETIC ACID, 2008
Monochlorobenzene, see HYDROCARBONS, HALOGENATED, 1003
Monoethanolamine (MEA), see AMINOETHANOL COMPOUNDS II, 3509
MONOMETHYLHYDRAZINE, 3510
MTBE, see METHYL tert-BUTYL ETHER, 1615
Muriatic acid, see ACIDS, INORGANIC, 7903
Muthmann's liquid, see 1,1,2,2-TETRABROMOETHANE, 2003

Naphthalene, see HYDROCARBONS, AROMATIC, 1501; POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
1-Naphthalenol N-methylcarbamate, see CARBARYL, 5006
NAPHTHAS (refined petroleum solvents), 1550
Napthene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
NAPHTHYLAMINES, 5518
a-Naphthylamine, see NAPHTHYLAMINES, 5518
ß-Naphthylamine, see NAPHTHYLAMINES, 5518
1-Naphthylamine, see NAPHTHYLAMINES, 5518
2-Naphthylamine, see NAPHTHYLAMINES, 5518
NG, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
Nickel, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
NICKEL CARBONYL, 6007
NICOTINE, 2544
Nitric acid, see ACIDS, INORGANIC, 7903
NITRIC OXIDE and NITROGEN DIOXIDE, 6014
2,2',2"-Nitrilotriethanol, see AMINOETHANOL COMPOUNDS II, 3509
p-NITROANILINE, 5033
4-Nitroaniline, see p-NITROANILINE, 5033
NITROBENZENES, 2005
Nitrocarbol, see NITROMETHANE, 2527
p-Nitrochlorobenzene, see NITROBENZENES, 2005
NITROETHANE, 2526

NITROGEN DIOXIDE, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen monoxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen peroxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
NITROMETHANE, 2527
2-NITROPROPANE, 2528
NITROSAMINES, 2522
N-Nitrosodibutylamine, see NITROSAMINES, 2522
N-Nitrosodiethylamine, see NITROSAMINES, 2522
N-Nitrosodimethylamine, see NITROSAMINES, 2522
N-Nitrosodipropylamine, see NITROSAMINES, 2522
N-Nitrosomorpholine, see NITROSAMINES, 2522
N-Nitrosopiperidine, see NITROSAMINES, 2522
N-Nitrosopyrrolidine, see NITROSAMINES, 2522
Nitrotoluene, see NITROBENZENES, 2005
NITROUS OXIDE, 6600
Nonanedioic acid, see AZELAIC ACID, 5019
Nuisance dust, respirable, see PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE, 0600
Nuisance dust, total, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500

Octalene, see ALDRIN and LINDANE, 5502
n-Octane, see HYDROCARBONS, BP 36-126 °C, 1500
Octachlor, see CHLORDANE, 5510
1-OCTANETHIOL, 2510
n-Octanethiol, see 1-OCTANETHIOL, 2510
Octylmercaptan, see 1-OCTANETHIOL, 2510
Octyl thiol, see 1-OCTANETHIOL, 2510
OIL MIST, MINERAL, 5026
Oil of turpentine, see TURPENTINE, 1551
Oil of vitriol, see ACIDS, INORGANIC, 7903
Oleum, see ACIDS, INORGANIC, 7903
ORGANOPHOSPHORUS PESTICIDES, 5600
ORGANOTIN COMPOUNDS, 5504
Ortho-phosphoric acid, see ACIDS, INORGANIC, 7903
Oxirane, see ETHYLENE OXIDE, 1614; ETHYLENE OXIDE, 3702
Oxiranemethanol, see GLYCIDOL, 1608
1,1'-Oxybisbenzene, see PHENYL ETHER, 1617
1,1'-Oxybis(2-chloroethane), see sym-DICHLOROETHYL ETHER, 1004
1,1'-Oxybisethane, see ETHYL ETHER, 1610
OXYGEN, 6601

PAC, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
PAH, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
PARAQUAT, 5003
Parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
Pb, see LEAD, 7082 (FAAS); 7105 (GFAAS); ELEMENTS by ICP, 7300; LEAD in blood and urine, 8003
PbB, see LEAD in blood and urine, 8003
PCB, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
PCP, see PENTACHLOROPHENOL, 5512; PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303
PCT, see CHLORINATED TERPHENYL, 5014
Pentachlorobenzene, see POLYCHLOROBENZENES, 5517
PENTACHLOROETHANE, 2517
PENTACHLOROPHENOL, 5512
PENTACHLOROPHENOL in blood, 8001
PENTACHLOROPHENOL in urine, 8303
Pentaerythritol, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Penta, see PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303

PENTACHLOROPHENOL, 5512, see also PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303
Pentanal, see VALERALDEHYDE, 2536; ALDEHYDES SCREENING, 2539
n-Pentane, see HYDROCARBONS, BP 36-126 °C, 1500
2-Pentanone, see KETONES I, 1300
Perchlorobutadiene, see HEXACHLOROBUTADIENE, 2543
Perchlorocyclopentadiene, see HEXACHLORO-1,3-CYCLOPENTADIENE, 2518
Perchloroethane, see HYDROCARBONS, HALOGENATED, 1003
Perchloroethylene, see HYDROCARBONS, HALOGENATED, 1003
Petroleum ether, see NAPHTHAS, 1550
Petroleum naphtha, see NAPHTHAS, 1550
Phenanthrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Phenol, see CRESOLS and PHENOL, 2546
PHENOL and p-CRESOL in urine, 8305
Phenyl chloride, see HYDROCARBONS, HALOGENATED, 1003
PHENYL ETHER, 1617
PHENYL ETHER - DIPHNEYL MIXTURE, 2013
PHENYL GLYCIDYL ETHER, 1619
PHENYLHYDRAZINE, 3518
Phenoxypropane oxide, see PHENYL GLYCIDYL ETHER, 1619
2,3-Phenylenepyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Phenylphosphonothioic acid O-ethyl O-p-nitrophenyl ester, see EPN, 5012
Phorate, see ORGANOPHOSPHORUS PESTICIDES, 5600
Phosdrin, see ORGANOPHOSPHORUS PESTICIDES, 5600
Phosphoric acid, see ACIDS, INORGANIC, 7903
Phosphoric acid dibutyl ester, see DIBUTYL PHOSPHATE, 5017
Phosphoric acid tributyl ester, see TRIBUTYL PHOSPHATE, 5034
Phosphoric acid triorthocresyl ester, see TRIORTHOCRESYL PHOSPHATE, 5037
Phosphoric acid triphenyl phosphate, see TRIPHENYL PHOSPHATE, 5038
Phosphorothioic acid O,O-diethyl O-[2-(ethylthio)ethyl]ester mixture with O,O-diethyl-S-[2-ethylthio)ethyl]phosphorothioate, see DEMETON, 5514
Phosphorothioic acid O,O-diethyl O-(4-nitrophenyl)ester, see ORGANOPHOSPHORUS PESTICIDES, 5600
PHOSPHORUS, 7905; ELEMENTS by ICP, 7300
PHOSPHORUS TRICHLORIDE, 6402
Phthalic acid dibutyl ester, see DIBUTYL PHTHALATE, 5020
Pinene, see TURPENTINE, 1551
Plaster of Paris, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Platinum, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Plictran, see ORGANOTIN COMPOUNDS, 5504
PNA (obsolete term), see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
POLYCHLORINATED BIPHENYLS in serum, 8004
POLYCHLOROBENZENES, 5517
POLYCHLOROBIPHENYLS, 5503
Polychloroterphenyl, see CHLORINATED TERPHENYL, 5014
POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Portland cement, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Potassium cyanide, see CYANIDES, 7904
Potassium hydroxide, see ALKALINE DUSTS, 7401
1,2,3-Propanetriol trinitrate, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
1-Propanol, see ALCOHOLS II, 1401
2-Propanol, see ALCOHOLS I, 1400
2-Propanone, see KETONES I, 1300
2-Propenal, see ACROLEIN, 2501
2-Propenoic acid methyl ester, see METHYL ACRYLATE, 1459
Propionaldehyde, see ALDEHYDES, SCREENING, 2539
2-Propenenitrile, see ACRYLONITRILE, 1604
2-Propenoic acid ethyl ester, see ESTERS I, 1450
2-Propen-1-ol, see ALCOHOLS III, 1402

n-Propyl acetate, see ESTERS I, 1450
sec-Propyl acetate, see ISOPROPYL ACETATE, 1454
n-Propyl alcohol, see ALCOHOLS II, 1401
Propylene aldehyde, see CROTONALDEHYDE, 3516
PROPYLENE DICHLORIDE, 1013
PROPYLENE OXIDE, 1612
Prussic acid, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904
Pyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Pyrethrin I, II, see PYRETHRUM, 5008
PYRETHRUM, 5008
PYRIDINE, 1613
Pyrophosphoric acid tetraethyl ester, see TETRAETHYL PYROPHOSPHATE, 2504

Quartz, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); SILICA in coal mine dust, 7603
Quicklime, see CALCIUM, 7020
Quicksilver, see MERCURY, 6009

Refrigerant 11, see FLUOROTRICHLOROMETHANE, 1006
Refrigerant 12, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, CHLORODIFLUOROMETHANE, 1018
Refrigerant 13B1, see TRIFLUOROBROMOMETHANE, 1017
Refrigerant 13B2, see DIFLUORODIBROMOMETHANE, 1012
Refrigerant 21, see DICHLOROFLUOROMETHANE, 2516
Refrigerant 112, see 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016
Refrigerant 112a, see 1,1,1,2-TETRACHLORO-2,2,-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016
Refrigerant 113, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Refrigerant 114, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, AND CHLORODIFLUOROMETHANE, 1018
RIBAVIRIN, 5027
Ronnel, see ORGANOPHOSPHORUS PESTICIDES, 5600
ROTENONE, 5007
Rouge, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Rubber solvent, see NAPHTHAS, 1550

Selenium, see ELEMENTS by ICP, 7300
Serpentine, see ASBESTOS (bulk) by PLM, 9002; ASBESTOS FIBERS by TEM 7402; ASBESTOS and OTHER FIBERS
by PCM, 7400
Sevin, see CARBARYL, 5006
SILICA, AMORPHOUS (XRD), 7501
SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); SILICA in coal mine dust, 7603 (IR)
Silica aerogel, see SILICA, AMORPHOUS, 7501
Silicic anhydride, see SILICA, AMORPHOUS, 7501
Silicon, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Silicon carbide, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Silicon dioxide, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); SILICA in coal mine dust, 7603
Silver, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue,8005; METALS in urine, 8310
Soda lime, see ALKALINE DUSTS, 7401
Sodium fluoride, see FLUORIDES by ISE, 7902; 7906 (IC)
Sodium hexafluoroaluminate, see FLUORIDES by ISE, 7902; 7906 (IC)
Sodium hydroxide, see ALKALINE DUSTS, 7401
Sodium, see ELEMENTS by ICP, 7300
Stannane, chlorotributyl-, see ORGANOTIN COMPOUNDS, 5504
Stannane, tetrabutyl-, see ORGANOTIN COMPOUNDS, 5504
Stannane, tricyclohexylhydroxy-; see ORGANOTIN COMPOUNDS, 5504
Starch, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600

STIBINE, 6008
Stoddard solvent, see NAPHTHAS, 1550
Strontium, see ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Strychnidin-10-one, see STRYCHNINE, 5016
STRYCHNINE, 5016
Styrene, see HYDROCARBONS, AROMATIC, 1501
Sucrose, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
SULFUR DIOXIDE, 6004
Sulfuretted hydrogen, see HYDROGEN SULFIDE, 6013
Sulfuric acid, see ACIDS, INORGANIC, 7903
SULFURYL FLUORIDE, 6012
Systox, see DEMETON, 5514

2,4,5-T, see 2,4-D and 2,4,5-T, 5001
TBTC, see ORGANOTIN COMPOUNDS, 5504
TCHH, see ORGANOTIN COMPOUNDS, 5504
2,4-TDA, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
2,6-TDA, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
2,4-TDI, see TOLUENE-2,4-DIISOCYANATE, 2535; ISOCYANATES, 5521
2,6-TDI, see ISOCYANATES, 5521
TEA, see AMINOETHANOL COMPOUNDS II, 3509
TeBT, see ORGANOTIN COMPOUNDS, 5504
TEL, see TETRAETHYL LEAD (as Pb), 2534
Tellurium, see ELEMENTS by ICP, 7300
TEPP, see TETRAETHYL PYROPHOSPHATE, 2504
Terbufos, see ORGANOPHOSPHORUS PESTICIDES, 5600
o-TERPHENYL, 5021
Tetraboron carbide, see BORON CARBIDE, 7506
1,1,2,2-TETRABROMOETHANE, 2003
sym-Tetrabromoethane, see 1,1,2,2-TETRABROMOETHANE, 2003
Tetrabutyltin, see ORGANOTIN COMPOUNDS, 5504
1,2,4,5-Tetrachlorobenzene, see POLYCHLOROBENZENES, 5517
1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016
1,1,2,2-TETRACHLOROETHANE, 1019
Tetrachloroethylene, see HYDROCARBONS, HALOGENATED, 1003
Tetrachloromethane, see HYDROCARBONS, HALOGENATED, 1003
TETRAETHYL LEAD (as Pb), 2533
TETRAETHYL PYROPHOSPHATE, 2504
Tetrahydrobenzene, see HYDROCARBONS, BP 36-126 °C, 1500
TETRAHYDROFURAN, 1609
TETRAMETHYL LEAD (as Pb), 2534
TETRAMETHYL THIOUREA, 3505
Tetramethylthioperoxydicarbonic diamide, see THIRAM, 5005
Tetramethylthiuram disulfide, see THIRAM, 5005
Tetraphene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
Thallium, see ELEMENTS, 7300; ELEMENTS in blood or tissue, 8005
THF, see TETRAHYDROFURAN, 1609
THIRAM, 5005
Tin, see METALS in urine, 8310; ORGANOTIN COMPOUNDS, 5504
Titanium, see ELEMENTS, 7300; METALS in urine, 8310
Titanium dioxide, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
TML, see TETRAMETHYL LEAD (as Pb), 2534
o-Tolidine, see DYES, 5013
TOLUENE, 4000; see HYDROCARBONS, BP 36-126 °C, 1500; HYDROCARBONS, AROMATIC, 1501; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
2,4- AND 2,6-TOLUENEDIAMINE, 5516
TOLUENE-2,4-DIISOCYANATE, 2535; see ISOCYANATES, 5521
Toluene 2,6-TDI, see ISOCYANATES, 5521

o-Toluidine, see AMINES, AROMATIC 2002
o-Tolyl phosphate, see TRIORTHOCRESYL PHOSPHATE, 5037
Toxaphene, see CHLORINATED CAMPHENE, 5039
Toxilis anhydride, see MALEIC ANHYDRIDE, 3512
Toxichlor, see CHLORDANE, 5510
Transformer oil, see OIL MIST, MINERAL, 5026
Tremolite, see ASBESTOS and OTHER FIBERS, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
Tribromomethane, see HYDROCARBONS, HALOGENATED, 1003
Tributyltin chloride, see ORGANOTIN COMPOUNDS, 5504
TRIBUTYL PHOSPHATE, 5034
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
1,2,4-Trichlorobenzene, see POLYCHLOROBENZENES, 5517
1,1,1-Trichloroethane, see HYDROCARBONS, HALOGENATED, 1003
1,1,2-Trichloroethane, see HYDROCARBONS, HALOGENATED, 1003
Trichloroethene, see TRICHLOROETHYLENE, 1022; 3701 (portable GC)
TRICHLOROETHYLENE, 1022; 3701 (portable GC)
Trichlorofluoromethane, see FLUOROTRICHLOROMETHANE, 1006
Trichloromethane, see HYDROCARBONS, HALOGENATED, 1003
(2,4,5-Trichlorophenoxy) acetic acid, see 2,4-D and 2,4,5-T, 5001
1,2,3-Trichloropropane, see HYDROCARBONS, HALOGENATED, 1003
Tricyclohexyltin hydroxide, see ORGANOTIN COMPOUNDS, 5504
Tridymite, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR)
Triethanolamine, see AMINOETHANOL COMPOUNDS II, 3509
TRIETHYLENETETRAMINE, see ETHYLENEDIAMINE, DIETHYLENETRIAMINE & TRIETHYLENETERAMINE, 2540
TRIFLUOROBROMOMETHANE, 1017
Trimellitic acid-1,2-anhydride, see TRIMELLITIC ANHYDRIDE, 5036
TRIMELLITIC ANHYDRIDE, 5036
3,3,5-Trimethyl-2-cyclohexen-1-one, see ISOPHORONE, 2508
2,4,7-TRINITROFLUOREN-9-ONE, 5018
TRIORTHOCRESYL PHOSPHATE, 5037
o-Triphenyl, see o-TERPHENYL, 5021
TRIPHENYL PHOSPHATE, 5038
Trolene, see ORGANOPHOSPHORUS PESTICIDES, 5600
TTE, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Tubatoxin, see ROTENONE, 5007
TUNGSTEN (soluble and insoluble), 7074
TURPENTINE, 1551

VALERALDEHYDE, 2536; see ALDEHYDES, SCREENING, 2539
Vanadic anhydride, see VANADIUM OXIDES, 7504
Vanadic oxide, see VANADIUM OXIDES, 7504
Vanadium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005
VANADIUM OXIDES, 7504
Vanadium pentoxide, see VANADIUM OXIDES, 7504
Vanadium sesquioxide, see VANADIUM OXIDES, 7504
Vanadium trioxide, see VANADIUM OXIDES, 7504
Vegetable oil mists (except castor, cashew nut, or similar irritant oils), see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Vikane, see SULFURYL FLUORIDE, 6012
VINYL ACETATE, 1453
Vinylbenzene, see HYDROCARBONS, AROMATIC, 1501
VINYL BROMIDE, 1009
VINYL CHLORIDE, 1007
Vinyl cyanide, see ACRYLONITRILE, 1604
VINYLIDENE CHLORIDE, 1015
Vinyl trichloride, see HYDROCARBONS, HALOGENATED, 1003
Vinyltoluene, see HYDROCARBONS, AROMATIC, 1501

VM&P naphtha, see NAPHTHAS, 1550
Virazole, see RIBAVIRIN, 5027

WARFARIN, 5002
Wolfram, see TUNGSTEN, 7074
Wood alcohol, see METHANOL, 2000
Wood turpentine, see TURPENTINE, 1551

Xylene, see HYDROCARBONS, AROMATIC, 1501
2,4-Xylidene, see AMINES, AROMATIC, 2002

Yttrium, see ELEMENTS by ICP, 7300

ZINC, 7030; see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310
Zincite, see ZINC OXIDE (XRD), 7502
ZINC OXIDE, 7502; see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600;
ZINC (FAAS), 7030
Zinc stearate, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Zinc white, see ZINC OXIDE (XRD), 7502
Zirconium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005

CAS # 50-00-0, see FORMALDEHYDE (2-HMP), 2541; (chromotropic acid), 3500; ALDEHYDES, SCREENING, 2539
CAS # 50-32-8, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 53-70-3, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 55-18-5, see NITROSAMINES (N-NITROSODIETHYLAMINE), 2522
CAS # 55-63-0, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
CAS # 56-23-5, see HYDROCARBONS, HALOGENATED, 1003
CAS # 56-38-2, see ORGANOPHOSPHORUS PESTICIDES, 5600
CAS # 56-55-3, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 56-81-5, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500; RESPIRABLE, 0600
CAS # 57-14-7, see 1,1-DIMETHYL HYDRAZINE, 3515
CAS # 57-24-9, see STRYCHNINE, 5016
CAS # 57-74-9, see CHLORDANE, 5510
CAS # 58-89-9, see ALDRIN and LINDANE, 5502
CAS # 59-89-2, see NITROSAMINES, 2522
CAS # 60-29-7, see ETHYL ETHER, 1610
CAS # 60-34-4, see MONOMETHYL HYDRAZINE, 3510
CAS # 62-53-3, see AMINES, AROMATIC, 2002
CAS # 62-75-9, see NITROSAMINES, 2522
CAS # 63-25-2, see CARBARYL, 5006
CAS # 64-17-5, see ALCOHOLS I, 1400; 2-BUTANONE, ETHANOL, and TOLUENE in blood, 8002
CAS # 64-18-6, see FORMIC ACID, 2011
CAS # 64-19-7, see ACETIC ACID, 1603
CAS # 66-25-1, see ALDEHYDES, SCREENING, 2539
CAS # 67-56-1, see METHANOL, 2000
CAS # 67-63-0, see ALCOHOLS I, 1400
CAS # 67-64-1, see KETONES I, 1300
CAS # 67-66-3, see HYDROCARBONS, HALOGENATED, 1003
CAS # 67-72-1, see HYDROCARBONS, HALOGENATED, 1003
CAS # 68-12-2, see DIMETHYLFORMAMIDE, 2004
CAS # 71-23-8, see ALCOHOLS II, 1401
CAS # 71-36-3, see ALCOHOLS II, 1401
CAS # 71-43-2, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126 °C, 1500; BENZENE by portable GC, 3700
CAS # 71-55-6, see HYDROCARBONS, HALOGENATED, 1003
CAS # 72-20-8, see ENDRIN, 5519
CAS # 74-83-9, see METHYL BROMIDE, 2520
CAS # 74-87-3, see METHYL CHLORIDE, 1001
CAS # 74-88-4, see METHYL IODIDE, 1014
CAS # 74-90-8, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904
CAS # 74-93-1, see MERCAPTANS, METHYL-, ETHYL-, and n-BUTYL; 2542
CAS # 74-96-4, see ETHYL BROMIDE, 1011
CAS # 74-97-5, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-00-3, see ETHYL CHLORIDE, 2519
CAS # 75-01-4, see VINYL CHLORIDE, 1007
CAS # 75-05-8, see ACETONITRILE, 1606
CAS # 75-07-0, see ACETALDEHYDE, (GC), 2538; (SCREENING), 2539; 3507 (HPLC)
CAS # 75-08-1, see MERCAPTANS, METHYL-, ETHYL-, and n-BUTYL, 2542
CAS # 75-09-2, see METHYLENE CHLORIDE, 1005
CAS # 75-15-0, see CARBON DISULFIDE, 1600
CAS # 75-21-8, see ETHYLENE OXIDE, 1614; ETHYLENE OXIDE, 3702
CAS # 75-25-2, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-34-3, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-35-4, see VINYLIDENE CHLORIDE, 1015
CAS # 75-43-4, see DICHLOROFLUOROMETHANE, 2516
CAS # 75-52-5, see NITROMETHANE, 2527
CAS # 75-56-9, see PROPYLENE OXIDE, 1612
CAS # 75-60-5, see ARSENIC, ORGANO-, 5022

CAS # 75-61-6, see DIFLUORODIBROMOMETHANE, 1012
CAS # 75-63-8, see TRIFLUOROBROMOMETHANE, 1017
CAS # 75-65-0, see ALCOHOLS I, 1400
CAS # 75-69-4, see FLUOROTRICHLOROMETHANE, 1006
CAS # 75-71-8, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE, 1018
CAS # 75-74-1, see TETRAMETHYL LEAD (as Pb), 2534
CAS # 75-86-5, see ACETONE CYANOHYDRIN, 2506
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