

SECOND SUPPLEMENT

To

NIOSH Manual of Analytical Methods (NMAM®)
Fourth Edition

Mary Ellen Cassinelli
Editor

Paula Fey O'Connor
Associate Editor

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16. Abstract (Limit: 200 words)

This supplement to the NIOSH Manual of Analytical Methods contains twenty new methods, eleven revised methods, twelve corrected methods, and one new chapter. The method finder, contents, and indexes have also been updated to coinside with the changes. The replacement pages are included. The manual is a collection of air, biological, bioaerosol, and bulk analytical methods that NIOSH has evaluated. NMAM will be upated as methods are developed, evaluated or revised by NIOSH. These methods are intended to promote accuracy, sensitivity, and specificity in industrial hygiene analyses. The introduction states the purpose and use of the manual. Subsequent sections discuss the quality assurance, sampling, measurements, methods, standards, blanks, blind samples, recovery studies, duplicates, tracking, and reporting. In addition, information to be considered when sampling for airborne contaminants; types and uses of solid sorbents; factors affecting the collection of gases, vapors, and aerosols; sampling strategy and calibration techniques; and samplers is presented.

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TRANSMITTAL NOTICE

This is the Second Supplement to the NIOSH Manual of Analytical Methods (NMAM®), 4th Edition, which was printed August 15, 1994. This supplement, dated January 15, 1998, includes 20 new methods, 11 revised methods, and 12 corrected methods, and one new chapter, as well as an updated Method Finder, Contents, and indexes.

INSTRUCTIONS FOR INSERTING 2ND SUPPLEMENT INTO YOUR MANUAL

Table of Contents - Remove Acknowledgments and Contents, pp. v to xiii, and replace with new pages.

Method Finder - Remove old Method Finder, pp. MF-1 to MF-17, and replace with new pages MF-1 to MF-27.
NOTE: Methods by number are listed at the end of the Method Finder.

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Methods - Insert methods alphabetically in NMAM. For new methods, insert in proper alphabetical order. For revised and corrected (errata) methods, remove old method and replace with new method.

Method	Method No.	Type
Acetonitrile	1606	Revision
Aerobic Bacteria by GC-FAME	0801	New
Alachlor in Air	5603	New
Aniline, *o*-Toluidine, Nitrobenzene	2017	New
Benzene Soluble Fraction & Total Particulate (Asphalt Fume)	5042	New
Benzothiazole in Asphalt Fume	2550	New
Bioaerosol Sampling	0800	New
n-Butyl Mercaptan	2525	Errata
Cobalt and Compounds, as Co	7027	Errata
Elemental Carbon	5040	Revision
Elements by ICP	7300	Errata
Epichlorhydrin	1010	Errata
Ethylene Oxide	1614	Errata
Fluorides by IC	7906	Errata
Formaldehyde (DNPH)	2016	New
Glutaraldehyde by HPLC/UV	2532	Errata
Glycols	5523	Errata

Method	Method No.	Type
Chlorinated and Organonitrogen Herbicides (Air Sampling)	5602	New
Chlorinated and Organonitrogen Herbicides (Patch)	9201	New
Chlorinated and Organonitrogen Herbicides (Hand wash)	9200	New
Isocyanates	5522	Revision
Lead by Flame AAS	7082	Errata
Lead by GFAAS	7105	Errata
Lead (Port XRF)	7702	New
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Methanol	2000	Revision
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N-Methyl-2-pyrrolidone	1302	New
Mycobacterium Tuberculosis, Airborne (PCR)	0900	New
Nicotine	2551	New
Nitroaromatic Compounds	2005	Revision
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Toluene (Diffusive Sampling)	4000	Errata
p-Toluenesulfonic acid	5043	New
Vinyl Acetate	1453	Revision

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The supplement was accomplished under the direction of Dennis M. O'Brien, Ph.D., Director, Division of Physical Sciences and Engineering, NIOSH.

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Calcium	Magnesium	Silver	Zinc
Cadmium	Manganese	Tellurium	Zirconium
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Benzo[b]fluoranthene Dibenz[a,h]anthracene Pyrene
Benzo[k]fluoranthene Fluoranthene
PROPYLENE DICHLORIDE 1013
PROPYLENE OXIDE 1612
PYRETHRUM 5008
PYRIDINE 1613

RESORCINOL 5701
RIBAVIRIN 5027
ROTENONE 5007

SILICA, AMORPHOUS 7501
SILICA in coal mine dust by IR 7603
SILICA, CRYSTALLINE, Respirable, by XRD 7500
SILICA, CRYSTALLINE by VIS 7601
SILICA, CRYSTALLINE by IR 7602
STIBINE 6008
STRYCHNINE 5016

SULFUR DIOXIDE 6004
SULFUR HEXAFLUORIDE by portable GC 6602
SULFURYL FLUORIDE 6012
SUPER ABSORBENT POLYMER 5035

TERPENES 1552
Limonene, d-, l- α-pinene β-pinene 3-carene
o-TERPHENYL 5021
1,1,2,2-TETRABROMOETHANE 2003
1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and
1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE 1016
1,1,2,2-TETRACHLOROETHANE 1019
TETRAETHYL LEAD 2533
TETRAETHYL PYROPHOSPHATE (TEPP) 2504
TETRAHYDROFURAN 1609
TETRAMETHYL LEAD 2534
TETRAMETHYL THIOUREA 3505
TETRANITROMETHANE 3513
THIRAM 5005
TOLUENE (diffusive sampler) 4000
2,4- & 2,6-TOLUENEDIAMINE (TDA) 5516
TOLUENE-2,4-DIISOCYANATE (TDI) 2535
P-TOLUENESULFONIC ACID 5043
TRIBUTYL PHOSPHATE 5034
TRICHLOROETHYLENE 1022
TRICHLOROETHYLENE (portable GC) 3701
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE 1020
TRIFLUOROBROMOMETHANE 1017
TRIMELLITIC ANHYDRIDE 5036
2,4,7-TRINITROFLUOREN-9-ONE 5018
TRIORTHOCRESYL PHOSPHATE 5037
TRIPHENYL PHOSPHATE 5038
TUNGSTEN (soluble and insoluble) 7074
TURPENTINE 1551

VALERALDEHYDE 2536
VANADIUM OXIDES 7504
VINYL ACETATE 1453
VINYL BROMIDE 1009
VINYL CHLORIDE 1007
VINYLIDENE CHLORIDE 1015
VOLATILE ORGANIC COMPOUNDS (SCREENING) 2549

WARFARIN 5002

ZINC 7030
ZINC OXIDE 7502

III. APPENDIXES

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Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Acenaphthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Acenaphthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Acenaphthylene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Acenaphthylene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Acetaldehyde	2538	ACETALDEHYDE	0.01-0.05	1-12	tol	GC-FID	XAD-2/HMP
Acetaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Acetaldehyde	3507	ACETALDEHYDE	0.1-0.5	6-60	reag	HPLC-UV	BuB
Acetic acid	1603	ACETIC ACID	0.01-0.1	20-300	formic a	GC-FID	CCT
Acetic anhydride	3506	ACETIC ANHYDRIDE	0.2-1.0	25-100	reag	VIS	BuB
Acetone	1300	KETONES I	0.01-0.2	0.5-3	CS_2	GC-FID	CCT
Acetone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Acetone cyanohydrin	2506	ACETONE CYANOHYDRIN	0.2	0.3-12	Et Ac	GC-NPD	Por QS
Acetonitrile	1606	ACETONITRILE	0.01-0.2	1-25	MeCl/MeOH	GC-FID	CCT
Acetylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2-5	CS_2	GC-FID	CCT
Acetylene tetrabromide	2003	1,1,2,2-TETRABROMOETHANE	0.2-1.0	50-100	THF	GC-FID	SG
Acetylene tetrachloride	1019	1,1,2,2-TETRACHLOROETHANE	0.01-0.2	3.0-30	CS_2	GC-FID	PCT
Acids, inorganic	7903	ACIDS, INORGANIC	0.2-0.5	3.0-100	HCO_3^-/CO_3^{2-}	IC	SG(washed)
ACN	1606	ACETONITRILE	0.01-0.2	1-25	MeCl/MeOH	GC-FID	CCT lg
Acrolein	2501	ACROLEIN	0.01-0.1	1.5-48	tol	GC-NPD	XAD-2/HMP
Acrolein	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Acrylonitrile	1604	ACRYLONITRILE	0.01-0.2	3.5-20	acet/CS_2	GC-FID	CCT
Aerobic bacteria	0801	AEROBIC BACTERIA by GC-FAME	28.3	50-300	hex/MTBE	GC-FID	impactor
Alachlor	5603	ALACHLOR in AIR	1	70-1750	methanol	ELISA	SPE disk
Alachlor	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Alachlor	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Alachlor	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Aldehydes, screening	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2
Aldicarb	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Aldrin	5502	ALDRIN & LINDANE	0.2-1.0	18-240	isooct	GC-ECN	GFF & BuB
Alkaline dusts	7401	ALKALINE DUSTS	1 - 4	70-1000	HCl	Titration	PTFE
Allyl alcohol	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	GC-FID	CCT
Allyl chloride	1000	ALLYL CHLORIDE	0.01-1.0	16-100	bz	GC-FID	CCT
Allyl glycidyl ether	2545	ALLYL GLYCIDYL ETHER	0.01-0.2	1.5-8	diethyl ether	GC-FID	Tenax
Allyl trichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	2-60	CS_2	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	HNO_3+	ICP-AES	MCEF
Aluminum	7013	ALUMINUM & CPDS, as Al	1 - 3	10-400	HNO_3	FAAS	MCEF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Amines, aliphatic	2010	AMINES, ALIPHATIC	0.01-1.0	3-30	H_2SO_4/aq MeOH	GC-FID	SG
Amines, aromatic	2002	AMINES, AROMATIC	0.2-1.0	30-150	Ethanol	GC-FID	SG
Aminobenzene	2002	AMINES, AROMATIC	0.2-1.0	30-150	Ethanol	GC-FID	SG
Aminobenzene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	Ethanol	GC-FID	GFF + SG
2-Aminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4-24	MeOH/H_2O	GC-FID	SG
2-Aminoethanol	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5-300	HSA	IC	IMP
2-aminotoluene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF + SG
p-Aminophenylarsonic acid	5022	ARSENIC, ORGANO-	1 - 3	50-1000	buffer	IC-HYAAS	PTFE
2-Aminotoluene	2002	AMINES, AROMATIC	0.02-1.0	10-150	Ethanol	GC-FID	SG
Ammonia	6015	AMMONIA by VIS	0.1-0.2	0.1-90	H_2O	VIS-Auto	SG + H_2SO_4
Ammonia	6016	AMMONIA by IC	0.1-0.5	0.1-96	H_2O	IC	SG + H_2SO_4
n- and sec-Amyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Amyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Aniline	2002	AMINES, AROMATIC	0.02-0.2	5-30	Ethanol	GC-FID	SG
Aniline	2017	ANILINE, O-TOLUIDINE, & NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF+SG
Anisidine	2514	ANISIDINE	0.5-1.0	24-320	MeOH	HPLC-UV	XAD-2
Anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
p-Arsanilic acid	5022	ARSENIC, organo-	1 - 3	50-1000	buffer	IC-HYAAS	PTFE
Arsenic	7900	ARSENIC & compounds, as As	1 - 3	30-1000	HNO_3 +	HYAAS	MCEF
Arsenic	7300	ELEMENTS by ICP	1 - 4	5-2000	HNO_3 +	ICP-AES	MCEF
Arsenic trioxide	7901	ARSENIC TRIOXIDE, as As	1 - 3	30-1000	HNO_3 +	GFAAS	MCEF
Arsine	6001	ARSINE	0.01-0.2	0.1-10	HNO_3	GFAAS	CCT
Asbestos	7400	ASBESTOS FIBERS by PCM	0.5-16	400-var	NA	PCM	MCEF open
Asbestos	7402	ASBESTOS FIBERS by TEM	0.5-16	400-var	NA	TEM	MCEF open
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	eluent	HPLC-UV	PTFE
Asphalt fume	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 - 4	28-400	benzene	GRAVIMETRIC	Tared PTFE
Atrazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Atrazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Atrazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/ diazomethane	GC-ECD	PUF pad
Azelaic acid	5019	AZELAIC ACID	1 - 3	200-1000	Ethanol	GC-FID	PVC
Azinphos methyl	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12-240	tol/acet	GC-FPD	OVS-2
Bacteria	0801	AEROBIC BACTERIA by GC-FAME	28.3	50-300	hex/MTBE	GC-FID	impactor
B[a]P	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
B[a]P	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Barium	7056	BARIUM, SOLUBLE COMPOUNDS	1 - 4	50-2000	H_2O	FAAS	MCEF
Benomyl	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Benzaldehyde	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Benz[a]anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benz(a)anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD 2
Benzene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Benzene	3700	BENZENE by portable GC	> 0.02	80% vol	NA	GC	air bag
Benzene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	5-30	CS_2	GC-FID	CCT
Benzene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2-30	CS_2	GC-FID	CCT
Benzene solubles	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1-4	28	benzene	Grav	Tared PTFE
1,3-benzenediol	5701	RESORCINOL	0.2-1	5-160	methanol	GC-FID	OVS-7
Benzidine Dyes	5013	DYES	1 - 3	150-500	H_2O	HPLC-UV	PTFE
Benzidine	5509	BENZIDINE and 3,3'-DICHLORO-BENZIDINE	0.2	20-100	triethyl amine /MeOH	HPLC-UV	GFF
Benzo[a]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(a)pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD 2
Benzo[a]fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(b)fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Benzo[e]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(e)pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-ID	PTFE & XAD-2
Benzo[k]fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(k)fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-ID	PTFE & XAD-2
Benzo[ghi]perylene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(ghi)perylene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-ID	PTFE & XAD-2
Benzosulfonazole	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0-2.0	480-960	hexane	GC-SCD	PTFE + XD-2
Benzothiazole	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0-2.0	480-960	hexane	GC-SCD	PTFE + XD-2
Benzoyl peroxide	5009	BENZOYL PEROXIDE	1 - 3	40-400	diethyl ether	HPLC-UV	MCEF
Benzyl chloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	6-50	CS_2	GC-FID	CCT
Beryllium	7300	ELEMENTS by ICP	1 - 4	1250-2000	HNO_3+	ICP-AES	MCEF
Beryllium & compounds	7102	BERYLLIUM and cpds, as Be	1 - 4	25-2000	HNO_3/H_2SO_4	GFAAS	MCEF
Bioaerosol	0800	BIOAEROSOL SAMPLING (Indoor Air)	28.3	varies	NA	varies	Impactor
Biphenyl	2530	DIPHENYL	0.01-0.5	15-30	CCl_4	GC-FID	Tenax GC
Bitumen fume	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1-4	28-400	benzene	Grav	Tared PTFE
Boron carbide	7506	BORON CARBIDE	1.7 or 2.2	100-1000	ash	XRD	CYC & PVC
Boron oxide	0500	PARTICULATES N.O.R.	1.5-2.0	25-133	NA	Grav	PVC
Bromine	6011	CHLORINE and BROMINE	0.3-1.0	8-360	$Na_2S_2O_3$	IC	Ag F

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Bromoform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	4-70	CS_2	GC-FID	CCT
Bromotrifluoromethane	1017	TRIFLUOROBROMOMETHANE	0.01-0.05	0.3-1.0	CH_2Cl_2	GC-FID	2 CCT (lg+sm)
Bromoxynil	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	2-400	CH_3CN	HPLC-UV	PTFE
Bromoxynil octanoate	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	90-400	CH_3CN	HPLC-UV	PTFE
1,3-Butadiene	1024	1,3-BUTADIENE	0.01-0.5	5-25	CH_2Cl_2	GC-FID	CCT
2-Butanone	2500	METHYL ETHYL KETONE	0.01-0.2	1-12	CS_2	GC-FID	Carbon beads
2-Butanone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
2-Butoxyethyanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
2-Butoxyethanol	1403	ALCOHOLS IV	0.01-0.05	2-10	CH_2Cl_2/MeOH	GC-FID	CCT
n-, *sec*-, & *t*-Butyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Butyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Butyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
tert-Butyl alcohol	1400	ALCOHOLS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
n- & sec-Butyl alcohol	1401	ALCOHOLS II	0.01-0.2	2-10	CS_2	GC-FID	CCT
n-Butylamine	2012	*n*-BUTYLAMINE	0.01-1.0	2-100	MeOH	GC-FID	SG + H_2SO_4
Butyl cellosolve	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Butyl cellosolve	1403	ALCOHOLS IV	0.01-0.05	1-10	CH_2Cl_2/MeOH	GC-FID	CCT
1,3-Butylene glygol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Butyl glycidyl ether	1616	BUTYL GLYCIDYL ETHER	0.01-0.2	15-30	CS_2	GC-FID	CCT
n-Butyl mercaptan	2525	*n*-BUTYL MERCAPTAN	0.01-0.05	1-4	acet	GC-FPD	Chrom 104
n-Butyl mercaptan	2542	MERCAPTANS	0.1-0.2	10-150	HCl/DCE	GC-FPD	GFF/HgAc
p-*tert*-Butyltoluene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-29	CS_2	GC-FID	CCT
Butyraldehyde	2539	ALDEHYDES, SCREENING	0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Cadmium	7300	ELEMENTS by ICP	1 - 4	13-2000	HNO_3+	ICP-AES	MCEF
Cadmium & compounds	7048	CADMIUM and cpds, as Cd	1 - 3	25-1500	HNO_3/HCl	FAAS	MCEF
Calcium	7300	ELEMENTS by ICP	1 - 4	5-200	HNO_3+	ICP-AES	MCEF
Calcium & compounds	7020	CALCIUM and cpds as Ca	1 - 3	20-400	HNO_3/$HClO_4$	FAAS	MCEF
Camphor	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Capsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	5-1000	CH_3CN	HPLC-FL	GFF
Captan	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Carbaryl	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Carbaryl (Sevin)	5006	CARBARYL	1 - 3	20-400	reagent	VIS	GFF
Carbendazim	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Carbitol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Carbofuran	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Carbon black	5000	CARBON BLACK	1 - 2	30-570	NA	Grav	PVC
Carbon, elemental	5040	ELEMENTAL CARBON (DIESEL PART.)	2 - 4	142-19000	thermal	EGA/TOA	QFF
Carbon dioxide	6603	CARBON DIOXIDE	0.02-0.1	80% vol	NA	GC-TCD	air bag
Carbon disulfide	1600	CARBON DISULFIDE	0.01-0.2	2-25	toluene	GC-FPD	CCT & dry tube

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Carbon monoxide	6604	CARBON MONOXIDE	NA	NA	NA	Sensor	Port Instr
Carbon tetrachloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	3-150	CS_2	GC-FID	CCT
δ-3-Carene	1552	TERPENES	0.01-0.02	2-30	CS_2	GC-FID	CCT
Chlordane	5510	CHLORDANE	0.5-1.0	10-200	tol	GC-ECD	MCEF & Chrom 102
Chlorinated camphene	5039	CHLORINATED CAMPHENE	0.2-1	2-30	pet ether	GC-ECD	MCEF
Chlorinated diphenyl oxide	5025	CHLORINATED DIPHENYL OXIDE	0.5-1.5	8-200	isooctane	GC-ECN	MCEF
Chlorinated terphenyl	5014	CHLORINATED TERPHENYL	1 - 3	100-1500	isooctane	GC-ECD	GFF
Chlorine	6011	CHLORINE and BROMINE	0.3-1.0	2-90	$Na_2S_2O_3$	IC	Ag F
Chloroacetaldehyde	2015	CHLOROACETALDEHYDE	0.05-0.2	3-16	MeOH	GC-ECD	SG
Chloroacetic acid	2008	CHLOROACETIC ACID	0.05-0.2	1-100	H_2O	IC	SG
Chlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1.5-40	CS_2	GC-FID	CCT
Chlorobromomethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5-8	CS_2	GC-FID	CCT
Chlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2CCT (lg+sm)
Chlorodiphenyl (42 & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05-0.2	1-50	hexane	GC-ECD	GFF & Florisil
2-Chloroethanol	2513	ETHYLENE CHLOROHYDRIN	0.01-0.2	2-35	IPA/CS_2	GC-FID	PCT
Chloroform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1-50	CS_2	GC-FID	CCT
4-Chloronitrobenzene	2005	NITROAROMATIC COMPOUNDS	0.01-1.0	1-150	MeOH	GC-FID	SG
p-Chlorophenol	2014	*p-CHLOROPHENOL*	0.05-0.2	1.5-40	CH_3CN	HPLC-UV	SG
Chloroprene	1002	β-CHLOROPRENE	0.01-0.1	1.5-8	CS_2	GC-FID	CCT
Chlorpropham	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Chlorpyrifos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12-240	tol/acet	GC-FPD	OVS-2
Chromic acid	7600	CHROMIUM, HEXAVALENT	1 - 4	8-400	reagent	VIS	PVC
Chromic acid	7604	CHROMIUM, HEXAVALENT	1 - 4	100-1000	NaOH/Na_2CO_3	IC	PVC
Chromium	7024	CHROMIUM and cpds, as Cr	1 - 3	10-1000	HCl/HNO_3	FAAS	MCEF
Chromium	7300	ELEMENTS by ICP	1 - 4	5-1000	HNO_3+	ICP-AES	MCEF
Chromium, hexavalent	7600	CHROMIUM, HEXAVALENT	1 - 4	8-400	reagent	VIS	PVC
Chromium, hexavalent	7604	CHROMIUM, HEXAVALENT	1 - 4	100-1000	NaOH/Na_2CO_3	IC	PVC
Chromium, hexavalent	9101	CHROMIUM, HEXAVALENT in settled dust	NA	NA	NA	Spot	Test strip
Chrysene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Chrysene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Coal tar naphtha	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Coal tar pitch volatiles	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1-4	28-400	benzene	Grav	tared PTFE
Cobalt	7300	ELEMENTS by ICP	1 - 4	25-2000	HNO_3+	ICP-AES	MCEF
Cobalt & compounds	7027	COBALT and cpds, as Co	1 - 3	30-1500	aq reg/HNO_3	FAAS	MCEF
Copper	7300	ELEMENTS by ICP	1 - 4	5-1000	HNO_3+	ICP-AES	MCEF
Copper (dust & fume)	7029	COPPER (dust & fumes)	1 - 3	50-1500	HNO_3/HCl	FAAS	MCEF
Cresol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Cresol, all isomers	2546	CRESOLS and PHENOL	0.01-0.1	1-24	MeOH	GC-FID	XAD-7
Crotonaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Crotonaldehyde	3516	CROTONALDEHYDE	0.1-0.2	1-49	buffer	DPP	BuB
Cryofluorane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE, & CHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2 CCT
Cumene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-30	CS_2	GC-FID	CCT
Cyanides	7904	CYANIDES, aerosol and gas	0.5-1.0	10-180	KOH	ISE	MCEF & BuB
Cyanides	6010	HYDROGEN CYANIDE	0.05-0.2	0.6-90	H_2O	VIS	soda lime
Cyanuric acid	5030	CYANURIC ACID	1 - 3	10-1000	reagents	HPLC-UV	PVC
Cyanazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Cyanazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Cyanazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Cyclohexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2.5-5	CS_2	GC-FID	CCT
Cyclohexanol	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	CG-FID	CCT
Cyclohexanone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Cyclohexanone	1300	KETONES I	0.01-0.2	1-10	CS_2	CG-FID	CCT
Cyclohexene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	5-7	CS_2	CG-FID	CCT
1,3-Cyclopentadiene	2523	1,3-CYCLOPENTADIENE	0.01-0.05	1-5	Et Ac	GC-FID	Chrom104/ maleic anhy
2,4-D	5001	2,4-D and 2,4,5-T	1 - 3	15-200	MeOH	HPLC-UV	GFF
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC-ECD	OVS-2
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
n-Decane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Demeton	5514	DEMETON	0.2-1.0	30-500	toluene	GC-FPD	MCEF &XAD 2
Diacetone alcohol	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	GC-FID	CCT
o-Dianisidine	5013	DYES	1 - 3	150-500	H_2O	HPLC-UV	PTFE
Diatomaceous earth	7501	SILICA, AMORPHOUS	1 - 3	50-400	ash	XRD	PVC/CYC
Diazinon	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	toluene/acetone	GC-FPD	OVS-2
Diazomethane	2515	DIAZOMETHANE	0.2	6-30	CS_2	GC-FID	XAD-2(coated)
Dibenz[a,h]anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Dibenz(a,h) anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Diborane	6006	DIBORANE	0.5-1.0	60-260	H_2O_2	PES	PTFE & CCT w/oxidizer
Dibromodifluoromethane	1012	DIFLUORODIBROMOMETHANE	0.01-0.2	2.5-10	IPA	GC-FID	2 CCT
2-Dibutylaminoethanol	2007	AMINOETHANOL COMPOUNDS	0.01-0.2	4-24	MeOH/H_2O	GC-FID	SG

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Dibutyl phosphate	5017	DIBUTYL PHOSPHATE	1-3	50-250	CH_3CN	GC-FPD	PTFE
Dibutyl phthalate	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	1-3	6-200	CS_2	GC-FID	MCEF
Dibutyltin bis(isooctyl mercaptoacetate)	5504	ORGANOTIN COMPOUNDS	1-1.5	50-500	Acetic a/CH_3CN	HPLC/GFAAS	GFF + XAD 2
o-, p-Dichlorobenzene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	varies	TD/GC-MS	TD
o-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1-60	CS_2	GC-FID	CCT
p-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1-10	CS_2	GC-FID	CCT
3,3'-Dichlorobenzidine	5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE	0.2	20-100	TEA/MeOH	HPLC-UV	GFF
Dichlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
1,1-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5-15	CS_2	GC-FID	CCT
1,2-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.5-50	CS_2	GC-FID	CCT
Dichloroethyl ether	1004	DICHLOROETHYL ETHER	0.01-1.0	2-15	CS_2	GC-FID	CCT
1,2-Dichloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2-5	CS_2	GC-FID	CCT
Dichlorofluoromethane	2516	DICHLOROFLUOROMETHANE	0.01-0.05	0.25-3	CS_2	GC-FID	2 CCT (lg)
Dichloromethane	1005	METHYLENE CHLORIDE	0.01-0.2	0.5-2.5	CS_2	GC-FID	2 CCT
Dichloromethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
1,1-Dichloro-1-nitroethane	1601	1,1-DICHLORO-1-NITROETHANE	0.01-1.0	1.5-15	CS_2	GC-FID	PCT
1,2-Dichloropropane	1013	PROPYLENE DICHLORIDE	0.01-0.2	0.1-3.5	Acet/cyclohexane	GC-ECN	PCT
1,2-Dichlorotetra-fluoroethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
Dicrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Diesel exhaust	5040	ELEMENTAL CARBON (DIESEL PART.)	1 - 4	142-19000	thermal	EGA/TOA	QFF
Diethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5-300	HSA	IC	IMP
Diethylamine	2010	AMINES, ALIPHATIC	0.01-1.0	3-30	H_2SO_4/MeOH	GC-FID	SG
2-Diethylaminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4-24	MeOH/H_2O	GC-FID	SG
Diethylene glycol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS 7
Diethylene glycol ether	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC MS	TD
Diethylenetriamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1-20	DMF	HPLC-UV	XAD-2 w/10% NITC
Di-(2-ethylhexyl) phthalate	5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE	1 - 3	10-200	CS_2	GC-FID	MCEF
Difluorodibromomethane	1012	DIFLUORODIBROMOMETHANE	0.01-0.2	2.5-10	IPA	GC-FID	2 CCT
Difluorodichloromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2 CCT
Dihydrocapsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	7-1000	CH_3CN	HPLC-FL	GFF
Diisobutyl ketone	1300	KETONES I	0.01-0.2	1-10	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Dimethylacetamide	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	0.01-1.0	15-80	MeOH	GC-FID	SG
Dimethylamine	2010	AMINES, ALIPHATIC	0.01-1.0	3-30	H_2SO_4/MeOH	GC-FID	SG
N,N-Dimethylaniline	2002	AMINES, AROMATIC	0.02-1.0	3-30	Ethanol	GC-FID	SG
Dimethylarsinic acid	5022	ARSENIC, ORGANO-	1 - 3	50-1000	buffer	IC-HYAAS	PTFE
Dimethylformamide	2004	DIMETHYLACETAMIDE & DIMETHYLFORMAMIDE	0.01-1.0	15-80	MeOH	GC-FID	SG
1,1-Dimethylhydrazine	3515	1,1-DIMETHYLHYDRAZINE	0.2-1.0	2-100	reagent	VIS	BuB (0.1 *M* HCl)
N,N-Dimethyl-*p*-toluidine	2002	AMINES, AROMATIC	0.02-1.0	20-100	Ethanol	GC-FID	SG
Dimethyl sulfate	2524	DIMETHYL SULFATE	0.01-0.2	0.25-12	diEt ether	GC-ECN	Por P
Dioxane	1602	DIOXANE	0.01-0.2	0.5-15	CS_2	GC-FID	CCT
Diphenyl	2530	DIPHENYL	0.01-0.5	15-30	CCl_4	GC-FID	Tenax GC
Disulfoton	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Diuron	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Dyes- benzidine-, o-tolidine-, o-dianisidine-	5013	DYES, BENZIDINE-, o- TOLIDINE- o- DIANISIDINE	1 - 3	150-500	H_2O	HPLC-UV	PTFE
Elemental carbon	5040	ELEMENTAL CARBON (DIESEL PART.)	2 - 4	142-19000	thermal	EGA-TOA	QFF
Elements	7300	ELEMENTS by ICP	1 - 4	Varies	HNO_3+	ICP-AES	MCEF
Endrin	5519	ENDRIN	0.5-1.0	12-400	tol	GC-ECD	MCEF & Chrom 102
Epichlorohydrin	1010	EPICHLOROHYDRIN	0.01-0.2	2-30	CS_2	GC-FID	CCT
EPN	5012	EPN	1 - 2	15-700	isooctane	GC-FPD	GFF
1,2-Epoxypropane	1612	PROPYLENE OXIDE	0.01-0.2	0.5-5	CS_2	GC-FID	CCT
Ethanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Ethanol	1400	ALCOHOLS I	0.01-0.05	0.1-1	2-butanol/CS_2	GC-FID	CCT
Ethanolamine	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4-24	5600	GC-FID	SG
Ethion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Ethoprop	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
2-Ethoxyethanol	1403	ALCOHOLS IV	0.01-0.05	1-6	MeOH	GC-FID	CCT
2-Ethoxyethyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Ethyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Ethyl acetate	1457	ETHYL ACETATE	0.01-0.2	0.1-10	CS_2	GC-FID	CCT
Ethyl acrylate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Ethyl amyl ketone	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Ethylbenzene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-24	CS_2	GC-FID	CCT
Ethyl bromide	1011	ETHYL BROMIDE	0.01-0.2	0.5-4	IPA	GC-FID	CCT
Ethyl butyl ketone	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Ethyl chloride	2519	ETHYL CHLORIDE	0.02-0.05	0.3-3	CS_2	GC-FID	2 CCT (lg)
Ethylene chlorohydrin	2513	ETHYLENE CHLOROHYDRIN	0.01-0.2	2-35	IPA/CS_2	GC-FID	PCT
Ethylenediamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1-20	DMF	HPLC-UV	XAD-2 w/10% NITC
Ethylene dibromide	1008	ETHYLENE DIBROMIDE	0.02-0.2	0.1-25	bz/MeOH	GC-ECD	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Ethylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1-50	CS_2	GC-FID	CCT
Ethylene glycol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Ethylene glycol dinitrate	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2-1.0	3-100	Ethanol	GC-ECD	Tenax GC
Ethylene oxide	1614	ETHYLENE OXIDE	0.05-0.15	1-24	DMF	GC-ECD	PCT w/HBr
Ethylene oxide	3702	ETHYLENE OXIDE by portable GC	> 0.02	80% vol	NA	GC-PID	air bag
Ethylene thiourea	5011	ETHYLENE THIOUREA	1 - 3	200-800	H_2O	VIS	PVC or MCEF
Ethylenimine	3514	ETHYLENIMINE	0.2	1-48	$CHCl_3$	HPLC-UV	BuB
Ethyl ether	1610	ETHYL ETHER	0.01-0.2	0.25-3	Et Ac	GC-FID	CCT
Ethyl formate	1452	ETHYL FORMATE	0.01-0.2	0.3-10	CS_2	GC-FID	CCT
Ethyl mercaptan	2542	MERCAPTANS	0.1-0.2	10-150	HCl/DCE	GC-FPD	GFF/HgAc
Fenamiphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Fibrous glass	7400	ASBESTOS & other FIBERS by PCM	0.5-16	400-varies		PCM	MCEF
Fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Fluorene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Fluorene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Fluorides	7902	FLUORIDES, aerosol & gas	1 - 2	12-800	NaOH	ISE	MCEF & pad w/ Na_2CO_3
Fluorides	7906	FLUORIDES by IC	1 - 2	s 1-800 i 120-800	NaOH	IC	MCEF & pad w/ Na_2CO_3
Fluorotrichloromethane	1006	FLUOROTRICHLOROMETHANE	0.01-0.05	0.3-7	CS_2	GC-FID	CCT (lg)
Fonofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12-240	tol/acet	GC-FPD	OVS-2
Formaldehyde	2016	FORMALDEHYDE	0.1-1.5	1-15	acetonitrile	HPLC-UV	SG/DNPH
Formaldehyde	2541	FORMALDEHYDE	0.01-0.1	1-36	tol	GC-FID	XAD-2/HMP
Formaldehyde	3500	FORMALDEHYDE	0.2-1.0	1-100	$NaHSO_3$	VIS	PTFE & 2 IMP
Formaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Formaldehyde	5700	FORMALDEHYDE on dust	2	240-1050	H_2O/DNPH/CH_3CN	HPLC-UV	IOM/PVC
Formetanate.HCl	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Formic acid	2011	FORMIC ACID	0.05-0.2	1-24	H_2O	IC	PTFE & SG (washed)
Furfural	2529	FURFURAL	0.01-0.05	1-12	tol	GC-FID	XAD-2/HMP
Furfural	2539	ALDEHYDES, SCREENING	0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Furfuryl alcohol	2505	FURFURYL ALCOHOL	0.01-0.05	3-25	acet	GC-FID	Por Q
Glutaraldehyde	2532	GLUTARALDEHYDE	0.01-0.08	4-39	CH_3CN	HPLC-UV	SG/DNPH
Glycerin mist	0500	PARTICULATES N.O.R.	1 - 2	7-133	NA	Grav	PVC
Glycidol	1608	GLYCIDOL	0.01-1.0	5-100	THF	GC-FID	CCT
Glycols	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Heptanal	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
n-Heptane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
n-Heptane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4-4	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Herbicides	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Herbicides	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Herbicides	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Hexachlorobutadiene	2543	HEXACHLOROBUTADIENE	0.05-0.2	1-100	hexane	GC-ECD	XAD-2
Hexachloro-1,3-cyclo pentadiene	2518	HEXACHLORO-1,3-CYCLOPENTA DIENE	0.01-0.2	0.25-90	hexane	GC-ECD	2 Por T
Hexachloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	3-70	CS_2	GC-FID	CCT
Hexamethylene-diisocyanate	5522	ISOCYANATES	1 - 2	15-360	tryptamine/DMSO	HPLC-FL	IMP
Hexamethylene-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5-500	reagents	HPLC-ECHD	IMP
Hexanal	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Hexanal	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
n-Hexane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
n-Hexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4-4	CS_2	GC-FID	CCT
2-Hexanone	1300	KETONES I	0.01-1.0	1-10	CS_2	GC-FID	CCT
Hydrazine	3503	HYDRAZINE	0.2-1.0	7-100	reagents	VIS	BuB
Hydrogen bromide	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_4^{2-}	IC	SG
Hydrogen chloride	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_4^{2-}	IC	SG
Hydrogen cyanide	6010	HYDROGEN CYANIDE	0.05-0.2	2-90	H_2O	VIS	soda lime
Hydrogen cyanide	7904	CYANIDES, AEROSOL & GAS	0.5-1.0	7-100	KOH	ISE	MCEF
Hydrogen flouride	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_4^{2-}	IC	SG
Hydrogen flouride	7902	FLUORIDES, AEROSOL & GAS	1 - 2	12-800	NaOH	ISE	MCEF & pad w/Na_2CO_3
Hydrogen flouride	7906	FLUORIDES by IC	1 - 2	1-800	NaOH	IC	MCEF & pad w/Na_2CO_3
Hydrogen sulfide	6013	HYDROGEN SULFIDE (withdrawn)	0.1-1.5	1.2-40	NH_4OH/H_2O_2	IC	PTFE & CCT (ig)
Hydroquinone	5004	HYDROQUINONE	1 - 4	30-180	acetic a	HPLC-UV	MCEF
Indeno[1,2,3-cd]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Indeno [1,2,3-cd] pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Iodine	6005	IODINE	0.5-1.0	15-225	Na_2CO_3	IC	CCT w/alkali
Iron	7300	ELEMENTS by ICP	1 - 4	5-100	HNO_3+	ICP-AES	MCEF
Isoamyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Isoamyl alcohol	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	GC-FID	CCT
Isobutyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Isobutyl alcohol	1401	ALCOHOLS II	0.01-0.2	2-10	IPA/CS_2	GC-FID	CCT
Isobutyraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Isocyanates	5521	ISOCYANATES, MONOMERIC	1.0	5-500	reagents	HPLC-ECHD	IMP
Isocyanates	5522	ISOCYANATES	1 - 2	15-360	tryptamine/DMSO	HPLC-FL/ECHD	IMP

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Isophorone	2508	ISOPHORONE	0.01-1.0	2-25	CS_2	GC-FID	PCT
Isopropyl acetate	1454	ISOPROPYL ACETATE	0.02-0.2	0.1-9	CS_2	GC-FID	CCT
Isopropyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Isopropyl alcohol	1400	ALCOHOLS I	0.01-0.2	0.2-3	2-butanone/CS_2	GC-FID	CCT
Isopropyl ether	1618	ISOPROPYL ETHER	0.01-0.05	0.1-3	CS_2	GC-FID	CCT
Isopropyl glycidyl ether	1620	ISOPROPYL GLYCIDYL ETHER	0.01-0.2	1-30	CS_2	GC-FID	CCT
Isovaleraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Kepone	5508	KEPONE	0.5-1.0	50-600	bz/MeOH	GC-ECD	MCEF & IMP
Kerosene	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC FID	CCT
Lead	7082	LEAD by FAAS	1 - 4	200-1500	HNO_3/H_2O_2	FAAS	MCEF
Lead	7702	LEAD BY FIELD PORTABLE XRF	1-4	570-1900	NA	XRF (port)	MCEF
Lead	7105	LEAD by GFAAS	1 - 4	1-1500	HNO_3/H_2O_2	GFAAS	MCEF
Lead	7701	LEAD BY ULTRASOUND/ASV	1-4	20-1500	HNO_3	Port ASV	MCEF
Lead	7300	ELEMENTS by ICP	1 - 4	1250-2000	HNO_3+	ICP AES	MCEF
Lead	7700	LEAD in Air by Chemical Spot Test	2	10-240	-	Spot	MCEF
Lead	9100	LEAD in Surface Wipe Samples	NA	NA	HNO_3+	AAS; ICP	Wipes
Lead sulfide	7505	LEAD SULFIDE	1.7 or 2.2	600-1000	THF	XRD	CYC & PVC
Limonene	1552	TERPENES	0.01-0.2	2-30	CS_2	GC-FID	CCT
Limonene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Lindane	5502	ALDRIN and LINDANE	0.2-1.0	18-240	isooctane	GC-ECN	GFF & BuB
Lithium	7300	ELEMENTS by ICP	1 - 4	100-2000	HNO_3+	ICP-AES	MCEF
Lithium hydroxide	7401	ALKALINE DUSTS	1 - 4	70-1000	HCl	Titration	PTFE
Magnesium	7300	ELEMENTS by ICP	1 - 4	5-67	HNO_3+	ICP-AES	MCEF
Malathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-60	tol/acet	GC-FPD	OVS-2
Maleic Anhydride	3512	MALEIC ANHYDRIDE	0.2-1.5	40-500	H_2O	HPLC-UV	BuB
Manganese	7300	ELEMENTS by ICP	1 - 4	5-200	HNO_3+	ICP-AES	MCEF
MBK	1300	KETONES I	0.01-0.2	1-10	CS_2	GC-FID	CCT
MDI (4,4'-methylene-bisphenyl isocyanate)	5521	ISOCYANATES, MONOMERIC	1.0	5-500	reagents	HPLC-ECHD	IMP
MDI (4,4'-methylene-bisphenyl isocyanate)	5522	ISOCYANATES	1 - 2	15-360	tryptamine	HPLC-FL/ECHD	IMP
Mercury	6009	MERCURY	0.15-0.25	2-100	HNO_3/HCl	AAS-cold vap	Hopcalite
Mercaptans	2542	MERCAPTANS	0.1-0.2	10-150	HCl/DCE	GC-FPD	GFF/HgAc
Mesityl oxide	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Metals in air	7300	ELEMENTS by ICP	1 - 4	var-2000	HNO_3+	ICP-AES	MCEF
Methanal	2016	FORMALDEHYDE	0.1-1.5	1-15	acetonitrile	HPLC-UV	SG/DNPH
Methamidophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Methanol	2000	METHANOL	0.02-0.2	1-5	H_2O/IPA	GC-FID	SG
Methanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Methiocarb	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Methomyl	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Metolachlor	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Metolachlor	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Metolachlor	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
2-Methoxyethyl acetate	1451	METHYL CELLOSOLVE ACETATE	0.01-0.2	0.2-20	CS_2	GC-FID	CCT
2-Methoxyethanol	1403	ALCOHOLS IV	0.01-0.05	6-50	MeOH/CH_2Cl_2	GC-FID	CCT
Methyl acetate	1458	METHYL ACETATE	0.01-0.2	0.2-10	CS_2	GC-FID	CCT
Methyl acrylate	1459	METHYL ACRYLATE	0.01-0.2	1-5	CS_2	GC-FID	CCT
Methyl alcohol	2000	METHANOL	0.02-0.2	1-5	H_2O/IPA	GC-FID	SG
Methylal	1611	METHYLAL	0.01-0.2	1-3	hexane	GC-FID	CCT
4-Methylbenzenesulfonic acid	5043	*p*-TOLUENESULFONIC ACID	1-3	10-1000	IPA/H_2O	HPLC-UV	GFF
N-Methyl-γ-butyrolactone	1302	*N*-METHYL-2-PYRROLIDINONE	0.05-0.2	0.5-125	CH_2Cl_2/MeOH	GC-NPD or FID	CCT
Methyl-(n-amyl)-ketone	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Methylarsonic acid	5022	ARSENIC, ORGANO-	1 - 3	50-1000	buffer	IC-HYAAS	PTFE
Methyl bromide	2520	METHYL BROMIDE	0.01-0.1	1-5	CS_2	GC-AED	PCT(2)+drytube
Methyl cellosolve	1403	ALCOHOLS IV	0.01-0.05	6-50	MeOH/CH_2Cl_2	GC-FID	CCT
Methyl cellosolve acetate	1451	METHYL CELLOSOLVE ACETATE	0.01-0.2	0.2-20	CS_2	GC-FID	CCT
Methyl chloride	1001	METHYL CHLORIDE	0.01-0.1	0.4-3	CH_2Cl_2	GC-FID	2 CCT (lg+sm)
Methyl chloroform	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.1-8	CS_2	GC-FID	CCT
Methyl chloroform	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Methyl cyanide	1606	ACETONITRILE	0.01-0.2	3-25	MECl/MEOH	GC-FID	CCT
Methyl cyclohexane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4-4	CS_2	GC-FID	CCT
Methylcyclohexanol	1404	METHYLCYCLOHEXANOL	0.01-0.2	1-15	CH_2Cl_2	GC-FID	CCT
Methylcyclohexanone	2521	METHYLCYCLOHEXANONE	0.01-0.05	1-6	acet	GC-FID	Por Q
Methylene chloride	1005	METHYLENE CHLORIDE	0.01-0.2	0.5-2.5	CS_2	GC-FID	2 CCT
Methylene chloride	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
4,4'-Methylenedianiline	5029	4,4'-METHYLENEDIANILINE	1 - 2	10-1000	KOH/MeOH	HPLC-UV	GFF/H_2SO_4
4,4-Methylene diphenyl diisocyanate	5522	ISOCYANATES	1 - 2	15-360	tryptamine	HPLC-FL/ECHD	IMP
Methyl ethyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Methyl ethyl ketone	2500	METHYL ETHYL KETONE	0.01-0.2	0.25-12	CS_2	GC-FID	Carbon beads
Methyl ethyl ketone peroxide	3508	METHYL ETHYL KETONE PEROXIDE	0.5-0.2	52-520	reagent	VIS	IMP
5-Methyl-3-heptanone	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
Methyl iodide	1014	METHYL IODIDE	0.01-1.0	15-50	tol	GC-FID	CCT
Methyl isoamyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
Methyl isobutyl carbinol	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	GC-FID	CCT
Methyl isobutyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Methyl isobutyl ketone	1300	KETONES I	0.01-0.2	1-10	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Methyl mercaptan	2542	MERCAPTANS	0.1-0.2	10-150	HCl/DCE	GC-FPD	GFF/HgAc
Methyl methacrylate	2537	METHYL METHACRYLATE	0.01-0.05	1-8	CS_2	GC-FID	XAD-2
Methyl parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Methyl phenol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
N-methyl-2-pyrrolidinone	1302	*N*-METHYL-2-PYRROLIDINONE	0.05-0.2	0.5-125	CH_2Cl_2/MeOH	GC-NPD or FID	CCT
α-Methyl styrene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-30	CS_2	GC-FID	CCT
Methyl *tert*-butyl ether	1615	METHYL *tert*-BUTYL ETHER	0.1-0.2	2-96	CS_2	GC-FID	2 CCT (lg)
Mevinphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12-240	tol/acet	GC-FPD	OVS-2
Mineral spirits	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Molybdenum	7300	ELEMENTS by ICP	1 - 4	5-67	HNO_3+	ICP-AES	MCEF
Monocrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS 2
Monomethylaniline	3511	MONOMETHYLANILINE	0.2-1.0	11-100	NaOH	GC-FID	BuB/H_2SO_4
Monomethylhydrazine	3510	MONOMETHYLHYDRAZINE	0.5-1.5	3-20	PMA/HCl	VIS	BuB/HCl
Mycobacterium	0900	MYCOBACTERIUM TUBERCULOSIS	>4	varies	PCR	reagent	PTFE
Naphtha (coal tar)	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Naphthalene	1501	HYDROCARBONS, AROMATIC	0.01-1.0	100-200	CS_2	GC-FID	CCT
Naphthalene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Naphthalene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Naphthylamines	5518	NAPHTHYLAMINES	0.2-0.8	30-100	acetic a /IPA	GC-FID	GFF & SG
Nickel	7300	ELEMENTS by ICP	1 - 4	25-1000	HNO_3+	ICP-AES	MCEF
Nickel carbonyl	6007	NICKEL CARBONYL	0.05-0.2	7-80	HNO_3	GFAAS	CCT (low Ni)
Nicotine	2544	NICOTINE	1.0	60-400	EtAc	GC-NPD	XAD-2
Nicotine	2551	NICOTINE	0.1-1.0	0.5-600	ethyl acetate	GC-NPD	XAD-4
Nitric acid	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_3^{2-}	IC	SG (washed)
Nitric oxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025	1.5-6	reagent	VIS	MS w/TEA & oxidizer
p-Nitroaniline	5033	*p*-NITROANILINE	1 - 3	20	IPA	HPLC-UV	MCEF
Nitrobenzene	2005	NITROAROMATIC COMPOUNDS	0.01-1	10-150	MeOH	GC-FID	SG
Nitrobenzene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF + SG
Nitrobenzol	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF + SG
p-Nitrochlorobenzene	2005	NITROAROMATIC COMPOUNDS	0.01-1	1-150	MeOH	GC-FID	SG
Nitroethane	2526	NITROETHANE	0.01-0.05	1.5-3	EtAc	GC-FID	2XAD-2
Nitrogen dioxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025-0.2	1.5-6	reagent	VIS	MS w/TEA
Nitrogen dioxide	6700	NITROGEN DIOXIDE	NA	NA	reagent	VIS	Diffusive
Nitrogen peroxide	6700	NITROGEN DIOXIDE	NA	NA	reagent	VIS	Diffusive
Nitroglycerin	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2-1.0	3-100	ethanol	GC-ECD	Tenax-GC
Nitromethane	2527	NITROMETHANE	0.01-0.05	1.2-3	EtAc	GC-FPD	Chrom 106
2-Nitropropane	2528	2-NITROPROPANE	0.01-0.05	0.1-2	EtAc	GC-FID	Chrom 106
Nitrosamines	2522	NITROSAMINES	0.2-2.0	15-1000	MeOH/CH_2Cl_2	GC-TEA	TD tube

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
o-,*m*-, *p*-Nitrotoluene	2005	NITROAROMATIC COMPOUNDS	0.01-0.2	1-30	MeOH	GC-FID	SG
Nitrous oxide	6600	NITROUS OXIDE	NA	80% vol	NA	IR	air bag
NMP	1302	N-Methyl-2-Pyrrolidinone	0.05-0.2	0.5-125	CH_2Cl_2/MeOH	GC-FID/NPD	CCT
Nuisance dusts	0500	PARTICULATES N.O.R.	1 - 2	7-133	NA	GRAV	PVC
n-Octane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
n-Octane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4-4	CS_2	GC-FID	CCT
Octamethylcyclotetra-siloxane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
1-Octanethiol	2510	1-OCTANETHIOL	0.01-0.2	1-15	acet	GC-FPD	Tenax GC
Oil mist (mineral)	5026	OIL MIST, MINERAL	1 - 3	20-500	CCl_4	IR	PVC or MCE
Organonitrogen pesticides	5601	ORGANONITROGEN PESTICIDES	0.1-1	varies-480	reagent	HPLC-UV	OVS-2
Organophosphorus Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Oxamyl	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Oxygen	6601	OXYGEN	NA	1-NA	NA	Sensor	portable
PAC	5800	POLY AROMATIC COMPOUNDS, TOTAL (PACs)	1-2	5-1000	hexane	FI-FL	PTFE + XAD-2
Paraquat	5003	PARAQUAT	1 - 4	40-1000	H_2O	HPLC-UV	PTFE
Parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1.0	12-240	tol/acet	GC-FPD	OVS-2
Particulates N.O.R.	0500	PARTICULATES N.O.R., TOTAL	1 - 2	7-133	NA	GRAV	PVC
Particulates N.O.R.	0600	PARTICULATES, N.O.R, RESPIRABLE	1.7, 2.2, 2.5	20-400	NA	Grav.	CYC & PVC
Pentachlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3-12	hexane	GC-ECD	PTFE & XAD-2
Pentachloroethane	2517	PENTACHLOROETHANE	0.01-0.2	1-10	hexane	GC-ECD	Por R
Pentachlorophenol	5512	PENTACHLOROPHENOL	0.5-1.0	48-480	MeOH	HPLC-UV	MCEF & BuB
Pentamidine	5032	PENTAMIDINE ISETHIONATE	1 - 2	50-1500	reagents	HPLC/FL	PVC/opaque
n-Pentane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
n-Pentane	1500	HYDROCARBONS, BP 36-126°C	0.01-0.05	2-2	CS_2	GC-FID	CCT
2-Pentanone	1300	KETONES I	0.01-2.0	1-10	CS_2	GC-FID	CCT
Perchloroethylene	3704	PERCHLOROETHYLENE (port GC) in exhaled breath and air	0.02-5	<80% cap	NA	GC (port)-PID	air bag
Perchloroethylene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Pesticides	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
Petroleum ether/naphtha	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Phenanthrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Phenanthrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD 2
Phenol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Phenol	2546	CRESOLS and PHENOL	0.01-0.1	1-24	MeOH	GC-FID	XAD-7
Phenyl ether	1617	PHENYL ETHER	0.01-0.2	1-50	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Phenyl ether-diphenyl mixture	2013	PHENYL ETHER-DIPHENYL MIXTURE	0.01-0.2	1-40	bz	GC-FID	SG
Phenyl glycidyl ether	1619	PHENYL GLYCIDYL ETHER	0.01-1	80-150	CS_2	GC-FID	CCT
Phenylhydrazine	3518	PHENYLHYDRAZINE	0.2-1.0	25-120	PMA	VIS	BuB/HCl
Phorate	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Phosdrin (mevinphos)	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-480	tol/acet	GC-FPD	OVS-2
Phosphine	6002	PHOSPHINE	0.01-0.2	1-16	reagent	VIS	SG/$Hg(CN)_2$
Phosphoric acid	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_3^{2-}	IC	SG (washed)
Phosphorus	7300	ELEMENTS by ICP	1 - 4	50-2000	HNO_3+	ICP-AES	MCEF
Phosphorus	7905	PHOSPHORUS	0.01-0.2	5-100	xylene	GC-FPD	Tenax GC
Phosphorus trichloride	6402	PHOSPHORUS TRICHLORIDE	0.05-0.2	11-100	reagents	VIS	BuB/H_2O
Pinene	1552	TERPENES	0.01-0.2	2-30	CS_2	GC-FID	CCT
Pinene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Platinum	7300	ELEMENTS by ICP	1 - 4	13-2000	HNO_3+	ICP-AES	MCEF
PAH	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	HPLC-FL/UV	PTFE & XAD-2
Polyacrylate	5035	SUPER ABSORBENT POLYMER	1 - 2	50-1500	$Cu(Ac)_2$	ICP or AAS	PVC
PACs	5800	POLYCYCLIC AROMATIC COMPOUNDS, TOTAL	1 - 2	5-1000	hexane	FI-FL	
Polychlorobiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05-0.2	1-50	hexane	GC-ECD	GFF & Florisil
Potassium hydroxide	7401	ALKALINE DUSTS	1 - 4	70-1000	HCl	titration	PTFE
Propham	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Propionaldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2/HMP
Propoxur	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
n-Propyl acetate	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
n-Propyl alcohol	1401	ALCOHOLS II	0.01-0.2	1-10	IPA/CS_2	GC-FID	CCT
Propylene dichloride	1013	PROPYLENE DICHLORIDE	0.01-0.2	0.1-3.5	acet/cychex	GC-ECN	PCT
Propylene glycol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Propylene oxide	1612	PROPYLENE OXIDE	0.01-0.2	0.5-5	CS_2	GC-FID	CCT
Pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
Pyrethrum	5008	PYRETHUM	1 - 4	20-400	CH_3CN	HPLC-UV	GFF
Pyridine	1613	PYRIDINE	0.01-1.0	18-150	CH_2Cl_2	GC-FID	CCT
Resorcinol	5701	RESORCINOL	0.2-1	5-160	MeOH	GC-FID	OVS-7
Ribavirin	5027	RIBAVIRIN	1 - 4	5-1000	H_2SO_4	HPLC-UV	GFF
Ronnel	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-60	tol/acet	GC-FPD	OVS-2
Rotenone	5007	ROTENONE	1 - 4	8-400	CH_3CN	HPLC-UV	PTFE
Rubber solvent	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Selenium	7300	ELEMENTS by ICP	1 - 4	5-2000	HNO_3+	ICP-AES	MCEF
Silica, amorphous	7501	SILICA, AMORPHOUS	1.7 or 2.2	50-400	ash	XRD	PVC (total) PVC&CYC

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Silica, crystalline	7500	SILICA, CRYSTALLINE, by XRD.	1.7, 2.2, 2.5	400-1000	ash or THF	XRD	CYC & PVC
Silica, crystalline	7601	SILICA, CRYSTALLINE	1.7, 2.2, 2.5	400-800	H_3PO_4/HF	VIS	CYC & MCE or PVC
Silica, crystalline	7602	SILICA, CRYSTALLINE (IR)	1.7, 2.2, 2.5	400-800	ash	IR	CYC & MCE or PVC
Silicon dioxide	7500	SILICA, CRYSTALLINE, by XRD.	1.7, 2.2, 2.5	400-1000	ash or THF	XRD	CYC & PVC
Silica in coal mine dust	7603	SILICA in coal mine dust	1.7, 2.2, 2.5	300-1000	ash	IR	CYC & PVC
Silver	7300	ELEMENTS by ICP	1 - 4	250-2000	HNO_3+	ICP-AES	MCEF
Simazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
Simazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Simazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Sodium hexafluoro-aluminate	7902	FLUORIDES, aerosol & gas	1 - 2	12-800	NaOH	ISE	MCEF& pad w/Na_2CO_3
Sodium hexafluoro-aluminate	7906	FLUORIDES by IC	1-2	120-800	NaOH	IC	MCEF& pad w/Na_2CO_3
Sodium hydroxide	7401	ALKALINE DUSTS	1 - 4	70-1000	HCl	Titration	PTFE
Stibine	6008	STIBINE	0.01-0.2	4-50	HCl	VIS	SG w/$HgCl_2$
Stoddard solvent	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
Strychnine	5016	STRYCHNINE	1 - 3	70-1000	reagents	HPLC-UV	GFF
Styrene	1501	HYDROCARBONS, AROMATIC	0.01-1.0	1-14	CS_2	GC-FID	CCT
Sulfur dioxide	6004	SULFUR DIOXIDE	0.5-1.5	4-200	HCO_3^-/CO_3^{2-}	IC	MCEF& pad w/Na_2CO_3
Sulfur hexafluoride	6602	SULFUR HEXAFLUORIDE	0.01-0.05	80% vol	NA	GC-ECD	air bag
Sulfuric acid	7903	ACIDS, INORGANIC	0.2-0.5	3-100	HCO_3^-/CO_3^{2-}	IC	SG(washed)
Sulfuryl fluoride	6012	SULFURYL FLUORIDE	0.05-0.1	1.3-10	NaOH	IC	CCT (lg)
Sulprofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
Super absorbent polymer	5035	SUPER ABSORBENT POLYMER	1 - 3	50-1500	$Cu(Ac)_2$	ICP or AAS	PVC
2,4,5-T	5001	2,4-D and 2,4,5-T	1 - 3	15-200	MeOH	HPLC-UV	GFF
TB	0900	MYCOBACTERIUM TUBERCULOSIS, AIRBORNE	≥4	varies	reagent	PCR	PTFE
Tellurium	7300	ELEMENTS by ICP	1 - 4	25-2000	HNO_3	ICP-AES	MCEF
Terbufos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FID	OVS-2
Terpenes	1552	TERPENES	0.01-2	2-30	CS_2	GC-FID	CCT
o-Terphenyl	5021	o-TERPHENYL	1 - 3	2-30	CS_2	GC-FID	PTFE
1,1,2,2-Tetrabromo ethane	2003	1,1,2,2-TETRABROMOETHANE	0.2-1.0	50-100	THF	GC-FID	SG
Tetrabutyltin	5504	ORGANOTIN COMPOUNDS	1-1.5	50-500	acetic a/CH_3CN	HPLC/GFAAS	GFF & XAD-2
1,2,4,5-Tetrachlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3-12	hexane	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-DIFLUOROETHANE	0.01-0.035	0.5-2	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	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	CS_2	GC-FID	CCT
1,1,2,2-Tetrachloroethane	1019	1,1,2,2-TETRACHLOROETHANE	0.01-0.2	3-30	CS_2	GC-FID	PCT
Tetrachloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.2-40	CS_2	GC-FID	CCT
Tetrachloroethylene	3704	PERCHLOROETHYLENE (port GC) in exhaled breath and air	0.1-1	<80% cap	NA	Port GC-PID	air bag
Tetraethylene glycol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Tetraethyl lead	2533	TETRAETHYL LEAD (as Pb)	0.01-1.0	30-200	pentane	GC PID	XAD 2
Tetraethyl pyrophosphate	2504	TETRAETHYL PYROPHOSPHATE	0.01-0.2	20-48	toluene	GC-FPD	2 Chrom 102
Tetrahydrofuran	1609	TETRAHYDROFURAN	0.01-0.2	1-9	CS_2	GC FID	CCT
Tetramethyl lead	2534	TETRAMETHYL LEAD (as Pb)	0.01-0.2	15-100	pentane	GC-PID	XAD-2
Tetramethyl thiourea	3505	TETRAMETHYL THIOUREA	0.2-1.0	50-250	reagents	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	HNO_3+	ICP-AES	MCEF
Thiobencarb	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC, UV	OVS-2
Thiram	5005	THIRAM	1 - 4	10-400	CH_3CN	HPLC-UV	PTFE
Tin, organic compds as Sn	5504	ORGANOTIN CPDS. (as Sn)	1-1.5	50-500	acetic a/CH_3CN	HPLC/GFAAS	GFF & XAD-2
Titanium	7300	ELEMENTS by ICP	1 - 4	5-100	HNO_3+	ICP-AES	MCEF
o-Tolidine	5013	DYES	1 - 3	150-500	H_2O	HPLC-UV	PTFE
Toluene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Toluene	4000	TOLUENE(Diffusive sampler)	NA	15 min-8h	CS_2	GC-FID	Diffusive
Toluene	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	2-8	CS_2	GC-FID	CCT
Toluene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-8	CS_2	GC-FID	CCT
2,4 & 2,6-Toluenediamine	5516	2,4- & 2,6-TOLUENEDIAMINE	1.0	30-500	acetylate/MeOH	HPLC UV	IMP
Toluene-2,4-diisocyanate	2535	TOLUENE-2,4-DIISOCYANATE	0.2-1.0	2-170	MeOH	HPLC-UV	GW coated
Toluene-2,4-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5-500	acetylate/MeOH	HPLC ECHD	IMP
Toluene-2,4-diisocyanate	5522	ISOCYANATES	1 - 2	15-360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
Toluene-2,6-diisocyanate	5522	ISOCYANATES	1 - 2	15-360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
Toluene-2,6-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5-500	acetylate/MeOH	HPLC-ECHD	IMP
p-Toluenesulfonic acid	5043	*P*-TOLUENESULFONIC ACID	1 - 3	10-1000	IPA/H_2O	HPLC-UV	GFF
o-Toluidine	2002	AMINES, AROMATIC	0.02-1.0	10-150	Ethanol	GC-FID	SG
o-Toluidine	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF + SG
Tribromomethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	4-70	CS_2	GC-FID	CCT
Tributyl phosphate	5034	TRIBUTYL PHOSPHATE	1 - 3	2-100	diethyl ether	GC-FPD	MCEF
Tributyltin chloride	5504	ORGANOTIN COMPOUNDS	1-1.5	50-500	acetic a/CH_3CN	HPLC/GFAAS	GFF & XAD-2
1,2,4-Trichlorobenzene	5517	POLYCHLOROBENZENES	0.01-0.2	3-12	hexane	GC-ECD	PTFE & XAD-2
1,1,2-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	2-60	CS_2	GC-FID	CCT
1,1,1-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.1-8	CS_2	GC-FID	CCT
1,1,1-Trichloroethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Trichloroethylene	1022	TRICHLOROETHYLENE	0.01-0.2	1-30	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Trichloroethylene	3701	TRICHLOROETHYLENE by port GC	> 0.02	80% vol	NA	GC-port	air bag
Trichlorofluoromethane	1006	FLUOROTRICHLOROMETHANE	0.01-0.05	0.3-7	CS_2	GC-FID	CCT(lg)
Trichloromethane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	1-50	CS_2	GC-FID	CCT
1,2,3-Trichloropropane	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	0.6-60	CS_2	GC-FID	CCT
Trichcylohexyltin hydroxide	5504	ORGANOTIN COMPOUNDS	1-1.5	50-500	acetic a/CH_3CN	HPLC-GFAAS	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	CS_2	GC-FID	CCT
1,1,2-Trichloro-1,2,2-trifluoroethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Triethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5-300	HSA	IC	IMP
Triethylene glycol	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
Triethylenetetramine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1-20	DMF	HPLC-UV	XAD-2 W/10% NITC
Trifluorobromomethane	1017	TRIFLUOROBROMOMETHANE	0.01-0.05	0.1-1	CH_2Cl_2	GC-FID	2 CCT(lg+sm)
Trimellitic anhydride	5036	TRIMELLITIC ANHYDRIDE	1.5-2	400-1000	MeOH	GC-FID	PVC
2,4,7-Trinitrofluoren-9-one	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	1 - 3	100-500	toluene	HPLC-UV	PTFE
Triorthocresyl phosphate	5037	TRIORTHOCRESYL PHOSPHATE	1 - 3	2-100	diethyl ether	GC-FPD	MCEF
Triphenyl phosphate	5038	TRIPHENYL PHOSPHATE	1 - 3	10-400	diethyl ether	GC-FPD	MCEF
Tubercle bacilli	0900	MYCOBACTRIUM TUBERCULOSIS	≥4	varies	reagent	PCR	PTFE
Tungsten, soluble/insoluble	7074	TUNGSTEN (soluble/insoluble)	1 - 4	200-1000	HF/HNO_3	FAAS	MCEF
Turpentine	1551	TURPENTINE	0.01-0.2	1-10	CS_2	GC-FID	CCT
Turpentine	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Valeraldehyde	2536	VALERALDEHYDE	0.01-0.04	0.5-10	toluene	GC-FID	XAD-2/HMP
Valeraldehyde	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	toluene	GC-FID/MS	XAD-2/HMP
Vanadium	7300	ELEMENTS by ICP	1 - 4	5-2000	HNO_3 +	ICP-AES	MCEF
Vanadium oxides	7504	VANADIUM OXIDES	1.7 or 2.2	200-1000	THF	XRD	CYC & PVC
Vinyl acetate	1453	VINYL ACETATE	0.1-0.2	0.75-24	CH_2Cl_2/MeOH	GC-FID	MS(carbon)
Vinyl benzene	1501	HYDROCARBONS, AROMATIC	.01-1	1-14	CS_2	GC-FID	CCT
Vinyl bromide	1009	VINYL BROMIDE	0.01-0.2	2-10	Ethanol	GC-FID	CCT (lg)
Vinyl chloride	1007	VINYL CHLORIDE	0.05	0.7-5	CS_2	GC-FID	2 CCT
Vinylidene chloride	1015	VINYLIDENE CHLORIDE	0.01-0.2	2.5-7	CS_2	GC-FID	CCT
Vinyl tolueneuene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	1-24	CS_2	GC-FID	CCT
VM&P naphtha	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
VOCs	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Warfarin	5002	WARFARIN	1 - 4	200-1000	MeOH	HPLC-UV	PTFE
Wood alcohol	2000	METHANOL	0.02-0.2	1-5	H_2O/IPA	GC-FID	SG
Xylene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
Xylene	1501	HYDROCARBONS, AROMATIC	0.01-0.2	2-23	CS_2	GC-FID	CCT
2,4-Xylidine	2002	AMINES, AROMATIC	0.02-0.2	3-20	Ethanol	GC-FID	SG
Yttrium	7300	ELEMENTS by ICP	1 - 4	5-1000	HNO_3 +	ICP-AES	MCEF
Zinc and compounds	7030	ZINC and compounds, as Zn	1 - 3	2-400	HNO_3 +	FAAS	MCEF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Zinc	7300	ELEMENTS by ICP	1 - 4	5-200	HNO_3 +	ICP-AES	MCEF
Zinc oxide	7502	ZINC OXIDE	1 - 3	10-400	--	XRD	PVC
Zirconium	7300	ELEMENTS by ICP	1 - 4	5-200	HNO_3 +	ICP-AES	MCEF
METHODS BY NUMBER							
	0500	PARTICULATES N.O.R.	1 - 2	7-133	NA	GRAV	PVC
	0600	PARTICULATES, N.O.R, RESP.	1.7, 2.2,2.5	20-400	NA	Grav.	CYC & PVC
	0800	BIOAEROSOL SAMPLING	28.3	varies	NA	varies	impactor
	0801	AEROBIC BACTERIA - GC-FAME	28.3	50-300	hex/MTBE	GC-FID	impactor
	0900	MYCOBACTERIUM TUBERCULOSIS	4	varies	reagent	PCR	PTFE
	1000	ALLYL CHLORIDE	0.01-1.0	16-100	bz	GC-FID	CCT
	1001	METHYL CHLORIDE	0.01-0.1	0.4-3	CH_2Cl_2	GC-FID	2 CCT (lg+sm)
	1002	β-CHLOROPRENE	0.01-0.1	1.5-8	CS_2	GC-FID	CCT
	1003	HYDROCARBONS, HALOGENATED	0.01-0.2	3-70	CS_2	GC-FID	CCT
	1004	DICHLOROETHYL ETHER	0.01-1.0	2-15	CS_2	GC-FID	CCT
	1005	METHYLENE CHLORIDE	0.01-0.2	0.5-2.5	CS_2	GC-FID	2 CCT
	1006	FLUOROTRICHLOROMETHANE	0.01-0.05	0.3-7	CS_2	GC-FID	CCT (lg)
	1007	VINYL CHLORIDE	0.05	0.7-5	CS_2	GC-FID	2 CCT
	1008	ETHYLENE DIBROMIDE	0.02-0.2	0.1-25	bz/MeOH	GC-ECD	CCT
	1009	VINYL BROMIDE	0.01-0.2	2-10	Ethanol	GC-FID	CCT (lg)
	1010	EPICHLOROHYDRIN	0.01-0.2	2-30	CS_2	GC-FID	CCT
	1011	ETHYL BROMIDE	0.01-0.2	0.5-4	IPA	GC-FID	CCT
	1012	DIFLUORODIBROMOMETHANE	0.01-0.2	2.5-10	IPA	GC-FID	2 CCT
	1013	PROPYLENE DICHLORIDE	0.01-0.2	0.1-3.5	acet/cyclohexane	GC-ECN	PCT
	1014	METHYL IODIDE	0.01-1.0	15-50	tol	GC-FID	CCT
	1015	VINYLIDENE CHLORIDE	0.01-0.2	2.5-7	CS_2	GC-FID	CCT
	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	0.01-0.035	0.5-2	CS_2	GC-FID	CCT
	1017	TRIFLUOROBROMOMETHANE	0.01-0.05	0.1-1	CH_2Cl_2	GC-FID	2 CCT(lg+sm)
	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE& CHLORODIFLUOROMETHANE	0.01-0.05	1-4	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
	1019	1,1,2,2-TETRACHLOROETHANE	0.01-0.2	3-30	CS_2	GC-FID	PCT
	1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	0.01-0.05	0.1-3	CS_2	GC-FID	CCT
	1022	TRICHLOROETHYLENE	0.01-0.2	1-30	CS_2	GC-FID	CCT
	1024	1,3-BUTADIENE	0.01-0.5	5-25	CH_2Cl_2	GC-FID	CCT
	1300	KETONES I	0.01-2.0	1-10	CS_2	GC-FID	CCT
	1301	KETONES II	0.01-0.2	1-25	MeOH/CS_2	GC-FID	CCT
	1302	N-METHYL-2-PYRROLIDINONE	0.05-0.2	0.5-125	CH_2CL_2/MeOH	GC-FID/NPD	CCT
	1400	ALCOHOLS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
	1401	ALCOHOLS II	0.01-0.2	2-10	IPA/CS_2	GC-FID	CCT
	1402	ALCOHOLS III	0.01-0.2	1-10	IPA/CS_2	CG-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	1403	ALCOHOLS IV	0.01-0.05	6-50	MeOH/CH_2Cl_2	GC-FID	CCT
	1404	METHYLCYCLOHEXANOL	0.01-0.2	1-15	CH_2Cl_2	GC-FID	CCT
	1450	ESTERS I	0.01-0.2	1-10	CS_2	GC-FID	CCT
	1451	METHYL CELLOSOLVE ACETATE	0.01-0.2	0.2-20	CS_2	GC-FID	CCT
	1452	ETHYL FORMATE	0.01-0.2	0.3-10	CS_2	GC-FID	CCT
	1453	VINYL ACETATE	0.1-0.2	0.75-24	CH_2Cl_2/MeOH	GC-FID	MS(carbon)
	1454	ISOPROPYL ACETATE	0.02-0.2	0.1-9	CS_2	GC-FID	CCT
	1457	ETHYL ACETATE	0.01-0.2	0.1-10	CS_2	GC-FID	CCT
	1458	METHYL ACETATE	0.01-0.2	0.2-10	CS_2	GC-FID	CCT
	1459	METHYL ACRYLATE	0.01-0.2	1-5	CS_2	GC-FID	CCT
	1500	HYDROCARBONS, BP 36-126°C	0.01-0.2	4-4	CS_2	GC-FID	CCT
	1501	HYDROCARBONS, AROMATIC	0.01-1.0	100-200	CS_2	GC-FID	CCT
	1550	NAPHTHAS	0.01-0.2	1.3-20	CS_2	GC-FID	CCT
	1551	TURPENTINE	0.01-0.2	1-10	CS_2	GC-FID	CCT
	1552	TERPENES	0.01-2	2-30	CS_2	GC-FID	CCT
	1600	CARBON DISULFIDE	0.01-0.2	2-25	tol	GC-FPD	CCT & dry tube
	1601	1,1-DICHLORO-1-NITROETHANE	0.01-1.0	1.5-15	CS_2	GC-FID	PCT
	1602	DIOXANE	0.01-0.2	0.5-15	CS_2	GC-FID	CCT
	1603	ACETIC ACID	0.01-0.1	20-300	formic a	GC-FID	CCT
	1604	ACRYLONITRILE	0.01-0.2	3.5-20	acet/CS_2	GC-FID	CCT
	1606	ACETONITRILE	0.01-0.2	1-25	CH_2Cl_2/MeOH	GC-FID	CCT
	1608	GLYCIDOL	0.01-1.0	5-100	THF	GC-FID	CCT
	1609	TETRAHYDROFURAN	0.01-0.2	1-9	CS_2	GC-FID	CCT
	1610	ETHYL ETHER	0.01-0.2	0.25-3	Et Ac	GC-FID	CCT
	1611	METHYLAL	0.01-0.2	1-3	hexane	GC-FID	CCT
	1612	PROPYLENE OXIDE	0.01-0.2	0.5-5	CS_2	GC-FID	CCT
	1613	PYRIDINE	0.01-1.0	18-150	CH_2Cl_2	GC-FID	CCT
	1614	ETHYLENE OXIDE	0.05-0.15	1-24	DMF	GC-ECD	PCT w/HBr
	1615	METHYL *tert*-BUTYL ETHER	0.1-0.2	2-96	CS_2	GC-FID	2 CCT (lg)
	1616	BUTYL GLYCIDYL ETHER	0.01-0.2	15-30	CS_2	GC-FID	CCT
	1617	PHENYL ETHER	0.01-0.2	1-50	CS_2	GC-FID	CCT
	1618	ISOPROPYL ETHER	0.01-0.05	0.1-3	CS_2	GC-FID	CCT
	1619	PHENYL GLYCIDYL ETHER	0.01-1	80-150	CS_2	GC-FID	CCT
	1620	ISOPROPYL GLYCIDYL ETHER	0.01-0.2	1-30	CS_2	GC-FID	CCT
	2000	METHANOL	0.02-0.2	1-5	H_2O/IPA	GC-FID	SG
	2002	AMINES, AROMATIC	0.2-1.0	30-150	Ethanol	GC-FID	SG
	2003	1,1,2,2-TETRABROMOETHANE	0.2-1.0	50-100	THF	GC-FID	SG
	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	0.01-1.0	15-80	MeOH	GC-FID	SG
	2005	NITROAROMATIC COMPOUNDS	0.01-1	1-150	MeOH	GC-FID	SG
	2007	AMINOETHANOL COMPOUNDS I	0.01-0.2	4-24	MeOH/H_2O	GC-FID	SG
	2008	CHLOROACETIC ACID	0.05-0.2	1-100	H_2O	IC	SG
	2010	AMINES, ALIPHATIC	0.01-1.0	3-30	H_2SO_4/aq MeOH	GC-FID	SG

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	2011	FORMIC ACID	0.05-0.2	1-24	H_2O	IC	PTFE & SG (washed)
	2012	*n*-BUTYLAMINE	0.01-1.0	2-100	MeOH	GC-FID	SG + H_2SO_4
	2013	PHENYL ETHER-DIPHENYL MIXTURE	0.01-0.2	1-40	bz	GC-FID	SG
	2014	*p-CHLOROPHENOL*	0.05-0.2	1.5-40	CH_3CN	HPLC-UV	SG
	2015	CHLOROACETALDEHYDE	0.05-0.2	3-16	MeOH	GC-ECD	SG
	2016	FORMALDEHYDE	0.1-1.5	1-15	acetonitrile	HPLC-UV	SG/DNPH
	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5-50	ethanol	GC-FID	GFF + SG w/H_2SO_4
	2500	METHYL ETHYL KETONE	0.01-0.2	0.25-12	CS_2	GC-FID	Carbon beads
	2501	ACROLEIN	0.01-0.1	1.5-48	tol	GC-NPD	XAD-2/HMP
	2504	TETRAETHYL PYROPHOSPHATE	0.01-0.2	20-48	toluene	GC-FPD	2 Chrom 102
	2505	FURFURYL ALCOHOL	0.01-0.05	3-25	acet	GC-FID	Por Q
	2506	ACETONE CYANOHYDRIN	0.2	0.3-12	Et Ac	GC-NPD	Por QS
	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2-1.0	3-100	Ethanol	GC-ECD	Tenax-GC
	2508	ISOPHORONE	0.01-1.0	2-25	CS_2	GC-FID	PCT
	2510	1-OCTANETHIOL	0.01-0.2	1-15	acet	GC-FPD	Tenax GC
	2513	ETHYLENE CHLOROHYDRIN	0.01-0.2	2-35	IPA/CS_2	GC-FID	PCT
	2514	ANISIDINE	0.5-1.0	24-320	MeOH	HPLC-UV	XAD-2
	2515	DIAZOMETHANE	0.2	6-30	CS_2	GC-FID	XAD-2 (coated)
	2516	DICHLOROFLUOROMETHANE	0.01-0.05	0.25-3	CS_2	GC-FID	2 CCT (lg)
	2517	PENTACHLOROETHANE	0.01-0.2	1-10	hexane	GC-ECD	Por R
	2518	HEXACHLORO-1,3-CYCLOPENTA-DIENE	0.01-0.2	0.25-90	hexane	GC-ECD	2 Por T
	2519	ETHYL CHLORIDE	0.02-0.05	0.3-3	CS_2	GC-FID	2 CCT (lg)
	2520	METHYL BROMIDE	0.01-0.1	1-5	CS_2	GC-AED	PCT(2)+dry tube
	2521	METHYLCYCLOHEXANONE	0.01-0.05	1-6	acet	GC-FID	Por Q
	2522	NITROSAMINES	0.2-2.0	15-1000	MeOH/CH_2Cl_2	GC-TEA	Thermalosorb/N
	2523	1,3-CYCLOPENTADIENE	0.01-0.05	1-5	Et Ac	GC-FID	Chrom104/ maleic anh.
	2524	DIMETHYL SULFATE	0.01-0.2	0.25-12	diEt ether	GC-ECN	Por P
	2525	*n*-BUTYL MERCAPTAN	0.01-0.05	1-4	acet	GC-FPD	Chrom 104
	2526	NITROETHANE	0.01-0.05	1.5-3	EtAc	GC-FID	2XAD-2
	2527	NITROMETHANE	0.01-0.05	1.2-3	EtAc	GC-FPD	Chrom 106
	2528	2-NITROPROPANE	0.01-0.05	0.1-2	EtAc	GC-FID	Chrom 106
	2529	FURFURAL	0.01-0.05	1-12	tol	GC-FID	XAD-2/HMP
	2530	DIPHENYL	0.01-0.5	15-30	CCl_4	GC-FID	Tenax GC
	2532	GLUTARALDEHYDE	0.01-0.08	4-39	CH_3CN	HPLC-UV	SG/DNPH
	2533	TETRAETHYL LEAD (as Pb)	0.01-1.0	30-200	pentane	GC-PID	XAD-2
	2534	TETRAMETHYL LEAD (as Pb)	0.01-0.2	15-100	pentane	GC-PID	XAD-2
	2535	TOLUENE-2,4-DIISOCYANATE	0.2-1.0	2-170	MeOH	HPLC-UV	GW coated
	2536	VALERALDEHYDE	0.01-0.04	0.5-10	toluene	GC-FID	XAD-2/HMP
	2537	METHYL METHACRYLATE	0.01-0.05	1-8	CS_2	GC-FID	XAD-2

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	2538	ACETALDEHYDE	0.01-0.05	1-12	tol	GC-FID	XAD-2/HMP
	2539	ALDEHYDES, SCREENING	0.01-0.05	5-5	tol	GC-FID/MS	XAD-2
	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01-0.1	1-20	DMF	HPLC-UV	XAD-2 w/10% NITC
	2541	FORMALDEHYDE	0.01-0.1	1-36	tol	GC-FID	XAD-2/HMP
	2542	MERCAPTANS	0.1-0.2	10-150	HCl/DCE	GC-FPD	GFF/HgAc
	2543	HEXACHLOROBUTADIENE	0.05-0.2	1-100	hexane	GC-ECD	XAD-2
	2544	NICOTINE	1.0	60-400	EtAc	GC-NPD	XAD-2
	2545	ALLYL GLYCIDYL ETHER	0.01-0.2	1.5-8	diethyl ether	GC-FID	Tenax
	2549	VOLATILE ORGANIC CPDS (Screening)	0.01-0.05	1-6	thermal	TD/GC-MS	TD
	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0-2.0	480-960	hexane	GC-SCD	PTFE + XD-2
	2551	NICOTINE	0.1-1.0	0.5-600	ethyl acetate	GC-NPD	XAD-4
	3500	FORMALDEHYDE	0.2-1.0	1-100	$NaHSO_3$	VIS	PTFE & 2 IMP
	3503	HYDRAZINE	0.2-1.0	7-100	reagents	VIS	BuB
	3505	TETRAMETHYL THIOUREA	0.2-1.0	50-250	reagents	VIS	IMP/H_2O
	3506	ACETIC ANHYDRIDE	0.2-1.0	25-100	reagent	VIS	BuB
	3507	ACETALDEHYDE	0.1-0.5	6-60	reagent	HPLC-UV	BuB
	3508	METHYL ETHYL KETONE PEROXIDE	0.5-0.2	52-520	reagent	VIS	IMP
	3509	AMINOETHANOL COMPOUNDS II	0.5-1.0	5-300	HSA	IC	IMP
	3510	MONOMETHYLHYDRAZINE	0.5-1.5	3-20	PMA/HCl	VIS	BuB/HCl
	3511	MONOMETHYLANILINE	0.2-1.0	11-100	NaOH	GC-FID	BuB/H_2SO_4
	3512	MALEIC ANHYDRIDE	0.2-1.5	40-500	--	HPLC-UV	BuB/H_2O
	3513	TETRANITROMETHANE	0.5-1.0	20-250	--	GC-FID	IMP/EtAc
	3514	ETHYLENIMINE	0.2	1-48	$CHCl_3$	HPLC-UV	BuB
	3515	1,1-DIMETHYLHYDRAZINE	0.2-1.0	2-100	reagent	VIS	BuB (.1 M HCl)
	3516	CROTONALDEHYDE	0.1-0.2	1-49	buffer	DPP	BuB
	3518	PHENYLHYDRAZINE	0.2-1.0	25-120	PMA	VIS	BuB/HCl
	3700	BENZENE by portable GC	> 0.02	80% vol	NA	GC	air bag
	3701	TRICHLOROETHYLENE by port GC	> 0.02	80% vol	NA	GC-port	air bag
	3702	ETHYLENE OXIDE by portable GC	> 0.02	80% vol	NA	GC-PID	air bag
	3704	PERCHLOROETHYLENE (portable GC) in exhaled breath and air	0.1-1	80% VOL	NA	Port GC-PID	air bag
	4000	TOLUENE (Diffusive sampler)	NA	15 min-8h	CS_2	GC-FID	Diffusive
	5000	CARBON BLACK	1 - 2	30-570	NA	Grav	PVC
	5001	2,4-D and 2,4,5-T	1 - 3	15-200	MeOH	HPLC-UV	GFF
	5002	WARFARIN	1 - 4	200-1000	MeOH	HPLC-UV	PTFE
	5003	PARAQUAT	1 - 4	40-1000	H_2O	HPLC-UV	PTFE
	5004	HYDROQUINONE	1 - 4	30-180	acetic a	HPLC-UV	MCEF
	5005	THIRAM	1 - 4	10-400	CH_3CN	HPLC-UV	PTFE
	5006	CARBARYL	1 - 3	20-400	reagent	VIS	GFF
	5007	ROTENONE	1 - 4	8-400	CH_3CN	HPLC-UV	PTFE
	5008	PYRETHUM	1 - 4	20-400	CH_3CN	HPLC-UV	GFF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	5009	BENZOYL PEROXIDE	1 - 3	40-400	diethyl ether	HPLC-UV	MCEF
	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	2-400	CH_3CN	HPLC-UV	PTFE
	5011	ETHYLENE THIOUREA	1 - 3	200-800	H_2O	VIS	PVC or MCEF
	5012	EPN	1 - 2	15-700	isooctane	GC-FPD	GFF
	5013	DYES	1 - 3	150-500	H_2O	HPLC-UV	PTFE
	5014	CHLORINATED TERPHENYL	1 - 3	100-1500	isooctane	GC-ECD	GFF
	5016	STRYCHNINE	1 - 3	70-1000	reagents	HPLC-UV	GFF
	5017	DIBUTYL PHOSPHATE	1-3	50-250	CH_3CN	GC-FPD	PTFE
	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	1 - 3	100-500	toluene	HPLC-UV	PTFE
	5019	AZELAIC ACID	1 - 3	200-1000	Ethanol	GC-FID	PVC
	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	1-3	6-200	CS_2	GC-FID	MCEF
	5021	o-TERPHENYL	1 - 3	2-30	CS_2	GC-FID	PTFE
	5022	ARSENIC, organo-	1 - 3	50-1000	buffer	IC-HYAAS	PTFE
	5025	CHLORINATED DIPHENYL OXIDE	0.5-1.5	8-200	isooctane	GC-ECN	MCEF
	5026	OIL MIST, MINERAL	1 - 3	20-500	CCl_4	IR	PVC or MCE
	5027	RIBAVIRIN	1 - 4	5-1000	H_2SO_4	HPLC-UV	GFF
	5029	4,4'-METHYLENEDIANILINE	1 - 2	10-1000	KOH/MeOH	HPLC-UV	GFF/H_2SO_4
	5030	CYANURIC ACID	1 - 3	10-1000	reagents	HPLC-UV	PVC
	5031	ASPARTAME	1 - 3	70-1200	eluent	HPLC-UV	PTFE
	5032	PENTAMIDINE ISETHIONATE	1 - 2	50-1500	reagents	HPLC/FL	PVC/opaque
	5033	p-NITROANILINE	1 - 3	20	IPA	HPLC-UV	MCEF
	5034	TRIBUTYL PHOSPHATE	1 - 3	2-100	diethyl ether	GC-FPD	MCEF
	5035	SUPER ABSORBENT POLYMER	1 - 3	50-1500	$Cu(Ac)_2$	ICP or AAS	PVC
	5036	TRIMELLITIC ANHYDRIDE	1.5-2	400-1000	MeOH	GC-FID	PVC
	5037	TRIORTHOCRESYL PHOSPHATE	1 - 3	2-100	diethyl ether	GC-FPD	MCEF
	5038	TRIPHENYL PHOSPHATE	1 - 3	10-400	diethyl ether	GC-FPD	MCEF
	5039	CHLORINATED CAMPHENE	0.2-1	2-30	pet ether	GC-ECD	MCEF
	5040	ELEMENTAL CARBON (DIESEL PARTICULATE)	2 - 4	142-19000	thermal	EGA/TOA	QFF
	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	5-1000	CH_3CN	HPLC-FL	GFF
	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1-4	28-400	benzene	Grav	tared PTFE
	5043	p-TOLUENESULFONIC ACID	1-3	10-1000	IPA/H_20	HPLC-UV	GFF
	5502	ALDRIN & LINDANE	0.2-1.0	18-240	isooct	GC-ECN	GFF & BuB
	5503	POLYCHLOROBIPHENYLS	0.05-0.2	1-50	hexane	GC-ECD	GFF & Florisil
	5504	ORGANOTIN COMPOUNDS	1-1.5	50-500	acetic a/CH_3CN	HPLC-GFAAS	GFF & XAD-2
	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
	5508	KEPONE	0.5-1.0	50-600	bz/MeOH	GC ECD	MCEF & IMP
	5509	BENZIDINE and 3,3'-DICHLORO- BENZIDINE	0.2	20-100	triethyl amine /MeOH	HPLC UV	GFF
	5510	CHLORDANE	0.5-1.0	10-200	tol	GC-ECD	MCEF & Chrom 102
	5512	PENTACHLOROPHENOL	0.5-1.0	48-480	MeOH	HPLC-UV	MCEF & BuB

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	5514	DEMETON	0.2-1.0	30-500	tol	GC-FPD	MCEF &XAD-2
	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200-1000	varies	GC-FID	PTFE & XAD-2
	5516	2,4- & 2,6-TOLUENEDIAMINE	1.0	30-500	acetylate/MeOH	HPLC-UV	IMP
	5517	POLYCHLOROBENZENES	0.01-0.2	3-12	hexane	GC-ECD	PTFE & XAD-2
	5518	NAPHTHYLAMINES	0.2-0.8	30-100	acetic a /IPA	GC-FID	GFF & SG
	5519	ENDRIN	0.5-1.0	12-400	tol	GC-ECD	MCEF & Chrom 102
	5521	ISOCYANATES, MONOMERIC	1.0	5-500	reagents	HPLC-ECHD	IMP
	5522	ISOCYANATES	1 - 2	15-360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
	5523	GLYCOLS	0.5-2	5-60	MeOH	GC-FID	OVS-7
	5600	ORGANOPHOSPHORUS PESTICIDES	0.2-1	12-240	tol/acet	GC-FPD	OVS-2
	5601	ORGANONITROGEN PESTICIDES	0.1-1	var-480	reagent	HPLC-UV	OVS-2
	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2-1	12-480	reagent	GC/ECD	OVS-2
	5603	ALACHLOR in AIR	1	70-1750	MeOH	ELISA	SPE disk
	5700	FORMALDEHYDE on dust	2	240-1050	H_2O/DNPH/CH_3CN	HPLC-UV	IOM/PVC
	5701	RESORCINOL	0.2-1	5-160	MeOH	GC-FID	OVS-7
	5800	POLY AROMATIC COMPOUNDS (PACs)	1-2	5-1000	hexane	FI-FL	PTFE + XAD-2
	6001	ARSINE	0.01-0.2	0.1-10	HNO_3	GFAAS	CCT
	6002	PHOSPHINE	0.01-0.2	1-16	reagent	VIS	SG/$Hg(CN)_2$
	6004	SULFUR DIOXIDE	0.5-1.5	4-200	HCO_3^-/CO_3^{2-}	IC	MCEF& pad w/Na_2CO_3
	6005	IODINE	0.5-1.0	15-225	Na_2CO_3	IC	CCT w/alkali
	6006	DIBORANE	0.5-1.0	60-260	H_2O_2	PES	PTFE & CCT w/oxidizer
	6007	NICKEL CARBONYL	0.05-0.2	7-80	HNO_3	GFAAS	CCT (low Ni)
	6008	STIBINE	0.01-0.2	4-50	HCl	VIS	SG w/$HgCl_2$
	6009	MERCURY	0.15-0.25	2-100	HNO_3/HCl	AAS-cold vap	Hopcalite
	6010	HYDROGEN CYANIDE	0.05-0.2	2-90	H_2O	VIS	soda lime
	6011	CHLORINE and BROMINE	0.3-1.0	2-90	$Na_2S_2O_3$	IC	Ag F
	6012	SULFURYL FLUORIDE	0.05-0.1	1.3-10	NaOH	IC	CCT (lg)
	6013	HYDROGEN SULFIDE (withdrawn)	0.1-1.5	1.2-40	NH_4OH/H_2O_2	IC	PTFE & CCT (lg)
	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025	1.5-6	reagent	VIS	MS w/TEA & oxidizer
	6015	AMMONIA by VIS	0.1-0.2	0.1-90	H_2O	VIS-Auto	SG + H_2SO_4
	6016	AMMONIA by IC	0.1-0.5	0.1-96	H_2O	IC	SG + H_2SO_4
	6402	PHOSPHORUS TRICHLORIDE	0.05-0.2	11-100	reagents	VIS	BuB/H_2O
	6600	NITROUS OXIDE	NA	80% vol	NA	IR	air bag
	6601	OXYGEN	NA	1-NA	NA	Sensor	portable
	6602	SULFUR HEXAFLUORIDE	0.01-0.05	80% vol	NA	GC-ECD	air bag
	6603	CARBON DIOXIDE	0.02-0.1	80% vol	NA	GC-TCD	air bag
	6604	CARBON MONOXIDE	NA	NA	NA	Sensor	Port Instr
	6700	NITROGEN DIOXIDE (Diffusive)	NA	NA	reagent	VIS	Diffusive

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	7013	ALUMINUM & CPDS, as Al	1 - 3	10-400	HNO_3	FAAS	MCEF
	7020	CALCIUM and cpds as Ca	1 - 3	20-400	$HNO_3/HClO_4$	FAAS	MCEF
	7024	CHROMIUM and cpds, as Cr	1 - 3	10-1000	HCl/HNO_3	FAAS	MCEF
	7027	COBALT and cpds, as Co	1 - 3	30-1500	aq reg/HNO_3	FAAS	MCEF
	7029	COPPER (dust & fumes)	1 - 3	50-1500	HNO_3/HCl	FAAS	MCEF
	7030	ZINC and compounds, as Zn	1 - 3	2-400	HNO_3 +	FAAS	MCEF
	7048	CADMIUM and cpds, as Cd	1 - 3	25-1500	HNO_3/HCl	FAAS	MCEF
	7056	BARIUM, SOLUBLE COMPOUNDS	1 - 4	50-2000	H_2O	FAAS	MCEF
	7074	TUNGSTEN (soluble/insoluble)	1 - 4	200-1000	HF/HNO_3	FAAS	MCEF
	7082	LEAD by FAAS	1 - 4	200-1500	HNO_3/H_2O_2	FAAS	MCEF
	7102	BERYLLIUM and cpds, as Be	1 - 4	25-2000	HNO_3/H_2SO_4	GFAAS	MCEF
	7105	LEAD by GFAAS	1 - 4	1-1500	HNO_3/H_2O_2	GFAAS	MCEF
	7300	ELEMENTS by ICP	1 - 4	Varies	HNO_3+	ICP-AES	MCEF
	7400	ASBESTOS FIBERS by PCM	0.5-16	400-var	NA	PCM	MCEF open
	7401	ALKALINE DUSTS	1 - 4	70-1000	HCl	Titration	PTFE
	7402	ASBESTOS FIBERS by TEM	0.5-16	400-var	NA	TEM	MCEF open
	7500	SILICA, CRYSTALLINE, by XRD.	1.7, 2.2,2.5	400-1000	ash or THF	XRD	CYC + PVC
	7501	SILICA, AMORPHOUS	1.7, 2.2,2.5	50-400	ash	XRD	PVC (total) PVC&CYC
	7502	ZINC OXIDE	1 - 3	10-400	NA	XRD	PVC
	7504	VANADIUM OXIDES	1.7, 2.2,2.5	200-1000	THF	XRD	CYC & PVC
	7505	LEAD SULFIDE	1.7, 2.2,2.5	600-1000	THF	XRD	CYC & PVC
	7506	BORON CARBIDE	1.7, 2.2,2.5	100-1000	ash	XRD	CYC & PVC
	7600	CHROMIUM, HEXAVALENT	1 - 4	8-400	reagent	VIS	PVC
	7601	SILICA, CRYSTALLINE	1.7, 2.2,2.5	400-800	H_3PO_4/HF	VIS	CYC & MCE or PVC
	7602	SILICA, CRYSTALLINE (IR)	1.7, 2.2,2.5	400-800	ash	IR	CYC & MCE or PVC
	7603	SILICA in coal mine dust	1.7, 2.2,2.5	300-1000	ash	IR	CYC & PVC
	7604	CHROMIUM, HEXAVALENT	1 - 4	100-1000	$NaOH/Na_2CO_3$	IC	PVC
	7700	LEAD in Air by Chemical Spot Test	2	10-240	NA	Spot	MCEF
	7701	LEAD BY ULTRASOUND/ASV	1-4	20-1500	HNO_3	Port ASV	MCEF
	7702	LEAD by Field Portable XRF	1-4	570-1900	NA	XRF (port)	MCEF
	7900	ARSENIC & compounds, as As	1 - 3	30-1000	HNO_3 +	HYAAS	MCEF
	7901	ARSENIC TRIOXIDE, as As	1 - 3	30-1000	HNO_3 +	GFAAS	MCEF
	7902	FLUORIDES, aerosol & gas	1 - 2	12-800	NaOH	ISE	MCEF & pad w/ Na_2CO_3
	7903	ACIDS, INORGANIC	0.2-0.5	3.0-100	HCO_3^-/CO_3^{2-}	IC	SG(washed)
	7904	CYANIDES, aerosol and gas	0.5-1.0	10-180	KOH	ISE	MCEF & BuB
	7905	PHOSPHORUS	0.01-0.2	5-100	xylene	GC-FPD	Tenax GC
	7906	FLUORIDES by IC	1 - 2	s 1-800 i 120-800	NaOH	IC	MCEF & pad w/ Na_2CO_3
	9000	ASBESTOS, CHRYSOTILE by XRD	NA	NA	NA	XRD	bulk
	9002	ASBESTOS (bulk) by PLM	NA	NA	NA	PLM	bulk

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	9100	LEAD in Surface Wipe Samples	NA	NA	HNO_3+	AAS; ICP	Wipes
	9101	CHROMIUM, HEXAVALENT in settled dust	NA	NA	NA	Spot	Test strip
	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad

METHOD FINDER KEY TO ABBREVIATIONS

Sampling Media/Devices

Ag F	Silver membrane filter
BuB	Bubbler
CCT	Coconut shell charcoal tube
Chrom	Chromosorb
CYC	Cyclone
DNPH	Dinitrophenylhydrazine HCl
Dry	Drying tube
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)
OVS-7	OSHA versatile sampler (glass fiber filter/XAD-7)
Pad	Cellulose backup pad
PCT	Petroleum charcoal tube
Por	Poropak
PTFE	Polytetrafluoroethylene (Teflon) filter
PUF	Polyurethane foam
PVC	Polyvinyl chloride filter
QFF	Quartz fiber filter
SG	Silica gel
TD	Thermalalal desorption tube
TEA	Triethanolamine

Extraction Media

a	acid
ac	acetate
ACN	acetonitrile
acet	acetone
al	alcohol
alk	alkali
aq	aqueous / water
aq reg	aqua regia
bz	benzene
cychex	cyclohexane
DCE	dichloroethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DNPH	dinitrophenyl hydrazine
Et	ethyl
hex	hexane
HSA	hexanesulfonic acid
IPA	isopropanol
isooct	isooctane
Me	methyl
MTBE	methyl-tert-butyl ether
pet	petroleum
PMA	phosphomolybdic acid
pyr	pyridine
reag	reagent
THF	tetrahydrofuran
tol	toluene

Analytical Techniques

AAS	Atomic absorption spectrophotometry
AMP	Amperometric detector
ASV	Anodic stripping voltammetry
CD	Conductivity detector
DPP	Differential Pulse Polargraphy
ECD	Electron capture detector
ECHD	Electrochemical detector
ECN	Electrolytic conductivity detector
EG	Evolved gas analysis
FAAS	Flame AAS
FI	Flow injection
FID	Flame ionization detector
FL	Fluorescence detector
FPD	Flame photometric detector
GC	Gas chromatography
Grav	Gravimetric (filter weight)
GFAAS	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
SCD	Sulfur chemiluminescence detector
SEM	Scanning electron microscopy
Spot	Spot test
TCD	Thermalalal conductivity detector
TEM	Transmission electron microscopy
TOA	Thermal optical analyzer
UV	Ultraviolet
VIS	Visible absorption spectrophotometry
XRD	X-ray diffraction
XRF	X-ray fluorescence

Other

cap	capacity
i	insoluble
NA	not applicable
port	portable
s	soluble
var	varies / variable

I. INTRODUCTION

A. PURPOSE AND SCOPE

The NIOSH Manual of Analytical Methods (NMAM®) is a collection of air, biological, bioaerosol, and bulk analytical methods that 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 202/512-1800), and in electronic form from various software companies that have entered into publishing agreements with NIOSH (as of the time of this printing):

ChemSW, Inc.
(Formerly WindowChem)
420-F Executive Court North
Fairfield, CA 94585
Telephone:800/536-0404 or
707/864-0845
FAX: 707/864-2815
[Diskettes]

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
[Diskettes]

American Conference of Governmental Industrial Hygienists (ACGIH)
1330 Kemper Meadow Drive
Cincinnati, OH 45240
Telephone: 513/742-2020
FAX: 513/742-3355
[CD-ROM with TLVs® & BEIs®]

John Wiley & Sons, Inc.
Distribution Center
1 Wiley Drive
Somerset, NJ 08876-1272
Telephone:800/CALL-WILEY
FAX: 908/302-2300
[CD-ROM with Patty's Industrial Hygiene and Toxicology, Version 2.0]

These methods are intended to promote accuracy, sensitivity, and specificity in industrial hygiene analyses. There will be situations where users of the NIOSH methods will need to modify them (e.g., to accommodate interfering compounds from the workplace, to take advantage of special capabilities of the laboratory, 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 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, Extraction Solvent, 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
0001-0799	General air samples
0800-0999	Bioaerosols
1000-1999	Organic vapors on charcoal
2000-3499	Organic vapors on other solid sorbents
3500-3999	Organic vapors on other samplers (e.g., liquids, direct-reading)
4000-4999	Organic vapors 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-16). [**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-17 through A-30).

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-31 through A-62).

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 method Accuracy. (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.

CHEMICAL NAME **METHOD #**

FORMULA Molecular Weight Chemical Abstracts Service # RTECS #

Method numbers are the same as those in the 3rd edition. described in Method Classification of these "blue pages." and previous 3rd edition versions, if any.

Evaluation (Full, Partial, Unrated, N/A) is assigned as
Issue date reflects current version (e.g., August 15, 1994)

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. 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 special samplers.

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 over the range of the method.

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) and current 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

The SPECIAL PRECAUTIONS section gives safe practices to be observed during sampling and measurement. Next are 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. 7 through 16 and 17 through 35 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.

5. METHOD CLASSIFICATION

Methods in the fourth edition of the NIOSH Manual of Analytical Methods are classified into Evaluation categories: Full, Partial, Unrated, and Not Applicable. 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 ±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).

Evaluation: N/A

The designation, Not Applicable (N/A), is applied to methods where no quantitative data are collected:

- Procedures for sample collection only. The collected samples are analyzed subsequently by an appropriate analytical method, e.g., the Lead Wipe procedure (NMAM 9100) where the samples are analyzed by one of the three lead analysis methods.

- Qualitative methods that indicate results as positive or negative, e.g., Lead spot test (NMAM 7700), or *Mycobacterium Tuberculosis* by PCR (NMAM 0900).

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.

11. REFERENCES

[1] Hunter, J. S. "The National System of Scientific Measurement," Science, 210, 869 (1980).

[2] Garfield, F. M. Quality Assurance Principles for Analytical Laboratories, Association of Official Analytical Chemists, AOAC International, Arlington, VA (1991).

[3] Taylor, J. K. Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, MI (1987).

[4] Keith, L. H. Environmental Sampling and Analysis: A Practical Guide, Lewis Publishers, Chelsea, MI (1991).
[5] Dux, J. P. Handbook of Quality Assurance for the Analytical Chemistry Laboratory, Van Nostrand Reinhold, New York (1986).
[6] Kratochvil, B. and J. K. Taylor. "Sampling for Chemical Analysis," Anal. Chem., 53, 924A-938A (1981).
[7] Cali, J. P. and W. P. Reed. Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. NBS Spec. Publication 422, Vol 1, 41 (1976).
[8] Kosta L. Talanta, 29, 985-992 (1982).
[9] Leidel, N. A., K. A. Busch, and J. R. Lynch. Occupational Exposure Sampling Strategy Manual, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-173 (1977).
[10] Leidel, N. A. and K. A. Busch. Statistical Design and Data Analysis Requirements, Chapter 3 in L. V. Cralley and L. J. Cralley, Eds., Patty's Industrial Hygiene and Toxicology, Vol. III, 2nd Edition, Theory and Rationale of Industrial Hygiene Practice, John Wiley & Sons, NY (1984).
[11] Youden W. J. and E. H. Steiner. Statistical Manual of the Association of Official Analytical Chemists, AOAC, Washington, DC (1975).
[12] Taylor, J. K. Statistical Techniques for Data Analysis, Lewis Publishers, Chelsea, MI (1990).
[13] Kelley, W. D., T. A. Ratliff, Jr., and C. Nenadic. Basic Statistics for Laboratories - A Primer for Laboratory Workers, Van Nostrand Reinhold, New York (1992).
[14] Horwitz, W., L. R. Kamps, and K. W. Boyer. "Quality Assurance in the Analysis of Foods for Trace Constituents," J. Assoc. Off. Anal. Chem., 63, 1344-54 (1980).
[15] DeVoe, J. R., Ed. ACS Symp. Ser. No. 63, American Chemical Society, Washington, DC (1977).
[16] Shulman, S. A., J. H. Groff, and M. T. Abell, "Performance of Laboratories Measuring Silica in the Proficiency Analytical Testing Program," Amer.Ind.Hyg. Assoc.J., 53: 49-56 (1992).
[17] American Association for Laboratory Accreditation, A2LA 1993 Directory of Accredited Laboratories, Gaithersburg, MD (1993).
[18] NIOSH/DPSE Standard Operating Procedure, "SOP018 Limits of Detection and Quantitation," Cincinnati, OH (1991).
[19] Kanare, H. M., Writing the Laboratory Notebook, American Chemical Society, Washington, DC (1985).

D. GENERAL CONSIDERATIONS FOR SAMPLING AIRBORNE CONTAMINANTS

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1. CHOOSING MEASUREMENT METHODS AND SAMPLING MEDIA

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 to conduct analysis of collected samples, 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 that 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, 2 and 3 for common types, characteristics and behavior of sampling media). 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 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 h. 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) because of 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. Humidity may affect the adsorption as well.

Silica gel

Less reactive than charcoal. Because of its polar nature, it is hygroscopic and shows a decrease in breakthrough capacity for non-water soluble substances with increasing humidity [3].

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 [4].

Molecular sieves

Zeolites and carbon molecular sieves 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 [5].

Thermal desorption

Thermal desorption tubes may contain several different sorbents in order to collect a wide range of different chemicals [6]. 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. TYPES AND USES OF AEROSOL SAMPLERS [6]

Membrane filters

By far the most frequently used filters. This class of filters includes those made from polyvinyl chloride, Teflon®, silver, and mixed cellulose esters. Filters from this class are used for sampling asbestos, minerals, PAH's, particulates not otherwise regulated, and elements for ICP analysis.

Glass and quartz fiber filters

Quartz filters have replaced glass in many applications. They are used in applications such as sampling for mercaptans and diesel exhaust.

Polycarbonate straight pore filters

Because of their characteristics, these filters are good for the collection of particles to be analyzed by electron microscopy and x-ray fluorescence.

Respirable dust samplers

The 10-mm nylon cyclone and (preferably) conductive cyclones with a 50% cut at 4 μm are used with polyvinyl chloride filters to collect various forms of silica.

Inhalable dust samplers

The Institute of Occupational Medicine's (IOM) sampler is used, in conjunction with a polyvinyl chloride filter, for sampling formaldehyde on dust [7].

TABLE 3. FACTORS AFFECTING THE COLLECTION OF GASES, VAPORS, and AEROSOLS [2, 7]

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.

Temperature stability of a filter must be considered when sampling hot environments such as stack effluents.

Humidity*

Water vapor is adsorbed by polar sorbents; their breakthrough capacity for the analyte is thereby reduced for most organic compounds. However, for water soluble compounds, the breakthrough capacity is increased, e.g., chlorine and bromine [8] and formaldehyde [3]. This effect varies from substantial for more polar sorbents, such as charcoal and silica gel, to a smaller effect for Ambersorbs™ and porous polymers.

Filter media may also be affected by humidity. Moisture may affect a filter's collection efficiency. Very low humidities (≤10% RH) may make some filters (e.g., cellulose ester) develop high charge levels, causing non-uniform deposits and repulsion of particles [9]. Water absorption by some filters (e.g., cellulose ester) can cause difficulty in obtaining tare weights for gravimetric analysis.

Sampling flow rate*/ Face velocity

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 for most organic compounds can be significantly reduced by high humidity, lower sampling flow rates may actually result in smaller breakthrough volumes [10]. The collection efficiency of filters will change with face velocity.

Concentration*

As the concentration of contaminant in air increases, breakthrough capacity (mg adsorbed) of a solid sorbent bed increases, but breakthrough volume (L of air sampled) decreases [10].

Particle Characteristics

Filter collection efficiency is a function of pore size [11]. Particles smaller than about 0.2 μm are collected primarily by diffusion, while particles larger than about 0.2 μm are collected primarily by impaction and interception. Most sampling filters are highly efficient (≥95%) for all particle sizes, with the minimum efficiency in the 0.2 μm size range. Polycarbonate straight pore filters exhibit poor collection by diffusion, so particles smaller than the pore size are not collected efficiently.

Filter considerations

The pressure drop of a filter can limit the sampling time, because of the load on the personal sampling pump. In addition, pressure drop increases with dust loading on the

filter. Fine particles (≤0.5 μm) will increase the pressure drop much faster than coarse particles (≥10 μm). Heavy loading (≥ about 1 mg) may result in poor adhesion of collected particles to the filter surface.

*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 affected significantly 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.

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2. FIGURING SAMPLING PARAMETERS

Once the sampling media and measurement method are chosen, then the specific sampling parameters need to be determined [12]. 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 h for most aerosols or 10 to 200 mL/min for 8 h 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-h samples for comparison to the 100 ppm TWA. If sampling were 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 h (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.

c. **Sampling for Dusts Using a Membrane Filter**

Given parameters:	Method 7401 for Alkaline Dusts
Recommended Sample Volume:	70 L @ 2 mg/m^3; 1000 L max.
Useful Range of the Method:	0.76 to 3.9 mg/m^3
OSHA PEL:	2 mg/m^3 (NaOH)
Recommended Flow Rate:	1 to 4 L/min

Suppose it is desired to determine both an exposure taking place during a specific 20 minute operation as well as a TWA exposure of workers exposed to sodium hydroxide and the concentrations are unknown.

20 Minute Process Sample: This sample would meet the method conditions by sampling for the 20 minutes at 4 L/min since this would collect 80 L. Sampling at 1, 2, or 3 L/min for 20 minutes would probably not allow for the collection of sufficient sample required for analysis.

TWA Determination: In this situation, it is necessary to collect an 8-h sample to compare with the 2 mg/m^3 OSHA PEL. Since an 8-h TWA sample covers 480 minutes, sampling can no longer be done at 4 L/min since this would collect 1920 L, almost twice the upper recommended sample volume. Sampling at 1 L/min would collect a 480 L sample, and sampling at 2 L/min would collect a 960 L sample, both acceptable per the conditions of the method.

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 sample 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 sample (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 labeling 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"). Do not ship volatiles together with air samples. 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

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, labeled 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. Media blanks should also be included. These unexposed, unopened samplers will give an estimate of media background. The laboratory should analyze at least six (6) media blanks from the same lot as the field samples. 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 the following chapter for a detailed discussion of spiking procedures.

5. DIRECT-READING METHODS

The variety of types 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 [13]. Many direct-reading instruments now used for personal or area measurements have evolved from laboratory or process control instruments [14].

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. Because of the severe conditions to which direct-reading instruments may be subjected, performance checks and preventive maintenance on a periodic 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.

*NOTE: A portable instrument is defined as weighing less than 4.5 kg (10 lbs.) and powered by self-contained batteries [15]. 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.

6. SAMPLING STRATEGY

To obtain the maximum amount of information during the course of a survey with a minimum number of samples, a statistical sampling strategy should be developed before conducting any survey [16]. 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 4. 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 4. Minimum sample size (n) for including (@ 90% confidence level) at least one high risk employee* [16]

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 AND CALIBRATION TECHNIQUES

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 determinating 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 after each repair and if they have been abused. 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 [17]. 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 [17]. 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
   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 [18]. The expression for this correction is as follows.

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

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

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).

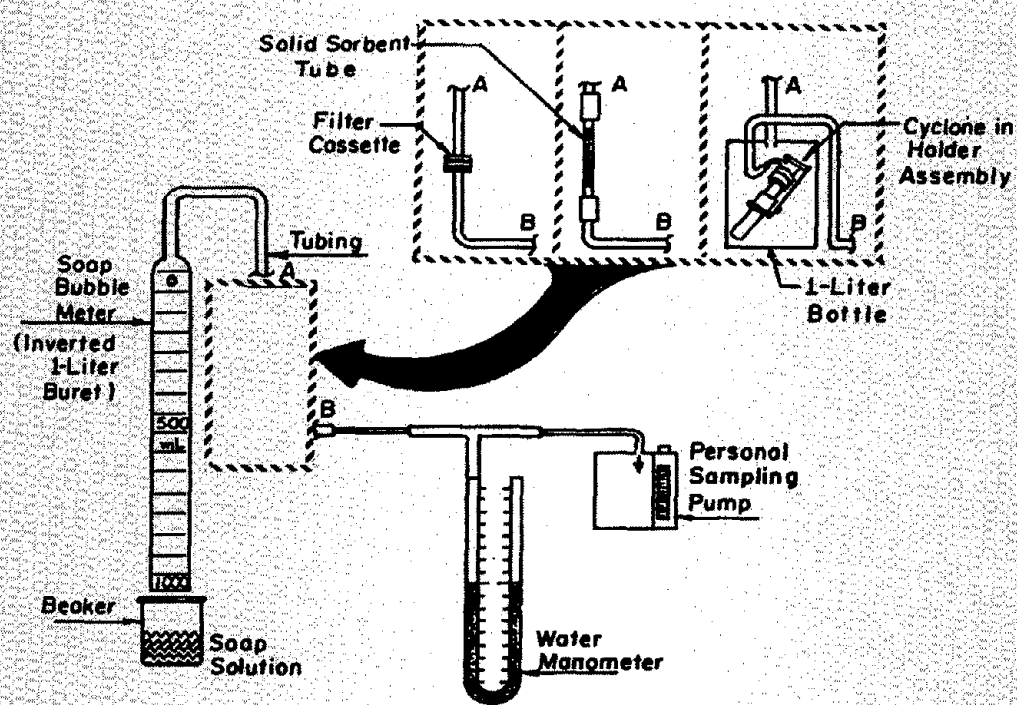


Figure 1. Calibration Apparatus.

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 cellulose backup pad or stainless steel screen. Close the cassette using a press [19] or other technique that ensures cassette parts mate evenly and positively to prevent leakage. Seal the filter holder with plastic tape or a shrinkable cellulose band to reduce contamination during filter removal.

(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 holder 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 [20]). 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, 2.2 L/min for the Higgins-Dewell cyclone [21], or 2.5 L/min for the aluminum cyclone), 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 cellulose backup pad or stainless steel screen. 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.

e. **Jarless Method of Calibration of Cyclone Assemblies [23]**

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter "calibration jar."

(1) Connect the pump to a pressure gauge or water manometer, a light load equal to 2 to 5" H_2O, and an electronic bubble meter or standard bubble tube.

(2) Adjust the pump to 1.7 L/min as indicated on the bubble meter/tube, under the light load conditions (2 to 5" H_2O) as indicated on the pressure gauge or manometer.

(3) Increase the load until the pressure gauge or water manometer indicates between 25 and 35" H_2O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min ± 5%.

(4) Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed. If the loading caused by the cyclone assembly is between 2 and 5" H_2O, the calibration is complete and the pump and cyclone are ready for sampling.

8. REFERENCES:

[1] First MW [1995]. Air Sampling and Analysis of Air Contaminants: An Overview. In: Cohen BS, Hering SV, Eds. Air Sampling Instruments, 8th ed. Cincinnati, OH: ACGIH, pp. 1-18.

[2] Melcher RG [1987]. Laboratory and Field Validation of Solid Sorbent Samplers. In: Taylor JK, Ed. Sampling and Calibration for Atmospheric Measurements, ASTM STP 957, Philadelphia PA: American Society for Testing and Materials, pp. 149-165.

[3] Iraneta PC, Collamati RA, Costello DN, Crowley RJ, Fernandez RL, Hopkins MR, Knowles CE, Martin DM [in press]. A validation study for a new active sampler for the analysis of formaldehyde in workplace and indoor air. Am Ind Hyg Assoc J.

[4] Kennedy ER [1988]. Sampling Reactive Materials. In: Advances in Air Sampling, ACGIH. Chelsea, MI: Lewis Publishers, pp.175-188.

[5] Langhorst M [1983]. A Hollow Fiber Device for Separating Water Vapor from Organic Vapors. Am Ind Hyg Assoc J *44* :592.

[6] Hodgson AT, Binenboym J, German JR [1988]. A Multisorbent Sampler for Volatile Organic Compounds in Indoor Air. In: Advances in Air Sampling, ACGIH. Chelsea, MI: Lewis Publishers, pp. 143-157.

[7] NIOSH [1994]. Formaldehyde on Dust: Method 5700. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[8] Lippmann M [1995]. Filters and Filter Holders. In: Cohen BS, Hering SV, Eds. Air Sampling Instruments, 8th ed. Cincinnati, OH: ACGIH, pp. 247 - 278.

[9] Cassinelli ME [1991]. Development of a solid sorbent monitoring method for chlorine and bromine with determination by ion chromatography. Appl Occup Environ Hyg *6*:215-226.

[10] Chen CC, Baron PA [1996]. Aspiration Efficiency and Wall Deposition in the Fiber Sampling Cassette," Am Ind Hyg Assos J, *52*: 142-152.

[11] Foerst D [1979]. A Sampling and Analytical Method for Vinylidene Chloride in Air. Am Ind Hyg Assoc J, *40*:, 888-893.

[12] Lee KW, Ramamurthi M [1993]. Filter Collection. In: Willeke KW, Baron PA, Eds. Aerosol Measurement. New York: Van Nostrand Reinhold.

[13] Eller PM [1986]. Operational Limits of Air Analysis Methods. Appl Ind Hyg *1(2)*: 91-94.

[14] Woebkenberg ML, McCammon CS [1995]. Direct-Reading Gas and Vapor Instruments. In: Cohen BS, Hering SV, Eds. Air Sampling Instruments, 8th ed. Cincinnati, OH: ACGIH, pp 439-510.

[15] Enviro Control, Inc. [1981]. Assessment of Engineering Control Monitoring Equipment, Final Report, NIOSH Contract 210-79-0011, available from NTIS, Springfield, VA 22161 as Order Nos. PB83-152629 (Vol. 1) and PB83-152637 (Vol. 2).

[16] Woebkenberg ML,Woodfin WJ [1983]. NIOSH-developed systems for monitoring equipment evaluations. In: Proceedings of third annual national symposium on recent advances in the measurement of pollutants in ambient air and stationary sources. Raleigh, NC: EPA-600/9-84-00 (1983).

[17] Busch KA, Leidel NA, Statistical Models for Occupational Exposure Measurements and Decision Making. In: Advances in Air Sampling, ACGIH. Chelsea, MI: Lewis Publishers, pp 319-336.
[18] Kovein RJ, Hentz PA [1988]. A Digital Current Capacity Tester for Rechargeable Batteries. Appl Ind Hyg *3(2)*:51-54.
[19] Okladek J [1988]. An Overview of Flow Metering Devices. Amer Lab *20*:84-90.
[20] Frazee PR, Tironi G [1987]. A Filter Cassette Assembly Method for Preventing Bypass Leakage. Am Ind Hyg Assoc J, *48*:176-180.
[21] ACGIH [1996]. 1996 TLVs® and BEIs® Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, pp. 45-48.
[22] Higgins RLJ, Dewell P [1967]. A Gravimetric Size Selecting Personal Dust Sampler. In: Davies CN, Ed. Inhaled Particles and Vapors II, Oxford: Pergammon Press, pp. 575-586.
[23] Feldman R [1997]. A Jarless Method for the Calibration of Cyclone Assemblies. Unpublished information, Occupational Safety and Health Administration, Cincinnati, OH.

E. DEVELOPMENT AND EVALUATION OF METHODS

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Table I Values of the Bias and the Precision Required to 51
Obtain Designated Accuracy in Percentage Units

1. METHOD DEVELOPMENT

The development and evaluation of analytical methods that are useful, reliable and accurate for industrial hygiene monitoring problems require the application of some general guidelines and evaluation criteria. The guiding objective in this work requires that, over a specified concentration range, the method provide a result that differs no more than ±25% from the true value 95 times out of 100. The application of consistent evaluation criteria and guidelines is particularly important when methods are developed by different individuals and organizations (e.g., contractors or outside laboratories) 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 method that is developed. This chapter provides an outline of a generalized set of evaluation criteria prepared by NIOSH researchers for the evaluation of sampling and analytical methodology [1].

In the development of a sampling and analytical method, there is a logical progression of events that cover a search of the literature to gather pertinent information and the preliminary experimentation for selection of analysis technique and sampling medium. To initiate the development of a method, the identity of the analyte must be as fully defined as possible. Physical and chemical properties of the analyte should be defined so that procedures for proper handling and use of the analyte can be prepared. These also aid in establishment of analyte

purity. Potential sources of this information include chemical reference books, health hazard evaluation reports, bulk sample analyses, material safety data sheets, chemical process information, etc.

Since innovation is a key element in the sampling and analytical method development process, detailed experiments for the initial development of the sampling approach and optimization of the analytical procedure are better left to the discretion of the researcher. During development, it should be recognized that appropriate, statistically designed experiments will optimize the amount of information obtained. Therefore, consultation with a statistician about appropriately designed experiments will be of value during this phase of the research.

a. Preliminary Experimentation

Several key points, including calibration and selection of measurement technique and sampling media, should be studied during the initial method development experiments. The selection of sampling medium and procedure is a decision that usually is made early in the method development process. The physical state of the analyte (i.e., gas, aerosol, vapor, or combination thereof) plays an important factor in the selection of an appropriate sampler. Analytes which can exist in more than one physical state may require a combination of sampling media in one sampler for efficient collection [1]. Where possible, commonly available and easily used samplers should be investigated initially. As the preliminary testing of a sampling method progresses, further modification in the sampling medium or sampler design may be required and may affect the measurement procedure. Sampler design and media selection considerations should include U.S. Department of Transportation regulations and restrictions for shipment back to a laboratory for analysis.

Since industrial hygiene analytical methods are geared toward measuring personal exposure, the size, weight, and convenience of the sampler are important elements in sampler design. The personal sampler should allow freedom of movement and should be unobtrusive, unbreakable, and not prone to leakage. The pressure drop across the sampler should not be so great as to limit sample collection times to $\leq$ 10 h with personal sampling pumps. For situations where only a short term sample will be required (i.e., 15 min for ceiling determinations), this $\leq$ 10 h recommendations can be reduced to $\leq$ 1 h. The use of potentially toxic reagents should be avoided unless they can be used safely. Reagents used should not pose any exposure hazard to the worker wearing the sampler or to the industrial hygienist taking the samples.

b. Recovery of the Analyte from the Medium

During the course of method development experiments, the ability to recover the analyte from the sampling medium should be determined. A suggested experiment to accomplish this entails the fortification of sets of 6 samplers with amounts of analyte equivalent to sampling concentrations of 0.1, 0.5, 1.0, and 2.0 (or higher) times the exposure limit for a minimum of 4 h at the typical sampling rate used for that type of sampler. If the analyte has a ceiling or short-term exposure limit, the amount of analyte fortified should be adjusted for the shorter sampling time required for this type of exposure limit. If the sampler has a backup section, then a like number of separate backup sections should be fortified with amounts of analyte

equivalent to 25% of the amount fortified on the front sections of the samplers, since this amount has been used to characterize the breakthrough limit of useful samples [2]. Samples (and backup sections) should be prepared for analysis and analyzed according to previously determined procedures. Results of these analyses should be expressed in terms of estimated percent recovery according to the following formula:

$$\text{Percent Recovery}_{(est.)} = \frac{\text{(Amount of analyte found on sampler)}}{\text{(Amount of analyte fortified on sampler)}} \times 100\%$$

After initial analyses of the samples, the samples should be resealed and analyzed on the following day, if possible. If the sample workup procedure results in a solution of the sample, these solutions should be recapped after the initial analysis if possible and reanalyzed on the following day using fresh standards.

The recovery of the analyte should be calculated for the primary and backup media in the sampler. Although complete recovery of the analyte from the sampler is most desirable, at a minimum, the estimated recovery of the analyte from the primary collection medium should be greater than or equal to 75% for concentrations equivalent to sampling 0.1, 0.5, 1.0, and 2.0 times the exposure limit. If recovery varies with analyte loading, results should be graphed as recovery versus loading during calibration of the method, so that appropriate correction can be made to sample results, as long as recovery is greater than 75% [3]. If estimated recovery does not exceed 75%, the method is not suitable for monitoring at this limit.

Estimated recovery from any backup media should be noted so that appropriate corrections can be applied if breakthrough of the sampler has occurred during sampling. The recovery of the analyte from the medium in the backup section of a sampler may be different from that of the front section, since the backup section of a sorbent-based sampler usually contains only half of the sorbent of the primary section. If the same volume of desorption solvent is used for both the primary and backup sections of the sampler, the desorption equilibrium can be shifted, since the backup section is being desorbed by twice the volume (i.e., on a mL solvent/mg sorbent basis) [4].

Reanalysis of the samples on the day after initial analysis indicates if immediate analysis after sample preparation is required. Often when processing a large number of samples, it may be necessary to prepare the samples for analysis as a batch. In these instances, the last samples may not be analyzed for up to 24 h or more after preparation because of the time required for analysis. If samples prepared for analysis exhibit time-dependent stability after desorption, analyses must be conducted within acceptable time constraints. Analysis and reanalysis results should agree within 5% of each other.

c. Stability of the Analyte on the Medium

An extension to the experiment described above may be performed to investigate potential stability problems early in the experimentation. An additional set of fortified samples at each of the 4 concentrations should be prepared and analyzed after 7-days' storage at room

temperature. Recovery should be similar to the above results within experimental error. Discrepancies larger than those expected by experimental error indicate sample stability problems that will need correcting by additional developmental effort (e.g., refrigerated storage). Comparison of results can be performed with statistical tests, such as an analysis of variance (ANOVA) [5] test of the "Day" difference or a paired t-test [6] of the means of the Day 1 and Day 7 storage results.

2. METHOD EVALUATION

After the initial development experiments for the method have been completed and a method has been proposed, the sampling and analysis approach should be evaluated to ensure that the data collected provides reliable, precise, and accurate results. Specifically, the goal of this evaluation is to determine whether, on the average, over a concentration range of 0.1 to 2 times the exposure limit, the method can provide a result that is within ±25% of the true concentration 95% of the time. For simplification, the true concentration is assumed to be represented by an independent method. An experimental approach for collecting the data necessary for this determination is described below.

As part of the evaluation of a method, the sampling of a generated atmosphere is needed to more adequately assess the performance of a method [8,9,10]. This allows the determination of 1) the capacity of the sampler; 2) the efficiency of analyte collection by the sampler; 3) the repeatability of the method; 4) the bias in the method; 5) interferences in the collection of the sample. Concentration ranges to be used in the evaluation of the method should be based on several factors. These ranges, at a minimum, should cover 0.1 to 2.0 times the exposure limit. In some instances, higher multiples of the exposure limit can be added if needed (e.g., 10 times the exposure limit). In situations where multiple exposure limits (i.e., from different authorities) exist for an analyte, the lowest exposure limit should be used to set the lower limit of the evaluation range (0.1 times lowest exposure limit) and the highest limit used to calculate the upper limit of evaluation range (2 times the highest exposure limit). Intermediate evaluation concentrations should be within these exposure limits. The toxicity of an analyte (e.g., suspected carcinogenicity) may indicate that a concentration lower than that calculated by the exposure limit should be included in the measurement and evaluation ranges. Previous monitoring information from other methods may indicate that typical concentrations of the analyte may be below or above a concentration range based on the exposure limit. In this case, this lower or upper level may be included in the method evaluation.

a. Feasibility of Analyte Generation

In order to provide a realistic test of the method under study, air concentrations covering the range from 0.1 to 2 times the exposure limit of the analyte should be generated. The generated atmospheres should be homogeneous in concentration and representative of the environment encountered when sampling for the analyte in the workplace.

When attempting to generate a concentration of an analyte, the impact of environmental conditions, such as temperature, pressure, humidity, and interferences, on sampler performance and/or generation should be considered. The effect of elevated temperature on the collection medium of a sampler may decrease the capacity of the sampler or may

decompose the analyte during generation and sampling. Reduced pressure may also reduce the capacity of a sampler. High relative humidity in many instances has been observed to reduce sampler capacity [3]. In other instances it has increased sampler capacity [11]. A typical interference(s) should be generated along with the analyte to approximate a typical workplace sampling environment.

Generation of particulate material can be extremely complex [12,13], especially if particles of a required size range must be generated for the evaluation of a specified sampler inlet design. The aerodynamic performance of the generator is a factor in the generation of this type of atmosphere and should be evaluated carefully. Appropriate, independent methods should be available to verify particle size, if this is a critical element in the generation.

The concentration of the generated atmosphere should be verified either by well characterized gravimetric/volumetric means or by analysis of replicate samples (if possible) by an independent method at each concentration used. Further details on this verification are included in the literature [1]. A statistician should be consulted for advice on the design and sample sizes to accomplish this validation. Ideally, the independent method should not be biased and should provide an accurate estimate of the concentration generated, assuming error is randomly distributed around the mean. Also the precision and bias of the independent method should be homogeneous over the concentrations investigated. (See Reference 1 for the definitions of these attributes.) In instances where the concentration of the generator can be based only on calculations using flow rates in the generator and the amount of analyte injected, the generation system should be well characterized [1] so that analyte losses are minimized.

In some instances, generation of an analyte may be difficult and even hazardous. As an alternative to direct generation in these cases, samplers may be fortified with an amount of analyte expected to be sampled over a specified period of time at a specific flow rate. When this is necessary, fortification of the sampler by vaporization of a known amount of analyte onto the sampling medium is a more appropriate method, since this approach more closely approximates a generated atmosphere. The alternative of direct application of a solution of analyte onto the collection medium is less desirable but may be necessary in some instances. After fortification, air, conditioned at both high and low humidity, should be drawn through samplers at the flow rate and time period used in the calculations for the amount of analyte expected to be collected. In the method report, the fact that samples were not collected from a generated atmosphere should be discussed.

b. Capacity of the Sampler and Sampling Rate

To determine the applicability of the sampling method, the capacity of the sampler should be determined as a function of flow rate and sampling time. This is particularly important if the analyte has both a short-term exposure limit (STEL) and a time-weighted average.

Flow rates typical for the media selected should be used. These may range from 0.01 - 4 L/min, depending on sampler type. At extremely low flow rates (ca. 5 mL/min), the effect of diffusion of the analyte into the sampler must be considered. Flow rates should be kept at a high enough rate to prevent diffusion from having a positive bias in the sampler. Sampling

should be performed at three different flow rates covering the range appropriate for the particular sampler type, unless the sampler is designed to operate at only one flow rate. Sampling times should range from 22.5 min for STELs to 900 min (15 h) for time-weighted averages. Shorter sampling times (e.g., 7.5 to 22.5 min) may be used for ceiling © measurements. Flow rates should be based on accurately calibrated sampling pumps or critical orifices. The amount of analyte collected at the lowest flow rate and shortest sampling time should be greater than the limit of quantitation of the method. The generated concentration used for capacity determination should be at least 2 times the highest published exposure limit and verified by an independent method.

Sampling should be conducted at ambient, elevated (>35 °C), and low (<20 °C) temperatures to assess the effect of temperature on sampling. To assess the effect of humidity on capacity, sampling should be performed at both low and high humidities (≤20% and ≥80%, since both have been observed to affect capacity [11,3]. Triplicate samplers at three different flow rates should be included to verify capacity at each of the six different humidity and temperature levels. For samplers which contain backup sampling media, only the front section of the sampler should be used. A means is required to quantitate analyte in the effluent from the sampler. This may involve the use of a backup sampler, continuous monitor or other appropriate means which can provide a measure of analyte concentration in the sampler effluent (ca. 1 - 5% of the influent concentration). If the mass of analyte found on a backup sampler totals 5% of the mass found on the front sampler or if the effluent concentration of the sampler contains 5% of the influent concentration, breakthrough has occurred and the capacity of the sampler has been exceeded.

If the analyte is a particulate material and collected with a filter, the capacity of the filter is defined by the pressure drop across the sampler or by the loading of the filter. For 37-mm filter-based samplers, pressure drop should be less than 40 inches (1016 mm) of water for total loading less than 2 mg. Larger filters may tolerate higher loadings.

If the collection process is based primarily on adsorption, breakthrough time should be proportional to the inverse of the flow rate [14]. This relationship can be checked by plotting the 5% breakthrough time versus the inverse of the flow rate. If the resulting plot is a straight line, then this relationship should hold for all flow rates in the flow rate range studied. Some nonlinearity in the plot may be noted due to experimental variability and assumptions made to simplify the relationship of breakthrough time and flow rate. Results from these experimental trials should provide a prediction of the capacity of the sampler at various flow rates and sampling times. If the flow rates and sampling times used in the experiment do not provide for sufficient capacity, a lower flow rate range may have to be studied and the experiment repeated.

With samplers which use reagents for collection of the analyte, the amount of the reagent in the sampler will also be a limiting factor in the capacity of the sampler, based on the stoichiometry of the reaction. Other factors, such as residence time in the sampler and kinetics of reaction between analyte and reagent, may affect the capacity of this type of sampler.

The combined temperature and humidity conditions that reduce sampler capacity to the greatest extent should be used in all further experiments. The Maximum Recommended Sampling Time (MRST) for a specific flow rate is defined as the time at which sampler capacity was reached, multiplied by 0.667. This adds a measure of safety to this determination. The relationship of breakthrough time with flow rate can be used to adjust flow rates to optimize specific sampling times.

c. Sampling and Analysis Evaluation

To assess the performance of a method, certain additional experimental parameters should be evaluated through a series of defined experiments. The effect of environmental conditions (e.g., pressure, interferences) on sampling efficiency of the sampling medium can be evaluated by a factorial design [15]. The temperature, relative humidity, flow rate, and sampling times, determined in the experiment described above to have most severely limited sampler capacity, should be used in these experimental runs. At a minimum, the effect of concentration on method performance should be investigated. Three sets of 12 samples should be collected from an atmosphere containing concentrations of 0.1, 1.0, and 2.0 times the exposure limit at the humidity determined above to have reduced sampler capacity for the MRST determined in the preceding experiment. If the analyte has a short-term or ceiling exposure limit in addition to a 8-hour time-weighted average, an additional 12 samplers should be collected at the STEL or C limit for the recommended sampling period at the appropriate flow rate. Potential interferences in the work environment should be included in the generation experiments to assess their impact on method performance. Concentrations up to 2 times the exposure limit value for the interference should be included. Other environmental factors may be studied, but will require a more comprehensive experimental design.

The effects of environmental conditions on analyte recovery should be assessed. A factorial design can be used to evaluate these factors to determine which exert a significant effect on analyte recovery. Those factors which are found to influence analyte recovery should be investigated further to determine if their impact is predictable. If these effects are not predictable, the utility of the method will be limited, based on the conditions defined by this experiment. If only concentration is evaluated, the analyte recovery should be the same at all concentrations after correctable biases have been included, such as desorption efficiency.

d. Sample Stability

To assess sample stability, samples should be collected from a generated atmosphere, stored under defined conditions (i.e., ambient or refrigerated, light or dark), and analyzed at specified time periods. A concentration of 0.5 times the lowest exposure limit should be sampled with 30 samplers for a minimum of ½ the MRST. The humidity and temperature of the generator should be at the same level as defined in the sample capacity experiment to reduce sample capacity. The samplers should be divided randomly into one group of 12, one group of 6, and four groups of 3, with the group of 12 analyzed as soon after collection as possible (Day 0). The group of 6 samplers should be analyzed after 7 days. The four remaining sets of 3 samplers should be analyzed after 10, 14, 21, and 30 days. The conditions of storage are determined by the nature of the analyte. If there is an indication of analyte instability on the

sampling medium, refrigeration of the samplers may be required. However, storage for the first 7 days should be at room temperature.

Samples should be stable for a minimum of 7 days under ambient conditions to simulate shipping to a laboratory for analysis. If the average analysis results of the samplers analyzed on day 7 differs from the set analyzed on day 0 by more than 10%, the method does not meet the sample stability criterion. Either additional precautions, such as shipment on ice and refrigerator storage, may be required or the method may have to be modified to address this problem. If a plot of recovery versus time indicates that recovery decreased by more than 10% after the initial 7-day storage period, sample instability is a problem. If samples need to be stored for longer periods, more restrictive storage conditions are required. Remedial action, such as cold storage may solve this longer term storage problem. After remedial precautions have been instituted in the method, the sample stability of the method must be redetermined.

e. Precision, Bias, and Accuracy

Results from four sets of samplers used in the analyte recovery experiment, the sampling and analysis experiments (e.g., the environmental parameters experiments), and the sample stability experiment can be used for the estimation of precision, bias, and accuracy of the method. A more exacting treatment of this is described elsewhere [1]. Sampler results from the multi-level factorial design at the 0.1, 1.0, and 2.0 times the exposure limit value; the sampler stability experiment (at 0.5 times the exposure limit); and the environmental factors experiment are used in the calculations of method precision. The calculations for the estimated method precision, $\hat{S}_{rT}$, have been described previously [1,16,17,18]. Before obtaining a pooled estimate of method precision from the four sets of samplers listed above, the homogeneity of the precision over the range of concentrations studied should be checked using a test, such as Bartlett's test [1,16,17]. If the precision is not found to be constant over concentrations, the sample set collected at 0.1 x exposure limit should be removed and Bartlett's test recalculated. Homogeneity of the method precision at all concentration levels is an assumption required to obtain pooled estimate of method precision.

Bias is assumed to be homogeneous over the evaluation range. This assumption should be tested by estimating the bias at each concentration and testing these for homogeneity using the procedures described in the literature [1]. Method bias should be less than 10%. A test for this is also described [18].

The bias and precision estimates can be used with the graph presented in Figure 1 or in Table I to estimate accuracy [19]. The bias and precision estimates are plotted on the x- and y-axes of the graph. The intersection of these points on the parabolic grid in the graph can be used to estimate the accuracy of the method. This procedure gives an estimate of method accuracy but does not yield the statistic required to test compliance of the method with the $\pm 25\%$ accuracy criterion. Techniques for the latter determination are discussed in the Appendix and elsewhere [1].

If the results for 4 concentrations fail the 25% accuracy criterion, then the set of samples collected at 0.1 x exposure limit should be excluded from the data set. The pooled $\hat{S}_{rT}$ and the

bias should be recalculated on this reduced data set before performing the accuracy analysis described in the previous paragraph.

For the 12 samplers collected at the ceiling limit, the accuracy analysis described above should be repeated using only the data collected at the ceiling limit.

3. FIELD EVALUATION

While field evaluation is not required in method evaluation, it does provide a further test of the method, since conditions which exist in the field are difficult to reproduce in the laboratory. Also unknown variables may affect sampling results when field samples are taken. This type of evaluation is recommended to further study the performance of the method in terms of field precision, bias, interferences and the general utility of the method.

Both the collection of area samples and personal samples should be included in the field evaluation of the method. Area samples should provide an estimate of field precision and bias. Personal samples may confirm these values and also provide a means to assess the utility of the method. A statistical study design should be prepared, based on the variability of the method and the statistical precision required for estimates of the differences in analyte concentrations yielded by the independent method and the method under evaluation [20].

If this type of statistically designed study is not feasible, a minimum of 20 pairs of samples of the method under study and an independent method should be used for personal sampling. Placement of the samplers on the workers should be random to prevent the biasing of results due to the "handedness" of the worker. Workers sampled should be in areas where both low and high concentrations of the analyte may be present.

As a minimum, sets of 6 area samplers paired with independent methods should be placed in areas of low, intermediate, and high analyte concentration. If the atmosphere sampled is not homogeneous, precautions may have to be taken to ensure that all samplers are exposed to the same concentrations. This can be done by using field exposure chambers, such as those described in the literature [21,22].

Field precision and bias of the area sampler results of the method under study should compare with laboratory evaluation results, provided that precautions have been taken to ensure that all samplers have been exposed to the same homogeneous atmosphere. Differences in precision and bias should be investigated. Sources of variation should be studied and corrections implemented where necessary. Evaluation of personal sampler results should be done cautiously, since observable differences may be due to work practices or other situations which are beyond the control of the method.

A field evaluation of a method also allows the developer of the method to determine its ruggedness. Although this may be a subjective judgement, first hand experience with the method in the field may suggest changes in the sampler or method that may make the method more easily used in the field and less subject to variability.

4. DOCUMENTATION

Development and evaluation research on a sampling and analytical method should be documented in a final report. The report should describe what was determined about the method. If the results of the statistical analysis of the data indicate there is not 95% confidence that the accuracy of the method is less than or equal to ±25%, the report should state this fact. In some instances, the method may actually have an accuracy of less than 25%, but a larger sample size must be used to prove this statistically (See Appendix 1 of Reference 1).

The final report can be either a technical report or a failure report. The technical report (acceptable method developed) documents the successful development of the method. This report may be prepared in a format appropriate for submission to a peer-reviewed journal for publication. The failure report (no acceptable method developed) documents the research performed on an attempted method development for an analyte or analytes. The report should describe the failure of the method, as well as other areas of the method research that were successful. Recommendations to solve the failure of the method may be included.

If an acceptable method is developed, a sampling and analytical method should be prepared in appropriate format. The format of the resulting method should provide clear instructions for the use of the method. Sampling, sample workup, and analysis procedures should be clearly described. The necessary equipment and supplies for the method should be listed clearly in the method. A summary of the evaluation of the method should be included, as well as a discussion of method applicability and lists of interferences and related references. As a check on the clarity and performance, new methods 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.

5. APPENDIX - ACCURACY AND ITS EVALUATION

In the development of a sampling and analytical method, one of the goals is to minimize the measurement error to the lowest feasible and practical levels. It is assumed that all feasible corrections to reduce error have been made in the laboratory experimentation process. Method evaluation requires adequate characterization of the magnitude and distribution of the uncorrectable error that cannot be prevented. One might consider a hypothetical experiment in which a method is used repeatedly to measure the same concentration, T, under the same conditions. These measurements would tend to exhibit a pattern or statistical distribution, here assumed to be normal, with a mean, μ, and standard deviation, σ. The distribution can be characterized in terms of two components: its location relative to T, which is the systematic error termed bias (B), is given by $(\mu\text{-}T)/T$; and its spread, which is the random error termed imprecision (S_{rT}), is given by σ/μ. The bias and imprecision are used to determine the inaccuracy of the method but they are also important characteristics of the error in and of themselves as will be discussed below.

Accuracy refers to the closeness of the measurements to T but it is defined in terms of the discrepancy of the measurements from T. Inaccuracy (I) is defined as the maximum error,

regardless of sign, expressed as a percentage of T that occurs with a probability of 0.95. Thus, an inaccuracy (or accuracy) of 20% means that on the average 95 of every 100 measurements will differ from T by no more than 0.2T. The accuracy criterion for single measurements mentioned at the beginning of this chapter, often termed the "NIOSH Accuracy Criterion," requires I to be less than or equal to 25%.

Accuracy, bias, and imprecision have the following relationship:

$$0.95 = \Phi\left(\frac{I-B}{(1+B)S_{rT}}\right) - \Phi\left(\frac{-I-B}{(1+B)S_{rT}}\right) \quad (1)$$

where $\Phi(x)$ denotes the probability that a standard normal random variable is less than or equal to x. A practically exact numerical solution to Equation (1) can be readily programmed in PC-SAS® [23]. A DOS program, ABCV. EXE, is also available which solves for I (denoted by A in the program), S_{rT} (denoted by CV in the program), or B when the values for the other two quantities are input. An estimate of I can be obtained in either case by entering estimates of B and S_{rT}. An approximate solution, which is accurate to about 1.1 percent, is given as follows [19]:

$$\left.\begin{aligned} I &= 1.57\ (B+1)\cdot S_{rT} + \sqrt{(0.39\ (B+1)\cdot S_{rT})^2 + B^2} \text{ for theoretical or true I} \\ \hat{I} &= 1.57\ (\hat{B}+1)\cdot \hat{S}_{rT} + \sqrt{(0.39\ (\hat{B}+1)\cdot \hat{S}_{rT})^2 + \hat{B})^2} \text{ for estimates of I} \end{aligned}\right\} \quad (2)$$

Also, the nomogram in Figure 1 can be used to solve for I or an estimate of I by entering B and S_{rT} or their estimates. Procedures for obtaining "best" single point and 95% confidence interval estimates of B, and S_{rT} and a 90% confidence interval estimate for I are given in Kennedy et al [1].

The 90% confidence interval for I can be used to infer whether the method passes or fails the 25% accuracy criterion for single measurements (AC) with 95% confidence as follows:

1) The method passes with 95% confidence if the interval is completely less than 25%.

2) The method fails with 95% confidence if the interval is completely greater than 25%.

3) The evidence is inconclusive if the interval includes 25% (there is not 95% confidence that the AC is true or that it is false).

When researchers interpret the results from analyses of the type described above, it is important to consider that most methods have many uses in addition to individual

measurement interpretation. Because accuracy is very important whenever any quantity is to be estimated, the ideal ("other things being equal") is to use the most accurate estimator regardless of its bias or imprecision. However, it is crucial to distinguish between the accuracy of the source or "raw" measurements and that of the final estimator, which might involve many intermediate analyses or operations. Unfortunately, the most accurate input or raw measurements do not always produce the most accurate final result unless the latter is a single measurement. The bias and imprecision of the source measurements can be differentially affected by intermediate operations in producing the final estimate. For example, if the final estimate is a function of a single average of many source measurements, its bias is not affected by the averaging while imprecision is reduced as a function of the square root of the number of measurements. Thus, a lower biased method might be preferable to another even if the inaccuracy of the latter is less. On the other hand, in comparative studies, the desired estimate is either a difference or ratio of means of measurements in which there can be partial or complete cancellation of the bias in the source measurements. Thus, the bias of the method used for the source measurements may be of little importance. If there are several methods applicable for a given user's project (regardless of whether all fulfill the AC for single measurements), the analyst would be well-advised to consult with the user (preferably in advance of measurement) to determine which of those methods would produce the most accuracy for the final results or estimates needed by that particular user. Accuracy, bias, and imprecision jointly form a complete or sufficient set for the efficient description of the measurement error characteristic of any method.

6. REFERENCES

[1] Kennedy, E.R., T.J. Fischbach, R. Song, P.M. Eller, and S.A. Shulman. Guidelines for Air Sampling and Analytical Method Development and Evaluation. NIOSH Technical report, (DHHS (NIOSH) Publication No. 95-117) Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, 1995.

[2] Streicher, R., E. Kennedy, and C. Lorberau: Strategies for the Simultaneous Collection of Vapours and Aerosols with Emphasis on Isocyanate Sampling. *Analyst 119*:89-97 (1994).

[3] Melcher, R., R. Langner, and R. Kagel: Criteria for the Evaluation of Methods for the Collection of Organic Pollutants in Air Using Solid Sorbents. *Am. Ind. Hyg. Assoc. J. 39*:349-361 (1978).

[4] Saalwaechter, A., C. McCammon, Jr., C. Roper, and K. Carlberg: Performance of the NIOSH Charcoal Tube Technique for the Determination of Air Concentrations of Organic Vapors. *Am. Ind. Hyg. Assoc. J. 38*:476-486 (1977).

[5] Posner, J., and J. Okenfuss: Desorption of Organic Analytes from Activated Carbon. *Am. Ind. Hyg. Assoc. J. 42*:643-646 (1981).

[6] Box, G.E.P., W.G. Hunter, and J.S. Hunter: *Statistics for Experimenters*. New York, NY: John Wiley & Sons, Inc., 1978. pp. 170-174.

[7] Box, G.E.P., W.G. Hunter, and J.S. Hunter: *Statistics for Experimenters*. New York, NY: John Wiley & Sons, Inc., 1978. pp. 97-102.

[8] National Institute for Occupational Safety and Health: Gas and Vapor Generating Systems for Laboratories by W. Woodfin (DHHS/NIOSH Publication No. 84-113). Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, 1984.

[9] Nelson, G.O.: *Controlled Test Atmospheres.* Ann Arbor, MI: Ann Arbor Science Publishers, 1971.

[10] Nelson, G.O.: *Gas Mixtures: Preparation and Control.* Ann Arbor, MI: Lewis Publishers, 1992.

[11] Cassinelli, M.E.: Development of a Solid Sorbent Monitoring Method for Chlorine and Bromine in Air with Determination by Ion Chromatography. *Appl. Occup. Environ. Hyg. 6*:215-226 (1991).

[12] Willeke, K., ed.: *Generation of Aerosols and Facilities for Exposure Experiments.* Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980.

[13] Hinds, W.C.: *Aerosol Technology.* New York, NY: John Wiley and Sons, 1982. pp. 379-395.

[14] Jonas, L.A., and J.A. Rehrmann: Predictive Equations in Gas Adsorption Kinetics. *Carbon 11*:59-64. [1973].

[15] Box, G.E.P., W.G. Hunter, and J.S. Hunter: *Statistics for Experimenters.* New York, NY: John Wiley and Sons, Inc., 1978. pp. 306-350.

[16] Anderson, C., E. Gunderson, and D. Coulson: Sampling and Analytical Methodology for Workplace Chemical Hazards. In: *Chemical Hazards in the Workplace*, edited by G. Choudhary. Washington, DC: American Chemical Society, 1981. pp. 3-19.

[17] Busch, K., and D. Taylor: Statistical Protocol for the NIOSH Validation Tests. In *Chemical Hazards in the Workplace*, edited by G. Choudhary. Washington, DC: American Chemical Society, 1981. pp. 503-517.

[18] National Institute for Occupational Safety and Health: *Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances with a Statistical Appendix by K. Busch* by E. Gunderson, C. Anderson, R. Smith, and L. Doemeny (DHHS/NIOSH Publication No. 80-133). Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, 1980.

[19] Fischbach, T., R. Song, and S. Shulman: Some Statistical Procedures for Analytical Method Accuracy Tests and Estimation. In preparation.

[20] European Committee for European Standardization (CEN), *Workplace atmospheres - Requirements and test method for pumped sorbent tubes for the determination of gases and vapours (prEN 1076).* Technical Committee 137, Working Group 2, 1993.

[21] Cassinelli, M.E., R.D. Hull, and P.A. Cuendet: Performance of Sulfur Dioxide Passive Monitors, *Am. Ind. Hyg. Assoc. J. 45*:599-608 (1985).

[22] Kennedy, E.R., D.L. Smith, and C.L. Geraci, Jr.: Field Evaluations of Sampling and Analytical Methods for Formaldehyde. In *Formaldehyde - Analytical Chemistry and Toxicology* edited by V. Turoski. Washington, DC: American Chemical Society, 1985. pp. 151-159.

[23] SAS Institute, Inc.: *SAS® Language Guide for Personal Computers, Release 6.03 Edition.* SAS Institute, Inc. Cary, NC, 1988.

Figure 1: Nomogram Relating Accuracy to Precision and Bias

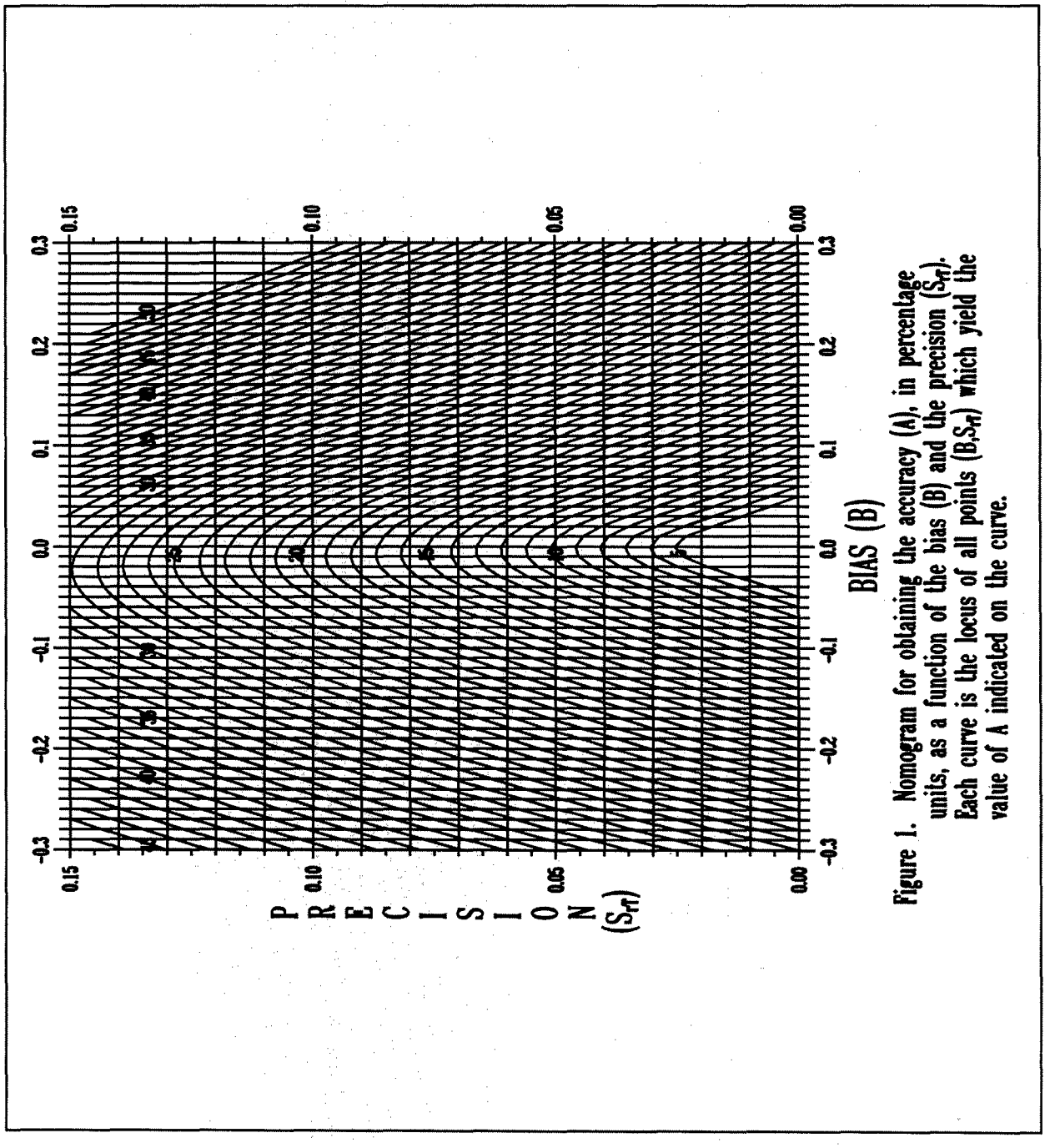


Figure 1. Nomogram for obtaining the accuracy (A), in percentage units, as a function of the bias (B) and the precision (S_{rt}). Each curve is the locus of all points (B,S_{rt}) which yield the value of A indicated on the curve.

Table I: Values of the Bias (B) and the Precision (S_{rT}) Required to Obtain Designated Values of Accuracy (A) in Percentage Units.[1]

A (%)	B (%)	S_{rT} (%)
5	-3.5	0.9450*
5	-2.5	1.5589*
5	0.0	2.5511*
5	2.5	1.4829*
5	3.5	0.8811*
10	-7.5	1.6432*
10	-5.0	3.1999*
10	0.0	5.1022
10	5.0	2.8952*
10	7.5	1.4139*
15	-10.0	3.3777*
15	-5.0	6.3814
15	0.0	7.6530
15	5.0	5.7736
15	10.0	2.7636*
20	-10.0	6.7554
20	-5.0	9.4476
20	0.0	10.2043
20	5.0	8.5478
20	10.0	5.5271
25	-10.0	10.1284
25	-5.0	12.3869
25	0.0	12.7548
25	5.0	11.2072
25	10.0	8.2869
30$	-15.0&	10.7287
30$	-7.5	14.5544
30$	0.0	15.3061
30$	7.5	12.5236
30$	15.0&	7.9299
35$	-15.0&	14.3038
35$	-7.5	17.5897
35$	0.0	17.8574
35$	7.5	15.1353
35$	15.0&	10.5724

* Below the minimum attainable precision with a 5% pump correction.
$ Does not fulfill the Accuracy Criterion (±25% of the true value).
& Does not fulfill the bias criterion (±10%).

[1] Note: the values shown in this table are population or theoretical values.

F. APPLICATION OF BIOLOGICAL MONITORING METHODS

by Alexander W. Teass, Ph.D., Raymond E. Biagini, Ph.D., D. Gayle DeBord, Ph.D., NIOSH/DBBS, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS

1. INTRODUCTION

Biological monitoring is the assessment of worker exposure to a hazardous agent through the measurement of a biomarker which results from contact with the agent. The biomarker typically is the agent or its metabolite in a biological specimen derived from the worker; examples are styrene in expired air, styrene in blood, and mandelic and phenylglyoxylic acids (metabolites of styrene) in urine. The biomarker also can be an effect of the agent, such as elevated levels of zinc protoporphyrin in blood, caused by exposure to lead. Industrial hygiene professionals use biological monitoring to assess the risk to workers from exposure hazards and to demonstrate the adequacy of control technologies and intervention strategies.

This chapter provides an overview of the effective and appropriate application of the biological monitoring analytical methods published herein. The analytical results should be interpreted in light of what is known about the uptake, metabolism, and excretion of the agent and the effect of the agent on the body. This chapter introduces these areas, provides other considerations, and gives references to sources of more comprehensive information on specific agents and situations. Additional resources on biological monitoring include reviews [1-10], books [11-17], and methods and quality assurance manuals [18-22].

2. GENERAL CONSIDERATIONS

A worker exposed to a chemical receives a dose of that chemical only if it is absorbed into the body. Absorption can occur after dermal contact, inhalation, ingestion, or from a combination of those routes. The extent of absorption from an exposure and the rate of absorption depend on the properties of the chemical (especially its solubility in lipids and water) and the route of exposure. Once absorbed, a chemical is distributed and partitions into various tissues due to tissue variations in pH, permeability, etc. Highly water-soluble chemicals may be distributed throughout the total body water, while more lipophilic substances may concentrate in the body fat or other lipid-rich tissues, such as the brain. The loss of chemical from the body can loosely be defined as elimination, which depends on metabolism and excretion. Chemicals may be eliminated by numerous routes, including fecal, urinary, exhalation, perspiration, and lactation. A chemical can be excreted from the body without metabolism, in which case the parent compounds may be detectable in the urine, breath, or fecal material. In other cases, the chemical may be metabolized through oxidation, reduction, hydrolysis, or a combination of these processes, often followed by conjugation with an endogenous substrate. Conjugation of a chemical or metabolite is a pathway for excretion. The more important conjugation reactions include glucuronidation, amino acid conjugation, acetylation, sulfate conjugation, and methylation. Metabolism and excretion and the rates of metabolism and excretion can be affected by age, diet, general health status, race, and other factors. In general, the metabolic products will be more water soluble than the parent chemical. Where metabolism yields more than one product, the relative amounts of each and the parent-metabolite ratios are affected by an individual's general health status, diet, genetic makeup, degree of hydration, time after

exposure, and other factors. The kidney is the major organ of excretion and is the primary route for water-soluble substances. These substances enter the urine by either glomerular filtration, tubular secretion, or sometimes both mechanisms.

Biological monitoring has the potential to assess worker exposure to industrial chemicals by all routes, including inhalation, skin absorption, and ingestion. Selection of an appropriate biomarker for an exposure requires knowledge of the distribution, metabolism, and excretion of the toxicant sufficient for selection of the proper compound to be determined, biological medium to be sampled, and time for obtaining a specimen. Often, most of the toxicological and pharmacological information available is from experimental animals and, thus, not always directly applicable to humans.

Monitoring Goals. Air monitoring (or workplace environmental monitoring) and biological monitoring have complementary goals and frequently are applied simultaneously in industrial hygiene investigations.

1. *Air monitoring.* Air monitoring provides an estimate of the potential for exposure to an agent. The presence of a health hazard is estimated by reference to environmental exposure limits, such as the NIOSH recommended exposure levels, the Occupational Safety and Health Administration (OSHA) permissible exposure levels, or the threshold limit values (TLVs™) of the American Conference of Governmental Industrial Hygienists (ACGIH). Compared with biological monitoring, air monitoring offers advantages in certain situations. If the agent has acute toxic effects on the respiratory tract or the eyes, air monitoring is the logical tool for controlling the exposure. Air monitoring can be conducted continuously and, thus, can detect peak exposures to dangerous chemicals.

2. *Biological monitoring of exposure.* A biomarker of exposure represents uptake of the agent through all routes of exposure. Thus, compared to air monitoring, biological monitoring offers a better estimate of the health risk in situations where routes of exposure other than inhalation are significant.

    a. The rate of disappearance of a biomarker determines the period of time after exposure during which the level of the biomarker is still affected by the exposure [7]. The levels of rapidly disappearing biomarkers primarily reflect exposures during the previous several hours. On the other hand, biomarkers which disappear over the course of several weeks reflect one, several, or numerous exposure incidents occurring anytime during a period of several weeks previous to the measurement.

    b. Some toxicants accumulate in one or several parts of the body and are in dynamic equilibrium with the sites of toxicity. In the case of polychlorinated biphenyl (PCB), which accumulates in fatty tissue, the blood level of PCB reflects the amount stored in the body.

    c. When the site of critical action for a toxicant is known, the concentration of the biomarker at that site can be used as a measure of the biologically effective dose.

Carboxyhemoglobin is such a biomarker for carbon monoxide poisoning. In this case, the biomarker level is correlated with the health effect.

3. *Biological monitoring of effect.* This term is defined as monitoring reversible biochemical changes resulting from exposures. The degree of change is less than that which leads to injury and is not associated with a known irreversible pathological effect [23]. Biological monitoring of effect is not health surveillance through which individuals with early signs of adverse health effects are identified. Some examples of biomarkers of effect are:

   a. Zinc protoporphyrin in blood, levels of which increase with lead exposure, because lead inhibits the biosynthesis of heme [24].

   b. Protein and DNA adducts of aromatic amines in blood. These adducts can both reflect the intensity of exposure and be correlated with the biologically effective dose.

   c. Antibodies produced against low-molecular-weight molecules [25]. Some chemicals, while not immunogenic in their own right because of small size and other limitations, may bind to constitutive polymers (such as host proteins) and become immunogenic, causing the production of specific antibodies. Alternatively, such exposures may lead to production of new antigenic determinants, through nonadduct-forming reactions of the agent with selected protein-carrier molecules. Antibodies can be made to these modified proteins or to the parent hapten-conjugate [26]. In both cases, the antibodies may remain in the human system much longer than the toxicant which initiated their development.

Biological Matrices. The most common matrices used for biological monitoring are exhaled air, blood, and urine.

1. Monitoring exhaled air is limited to volatile chemicals. Exhaled air monitoring is not suitable for chemicals inhaled as aerosols or for gases and vapors, which decompose upon contact with body fluids or tissues, or which are highly soluble in water, such as ketones and alcohols [3].

2. Blood is the medium which transports chemicals and their metabolites in the body. Therefore, most biomarkers present in the body can be found in the blood during some period of time after exposure [4].

   a. A chemical in the blood is in dynamic equilibrium with various parts of the body: the site of entry, tissues in which the chemical is stored, and organs in which it is metabolized or from which it is excreted. Thus, the concentration of a biomarker in the blood may differ between regions of the circulatory system. This would be the case during pulmonary uptake or elimination of a solvent, which would cause differences in concentration between capillary blood (mainly arterial blood) and venous blood.

b. Two advantages of blood monitoring are: (1) The gross composition of blood is relatively constant between individuals. This eliminates the need to correct measured biomarker levels for individual differences. (2) Obtaining specimens is straightforward and with proper care can be accomplished with relatively little risk of contamination.

c. An important consideration in blood monitoring is that obtaining blood specimens requires an invasive procedure and should be performed only by trained persons.

3. Urine is more suitable for monitoring hydrophilic chemicals, metals, and metabolites than for monitoring chemicals poorly soluble in water. The concentration of the biomarker in urine usually is correlated to its mean plasma level during the period the urine dwells in the bladder [5].

a. In some instances the urine concentration is affected by the amount of the biomarker stored in the kidneys. Examples are cadmium and chromium.

b. The accuracy of the exposure estimate, using urine monitoring, depends upon the sampling strategy. The most influential factors are time of collection and urine output.

c. Measurements from 24-hour specimens are more representative than from spot samples and usually correlate better with intensity of exposure. However, collection, stabilization, and transportation of 24-hour specimens in the field are difficult and often not feasible.

3. PRACTICAL CONSIDERATIONS

Selection of Methods. The occupational health professional and the laboratory scientist should decide on appropriate methods so that the test results are interpretable to the exposure situation. The following issues should be addressed:

1. The goal of the biological monitoring method should be consistent with the goal of the industrial hygiene investigation. Is the goal to measure exposure or a health effect related to the exposure?

2. The method needs to be evaluated for the required specificity and possible interferences. If interferences from diet, drugs, alcohol, disease states, or other workplace chemicals or agents exist, they must be accounted for.

3. The method should have a sufficiently low limit of detection to differentiate exposed from nonexposed workers. A method developed when biological monitoring reference levels were higher may be inadequate for measuring exposures at and below the current guidelines.

4. Limitations of the sample matrix and its affect on the analysis need to be assessed. In general, blood serum and urine specimens require different sample preparations and may require separate methodologies to eliminate matrix effects.

5. Because of sample instability, some methods may be impractical or not feasible.

6. The method should have guidelines for interpretation of collected data. Such guidelines are discussed in **Interpretation of Results** below.

7. To minimize the risk of harm to workers, when two biological monitoring methods will provide the same information, the less invasive method should be used. Thus, methods monitoring urine or exhaled breath are preferred over those monitoring blood.

Sampling Strategy. Strict attention to specimen handling and collection is essential for quality data. The analytical laboratory should be consulted for sampling instructions. Analytical methods should provide specific directions on the collection, storage, and transportation of specimens to the laboratory. Adherence to these directions is of the utmost importance to ensure sample integrity.

1. Timing of specimen collection should be appropriate. The method should include instructions for the timing of specimen collection, that is, whether specimens should be obtained during the work shift, at the end of the shift, or at some other time during the work week. The longer the half-life of the xenobiotic, the less critical is the timing of the collection [11].

2. The baseline of a biomarker should be evaluated when the toxicant accumulates in the body, as do cadmium, lead, and polychlorinated biphenyl [11]. The baseline should also be assessed, if there is large intersubject variability in the population, such as when pseudocholinesterase in plasma is measured.

3. Care should be taken not to contaminate the specimen with either chemicals or bacteria.

4. The proper preservative (for urine or blood samples) or anticoagulant (blood) should be used, if appropriate.

5. Stability of the biomarker is assured through proper storage and shipment of the specimen to the laboratory and proper storage by the laboratory.

Correction of Urinalysis Data for Dilution. Determination of biomarkers in individual urine samples is confounded by urine dilution, which can vary substantially with fluid intake and physical work load. In practice, this effect of urine dilution is reduced by adjusting the measured concentration of the biomarker to a normal value [5,27], such as:

1. Specific gravity. This adjustment is made by multiplying the measured concentration of the biomarker by the ratio of [(1.024 - 1)/(sp.g. - 1)], where sp.g. is the specific gravity of the urine sample and 1.024 is the assumed normal specific gravity value.

2. Urine output. The measured concentration of the biomarker is multiplied by the ratio R/0.05, where R is the output for the sample in liters per hour. The urine output for the sample is computed from the volume (liters) of the sample and the time (hours) elapsed since the last voiding. The adjustment is to a mean output of 0.05 L/h.

3. Creatinine concentration. This is the most frequently used adjustment. Creatinine is excreted by glomerular filtration at a relatively constant rate of 1.0-1.6 g/day. Urinary creatinine concentration can be determined by spectrometric or kinetic methods based on the Jaffé alkaline picrate reaction, enzymatic methods, and methods based on mass spectrometry and liquid chromatography [28]. The adjusted value is the quantity of the biomarker per unit quantity of creatinine.

There are other considerations to be taken into account when adjusting urinalysis data for dilution:

1. Adjustment to the creatinine level is not appropriate for compounds, such as methanol, that are excreted in the kidney primarily by tubular secretion.

2. Since the mechanism of excretion of a biomarker can be altered if the urine is very concentrated or very dilute, measurements on samples, having creatinine concentrations outside the range 0.5 to 3 g/L or having specific gravities outside the range 1.010 to 1.030, are unreliable [5].

3. Adjustment for creatinine concentration, while correcting for dilution, introduces additional variation, which must be considered when the data are evaluated. Among the factors affecting the rate of creatinine excretion are the muscularity of the subject, physical activity, urine flow, time of day, diet, pregnancy, and disease [27].

Quality Assurance. Good data require the utilization of an effective quality assurance program. In 1992, regulations implementing the Clinical Laboratory Improvement Amendments (CLIA) of 1988 were published by the Health Care Finance Administration and the Public Health Service to ensure that analysis of human specimens was done accurately and under good quality control procedures [29]. Any analysis of human specimens that can be used by a health care practitioner to assess the health of the individual or used in the diagnosis, prevention, or treatment of disease or impairment falls under the CLIA guidelines. Since, as a minimum, biological monitoring data are used to prevent occupational disease or impairment, CLIA guidelines apply. Key components of the CLIA quality assurance program include:

1. Strict management of specimen collection, handling, storage, and transportation, thus ensuring sample integrity

2. Thorough verification of a method by the laboratory before use on field specimens

3. High level of analytical quality control

4. Participation in proficiency testing programs, if available

5. Documented instrument evaluation and maintenance programs

6. Investigation of communication failures and complaints

7. Documentation of performance and corrective actions

Ethical Considerations. There are several ethical issues that must be considered before initiating a biological monitoring procedure [30, 31]:

1. Method should be appropriate for the requirements of the investigation.

2. Procedures should not threaten the health of the participant.

3. Risk of using invasive methods must be justified by the benefits.

4. Informed consent from the participant is required. This consent must be given when the participant feels no fear of reprisals, if consent is withheld.

5. Results should be kept confidential and shared only with the occupational health professional and the participant.

Laboratory Safety. When dealing with human specimens, a biosafety program is essential. Pathogens such as hepatitis B and human immunodeficiency virus (HIV) may be present in blood, saliva, semen, and other body fluids. Transmission can be by an accidental nick with a sharp object; exposure through open cuts, skin abrasions, and even dermatitis or acne; and indirectly through contact with a contaminated environmental surface. There are five major ways to reduce the potential for exposure to biological pathogens [32, 33]:

1. Engineering controls, which include mechanical or physical systems used to eliminate biological hazards, must be available. These are items such as biosafety cabinets or self-sheathing needles.

2. Employee work practices are essential to minimize exposure to pathogens. Good personal hygiene procedures and avoidance of needle recapping can lessen exposure to pathogens.

3. Personal protective equipment, such as gloves and masks, should be used when necessary.

4. Good housekeeping procedures, which involve cleanup of the work area, are essential to avoid contamination of the laboratory.

5. Employees, who have been identified as potential exposure candidates, should be vaccinated for hepatitis B.

Universal precautions that take into account the above five measures should be practiced with every biological sample received. It is not possible to know if a particular sample may contain pathogens; therefore, each sample should be treated as if contaminated.

4. INTERPRETATION OF RESULTS

A biological monitoring analytical result is a determination of the level of the biomarker in the biological matrix from which the sample was taken, at the time it was taken. Extrapolation from that datum to insight on the exposure of the worker requires knowledge of how the human body responds to the agent.

1. Exposure can be estimated when a quantitative relationship between environmental level and biomarker level has been demonstrated.

2. Health risk can be estimated when a quantitative relationship between a health effect and biomarker level has been demonstrated.

3. Where knowledge of a biomarker is limited, one can only infer from its presence above the background level that exposure has occurred.

Reference Levels. For a number of agents there exist published reference levels, termed "biological action levels" by the World Health Organization [18], which serve as guidelines for interpreting biological monitoring data. In the absence of published biomonitoring action levels, biomarker levels indicating occupational exposure have been inferred by comparison with the normal background levels of the biomarker.

1. Biomonitoring action levels vary in their derivation, some being from correlations with exposure, others with health effects. These reference levels should be used only when one has full understanding of their derivation. Sources of biomonitoring action levels include:

    a. Biological Exposure Indices (BEI) adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) [34];

    b. Biological Tolerance Values for Working Materials (BAT) published by the Deutsche Forschungsgemeinschaft's (DFG) Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area [35];

    c. Lauwerys' and Hoet's "Summary of Recommendations" in *Industrial Chemical Exposure. Guidelines for Biological Monitoring* [11];

    d. Occupational Safety and Health Administration (OSHA) standards [36, 37].

2. When biomarker data are available for exposed and nonexposed populations that are otherwise similar, the upper limit of the range for the nonexposed population may serve as a reference level. Levels of biomarker significantly above that limit suggest occupational exposure to the agent. For those biomarkers for which there is no measurable background level in nonexposed humans, this reference level is effectively the detection limit of the analytical method. In any case, levels of the biomarker above the reference level suggest there was occupational exposure, but give no information on the potential health effect.

Variability. Biological monitoring data are subject to a number of sources of variability [2], including:

1. Rates at which an agent is taken up by the body, metabolized, and excreted. These vary from person to person and are affected by the person's age, sex, and physical workload.

2. Route of exposure. For example, absorption through the lungs is much faster than adsorption through the skin. Thus, the appearance and elimination of a biomarker will be slower if the agent entered through the skin. If the biomarker is rapidly excreted, the optimum timing for collection of biological samples will be different for the two routes of entry.

3. Fluctuation in environmental exposure. Such fluctuations will be tracked by the levels of rapidly eliminated biomarkers, those reflecting exposure of the immediately previous several hours.

4. Personal protective equipment worn and a person's work practices.

5. Existence of a biomarker in both a free and a conjugated form, the relative proportions of which can vary substantially from person to person. For example, aniline is present in urine as both the free amine and as acetanilide, its acetyl derivative. Some persons are genetically predisposed to excrete primarily free aniline; while others, primarily, acetanilide.

6. Concurrent exposure to several agents that compete for the same biotransformation sites in the body. This may lead to altered metabolism and excretion, which would change the relationship between exposure or health effect and the level of the biomarker [8].

7. Concurrent exposure to several agents, which are metabolized to the same biomarker. This frustrates the interpretation of the biological monitoring data. For example, trichloroacetic acid is a biomarker for trichloroethylene, 1,1,1-trichloroethane, and perchloroethylene.

8. Consumption of alcoholic beverages [9], since ethanol is metabolized by three pathways used for metabolism of other organic agents. After consumption of one drink, the ethanol concentration in the blood is about 1000 times higher than from a normal occupational exposure and may affect significantly the metabolism of industrial chemicals.

9. Medications [10], health, and diet.

Because of the variability of biomarkers, judgments on the exposure or health risk of workers frequently cannot be made based on a single determination. It may be necessary to base conclusions on the data for a group of similarly exposed workers or on data from a series of samples from a single worker.

5. REFERENCES

[1] Aitio, A. Biological Monitoring Today and Tomorrow, *Scand. J. Work Environ. Health, 20 special issue,* 46-58 (1994).

[2] *Droz,* P.O. Biological Monitoring I: Sources of Variability in Human Response to Chemical Exposure, *Applied Industrial Hygiene, 4*(1), F-20 (1989).

[3] Fiserova-Bergerova (Thomas), V., L. K. Lowry, J. Rosenberg. Biological Monitoring II: Measurements in Exhaled Air, *Applied Industrial Hygiene, 4*(2), F-10 (1989).

[4] Lowry, L. K., J. Rosenberg, V. Fiserova-Bergerova (Thomas). Biological Monitoring III: Measurements in Urine, *Applied Industrial Hygiene, 4*(3), F-11 (1989).

[5] Rosenberg, J., V. Fiserova-Bergerova (Thomas), L. K. Lowry. Biological Monitoring IV: Measurements in Urine, *Applied Industrial Hygiene, 4*(4), F-16 (1989).

[6] Fiserova-Bergerova (Thomas), V., J. T. Pierce. Biological Monitoring V: Dermal Absorption, *Applied Industrial Hygiene, 4*(8), F-14 (1989).

[7] Droz, P. O., V. Fiserova-Bergerova (Thomas). Biological Monitoring VI: Pharmacokinetic Models Used in Setting Biological Exposure Indices, *Applied Occupational & Environmental Hygiene, 7*(9), 574 (1992).

[8] Ogata, M., V. Fiserova-Bergerova, P. O. Droz. Biological Monitoring VII: Occupational Exposures to Mixtures of Industrial Chemicals, *Applied Occupational & Environmental Hygiene, 8*(7), 609 (1993).

[9] Fiserova-Bergerova, V. Biological Monitoring VIII: Interference of Alcoholic Beverage Consumption with Biological Monitoring of Occupational Exposure of Industrial Chemicals, *Applied Occupational & Environmental Hygiene, 8*(9), 757 (1993).

[10] Rosenberg, J. Biological Monitoring IX: Concomitant Exposure to Medications and Industrial Chemicals, *Applied Occupational & Environmental Hygiene, 9*(5), 341 (1994).

[11] Lauwerys, R. R., P. Hoet. *Industrial Chemical Exposure. Guidelines for Biological Monitoring,* Ch. 1, Lewis Publishers, Ann Arbor, Michigan (1993).

[12] *Biological Monitoring of Exposure to Chemicals. Organic Compounds,* M. H. Ho, H. K. Dillon, Eds., John Wiley & Sons, Inc., New York (1987).

[13] *Biological Monitoring of Exposure to Chemicals. Metals,* H. K. Dillon, M. H. Ho, Eds., John Wiley & Sons, Inc., New York (1991).

[14] *Biological Monitoring and Surveillance of Workers Exposed to Chemicals,* A. Aitio, V. Riihimaki, H, Vainio, Eds., hemisphere Publishing Corporation, Washington, D. C.

[15] *Biological Monitoring for Pesticide Exposure. Measurement, Estimation, and Risk Reduction,* R. G. M. Wang, C. A. Franklin, R. C. Honeycutt, J. C. Reinert, Eds., ACS Symposium Series 382, American Chemical Society, Washington, D. C. (1989).

[16] *Biological Monitoring. An Introduction,* S. Que Hee, Ed., Van Nostrand Reinhold, New York (1993).

[17] Proceedings of International Symposium on Biological Monitoring, 12-15 October 1992, Kyoto, Japan, M. Ikeda, Ed., *International Archives of Occupational and Environmental Health, 65(1 Supplement)* (1993).

[18] World Health Organization. *Guidelines on Biological Monitoring of Chemical Exposure at the Work Place, Volumes 1 & 2,* WHO, Geneva (in press).

[19] DFG German Science Foundation. *Analyses of Hazardous Substances in Biological Materials, Volumes 1-4,* J. Angerer, K. H. Schaller, VCH Verlagsgesellschaft mbH, Weinheim (1985-1994).

[20] *Methods for Biological Monitoring. A Manual for Assessing Human Exposure to Hazardous Substances,* T. J. Kneip, J. V. Crable, American Public Health Association, Washington, D. C. (1988).

[21] Baselt, R. C. *Biological Monitoring Methods for industrial Chemicals,* Biomedical Publications, Davis (1980).

[22] Quality Assurance Considerations for Biological Monitoring, Chapter 12. In *"Quality Assurance Manual for Industrial Hygiene Chemistry,"* AIHA Laboratory Analysis Committee. American Industrial Hygiene Association, Fairfax, pp. 77-89 (1995).

[23] Health & Safety Executive, United Kingdom. Biological Monitoring for Chemical Exposures in the Workplace. Guidance Note EH56 from Environmental hygiene Series HMSO, London (1992) in World Health Organization. *Guidelines on Biological Monitoring of Chemical Exposure at the Workplace, Volumes 1 & 2,* WHO, Geneva (in press).

[24] Alessio, L., V. Foa. Lead, *Human Biological Monitoring of Industrial Chemical Series,* L. Alessio, A. Berlin, R. Roi, M. Boni, Eds., Commission of the European Communities, Luxembourg (1983).

[25] Biagini, R. E., S. L. Klincewicz, G. M. Henningsen, B. MacKenzie, J. S. Gallagher, I. L. Bernstein, D. I. Bernstein. Antibodies to Morphine in Workers Occupationally Exposed to Opiates at a Narcotics Manufacturing Facility and Evidence for Similar Antibodies in Heroin Abusers, *Life Sciences, 47,* 897-908 (1990).

[26] Biagini, R. E., J. S. Gallagher, W. M. Moorman, E. A. Knecht, W. Smallwood, I. L. Bernstein, D. I. Bernstein. Immune Responses of Cynomlogus Monkeys to Phthalic Anhydride, *Journal of Allergy and Clinical Immunology, 82,* 23-29 (1988).

[27] Boeniger, M. F., L. K. Lowry, J. Rosenberg. Interpretation of Urine Results Used to Assess Chemical Exposure with Emphasis on Creatinine Adjustments: A Review, *Am. Ind. Hyg. Assoc. J., 54,* 615 (1993).

[28] Spencer, K. Analytical Reviews in Clinical Biochemistry: The Estimation of Creatinine, *Ann. Clin. Biochem., 23,* 1-25 (1986).

[29] Health Care Financing Administration and Public Health Service. 42 Code of Federal Regulations Part 493--Laboratory Requirements. Clinical Laboratory Improvement Amendments of 1988; Final Rule, in *Federal Register, 57*(40), 7137-7185 (February 28, 1992).

[30] International Commission on Occupational Health. *International Code of Ethics for Occupational Health Professionals,* Singapore (1992).

[31] Zielhuis, R. L. Biological Monitoring. Guest lecture given at the 26th Nordic Symposium on Industrial Hygiene, Helsinki, October 1977, *Scand. J. Work, Environ. & Health, 4,* 1 (1978).

[32] *Bloodborne Pathogens,* Catalog No. 858, Coastal Video Communications, Corp. Virginia Beach, Virginia (1992).

[33] *Biosafety in Microbiological and Biomedical Laboratories,* 3rd ed., J. Y. Richmond, R. W. McKinney, Eds., HHS Publication No. (CDC) 93-8395, Centers for Disease Control And Prevention and National Institutes of Health, U. S. Government Printing Office, Washington, D. C. (1993).

[34] American Conference of Governmental Industrial Hygienists (ACGIH). *1994-1995 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices,* 51-66, ACGIH, Cincinnati (1994).

[35] Deutsche Forschungsgemeinschaft (DFG). *MAK- and BAT-Values 1992. Maximum Concentrations at the workplace and Biological Tolerance Values for Working Materials Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area. Report No. 28,* 99-104, VCH Verlagsgesellschaft mbH, Weinheim (1992).

[36] *Code of Federal Regulations, Title 29,* Parts 1910.1025 Lead and 1910.1027 Cadmium, U.S. Government Printing Office, Washington, D. C.

[37] Murthy, L. I., W. E. Halperin. Medical Screening and Biological Monitoring. A Guide to the Literature for Physicians, *Journal of Occupational and Environmental Medicine, 37*(2), 170-184 (1995).

G. AEROSOL PHOTOMETERS FOR RESPIRABLE DUST MEASUREMENTS

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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 *aerodynamic	5
10 diameter	1

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.

6. REFERENCES

[1] Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices for 1993-94, 42-45, ACGIH, Cincinnati, OH (1993).

[2] British Medical Research Council: Recommendations of the MRC Panels Relating to Selective Sampling, Inhaled Particles and Vapours, Pergammon Press, Oxford (1961).

[3] Ad Hoc Working Group Report to Technical Committee 146-Air Quality, International Standards Organization, Recommendations on Size Definitions for Particle Sampling, Am. Ind. Hyg. Assoc. J., 42(5), A-64 (1981).

[4] Air Quality - Particle Size Fraction Definitions for Health Related Sampling, Technical Report ISO/TR 7708-1983(E), International Standards Organization, Geneva, Switzerland (1983).

[5] Bartley, D. L., and Breuer, G. M. Analysis and Optimization of the Performance of the 10-mm Cyclone, Am. Ind. Hyg. Assoc. J. 43, 520 (1982).

[6] Marple, V. A., and Rubow, K. L, Respirable Dust Measurements, Report for U.S. Bureau of Mines Contract No. JO113042 (1984).

[7] Hering, S., Ed., Air Sampling Instruments, 7th ed., ACGIH, Cincinnati, OH (1989).

[8] Willeke, K. and P. A. Baron, Eds., Aerosol Measurement: Principles, Techniques, and Applications, Van Nostrand-Reinhold, New York (1993).

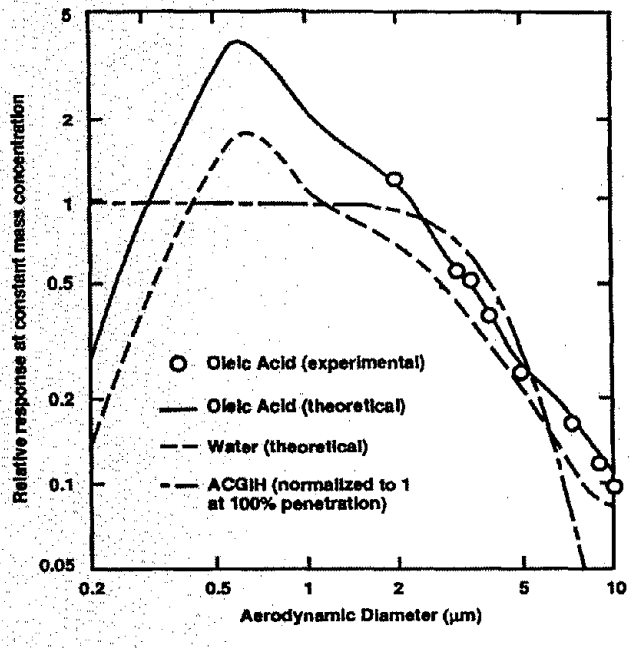


Figure 1. Experimentally determined and theoretically predicted "mass sensitivity" of the GCA RAM-1 to oleic acid and water droplets. Included for comparison is the ACGIH respirable dust penetration curve [1] normalized to one at 100% penetration.

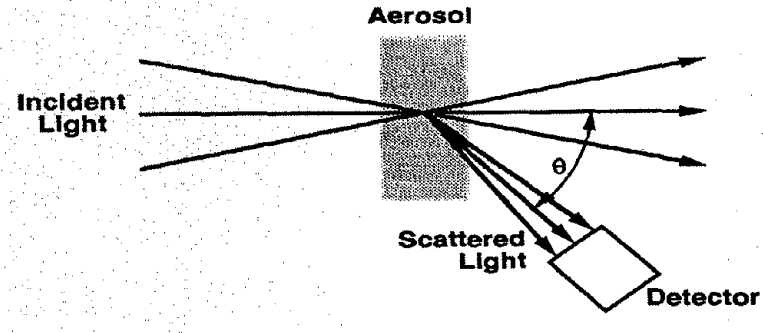


Figure 2. Diagram showing the components of an aerosol photmeter.

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].

6. REFERENCES

[1] Woodfin, W. J. and M. L. Woebkenberg. An Evaluation Of Portable Direct-Reading Oxygen Deficiency Monitors, (NIOSH, unpublished, 1984).
[2] Air Sampling Instruments, 7th ed., Ch. V, ACGIH, Cincinnati, OH (1989).
[3] Methods of Air Sampling and Analysis, 2nd ed., Morris Katz, Ph.D., Editor, Library of Congress No. 77-6826, American Public Health Association (1977).
[4] NIOSH Criteria for a Recommended Standard...Working in Confined Spaces, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-106 (1979).
[5] Parker, C. D., et al. An Evaluation of Personal Sampling Pumps in Sub-Zero Temperatures, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-117 (1978).
[6] Evaluation of Rechargeable Batteries Used in Industrial Hygiene Equipment, Final NIOSH Contract Report No. 210-78-0090 (1980).
[7] American Laboratory 1993 Buyers Guide, Am. Lab., 25(5) (February 28, 1993).
[8] Pollution Equipment News 1993 Catalog and Buyers Guide, Rimbach Publishing, Inc., 25(6) (November, 1992).

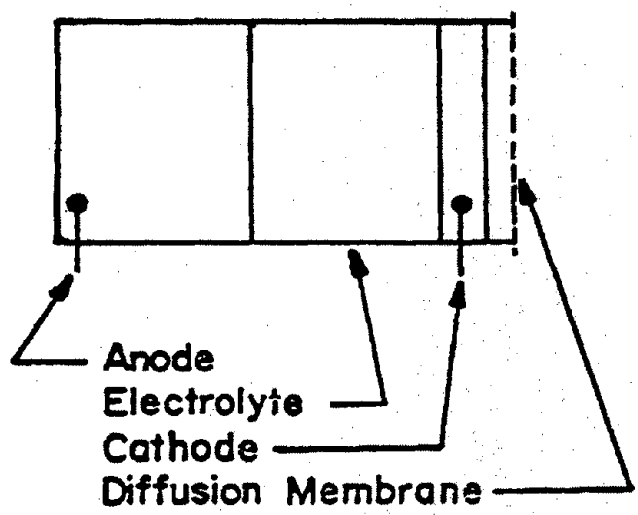


Figure 1. Electrochemical cell schematic.

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.

5. REFERENCES

[1] Jerpe, J. and A. Davis, J. Chromatog. Sci. 25(4): 154-57 (1987).

[2] Gaind, V. S., K. Vohra and F. Chai, Analyst 117(2): 161 (1992).

[3] Hinshaw, J.V., LC-GC 10(11): 851-55 (1992).

[4] Giddings, J.C., J. Chem. Ed. 39(11): 569-73 (1962).

[5] McNair, H.M. and E.J. Bonelli, Basic Gas Chromatography, p. 118 (1967).

[6] Berkley, R.E., J.L. Varns and J. Plell, Envron. Sci. Technol. 25(8): 1429-1444, (1991).

J. SAMPLING AND CHARACTERIZATION OF BIOAEROSOLS[‡]

by Paul A. Jensen, Ph.D., PE, CIH and Millie P. Schafer, Ph.D., NIOSH/DPSE

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‡Revision of Jensen PA, Lighthart B, Mohr AJ, Shaffer BT [1994]. Instrumentation used with microbial bioaerosol. In: Lighthart B, Mohr AJ, eds. Atmospheric microbial aerosols: theory and applications. New York, NY: Chapman & Hall, pp. 226-284.

1. INTRODUCTION

a. General

Bioaerosol monitoring is a rapidly emerging area of industrial hygiene. Bioaerosol monitoring includes the measurement of viable (culturable and nonculturable) and nonviable microorganisms in both indoor (e.g., industrial, office or residential) and outdoor (e.g., agricultural and general air quality) environments. In general, indoor bioaerosol sampling need not be performed if visible growth is observed. Monitoring for bioaerosols in the occupational environment is one of the many tools the industrial hygienist uses in the assessment of indoor environmental quality, infectious disease outbreaks, agricultural health, and clean rooms. Contamination (microbial growth on floors, walls, or ceilings, or in the HVAC system) should be remedied. If personnel remain symptomatic after remediation, air sampling may be appropriate, but the industrial hygienist should keep in mind that false negative results are quite possible and should be interpreted with caution. Other exceptions for which bioaerosol sampling may be appropriate include epidemiological investigations, research studies, or if situations indicated by an occupational physician and/or immunologist.

Sampling for fungi and bacteria (including *Actinomycetes*) is included in this chapter. Less developed methods for bioaerosols such as viruses, protozoa, antigenic fragments, algae, arthropods, and mycoplasmas are not addressed at this time.

b. Indoor and Outdoor Bioaerosols

In general, indoor microflora concentrations of a healthy work environment are lower than outdoor concentrations at the same location [ACGIH 1989, Step two; Macher et al. 1995]. If one or more genera are found indoors, in concentrations greater than outdoor concentrations, then the source of amplification must be found and remedied. Bioaerosol sampling is often performed out of doors for pollen and fungi to assist allergists in their treatment of patients by identifying taxa distribution and concentration in air over time. On occasion, outdoor bioaerosol sampling is conducted in an occupational environment (e.g., agricultural investigations and sewage treatment plants). Indoor bioaerosol sampling is often conducted in occupational (industrial and office environments) and nonoccupational (residential and educational buildings) settings. When sampling is indicated, it is advisable to sample before, during, and after the sampling area is occupied, including times when the heating, ventilating, and air conditioning system is activated and inactivated.

c. Viable and Nonviable Bioaerosols

Viable microorganisms are metabolically active (living) organisms with the potential to reproduce. Viable microorganisms may be defined in two subgroups: culturable and nonculturable. Culturable organisms reproduce under controlled conditions.

Information regarding environmental conditions and media to culture microorganisms is shown in Sections 3.a. and 3.c. Nonculturable organisms do not reproduce in the laboratory because of intracellular stress or because the conditions (e.g., culture medium or incubation temperature) are not conducive to growth. As the name implies, viable bioaerosol sampling involves collecting a bioaerosol and culturing the collected particulate. Only culturable microorganisms are enumerated and identified, thus leading to an underestimation of bioaerosol concentration.

Nonviable microorganisms are not living organisms; as such, they are not capable of reproduction. The bioaerosol is collected on a "greased" surface or a membrane filter. The microorganisms are then enumerated and identified using microscopy, classical microbiology, molecular biological, or immunochemical techniques. When sampling for culturable bacteria and fungi, the bioaerosol is generally collected by impaction onto the surface of a broad spectrum solid medium (agar), filtration through a membrane filter, or impingement into an isotonic liquid medium (water-based). Organisms collected by impaction onto an agar surface may be incubated for a short time, replica-plated (transferred) onto selective or differential media, and incubated at different temperatures for identification and enumeration of microorganisms [Tortora et al. 1989]. Impingement collection fluids are plated directly on agar, serially diluted and plated, or the entire volume of fluid is filtered through a membrane filter. The membrane filter is then placed on an agar surface and all colonies may be replica-plated. Culturable microorganisms may be identified or classified by using microscopy, classical microbiology, or molecular biology techniques such as restriction fragment length polymorphic (RFLP) analysis. Classical microbiology techniques include observation of growth characteristics; cellular or spore morphology; simple and differential staining; and biochemical, physiological, and nutritional testing for culturable bacteria. Analytical techniques which may be applied to both nonviable and viable microorganisms, but not distinguish between them, include polymerase chain reaction (PCR) and enzyme-linked immunosorbent assay (ELISA). Such methods may be used to identify specific microorganisms and to locate areas of contamination. Though these latter methods are generally qualitative, current research efforts involve modifying the methods to obtain semi-quantitative or quantitative results.

2. PRINCIPLES OF BIOAEROSOL COLLECTION

a. General Principles

Most aerosol sampling devices involve techniques that separate particles from the air stream and collect them in or on a preselected medium. Impaction, filtration, and impingement are three common sampling techniques used to separate and collect the bioaerosol.

b. Impaction

Impaction is used to separate a particle from a gas stream based on the inertia of the particle. An impactor consists of a series of nozzles (circular- or slot-shaped) and a target. Perfect impactors have a "sharp cutoff" or step-function efficiency curve. Particles larger than a particular aerodynamic size will be impacted onto a collection surface while smaller particles proceed through the sampler [Hinds 1982]. Marple and Willeke [1976] have reported that high velocity, inlet losses, interstage losses, and particle reentrainment affect the performance characteristics of an impactor. The cut-diameter (d_{50}) is a function of the Stk_{50}. In other words, the mass of the particles smaller than the d_{50} that are collected equals the mass of the particles larger than the d_{50} that pass through the impactor. The collection efficiency of the impactor approaches 100% when the aerodynamic diameter is greater than the d_{50} [Hinds 1982]. Aerodynamic diameter (d_{ae}) is defined as the diameter of a hypothetical sphere of unit density (ρ_p = 1 g/cm^3) that has the same settling velocity as the particle [Hinds 1982]. Impactors are selected so that the desired size particles will be collected. For the same aerosol sample, the mass and count particle distributions will have distinctive means and medians; however, they share the identical geometric standard deviation. The mass median aerodynamic diameter (MMAD) is descriptive of the mass distribution. In other words, the MMAD equals the diameter where particles larger than MMAD contribute half the collected mass; and those particles smaller than MMAD contribute the other half. The count median aerodynamic diameter (CMAD) is the median of the number of particles in a given particle distribution.

Investigators are likely to employ stationary cascade impactors or individual impactors used in survey instruments, either as the primary collection mechanism, or as a preclassifier (for example to remove nonrespirable particles from the sampled air stream). Cascade impactors consist of a stack of impaction stages: each stage consists of one or more nozzles and a target or substrate. The nozzles may take the form of holes or slots. The target may consist of a greased plate, filter material, or growth media (agar) contained in petri dishes. Each succeeding stage collects smaller particles. A filter may be used as the final stage so that all particles not impacted on the previous stages are collected. The target may be weighed to determine the collected mass, or it may be washed and the wash solution analyzed. Filters may induce more particle bounce than greased or oiled plates. Although personal cascade impactors are available, these devices are not as widely used in personal sampling for bioaerosols as are filters [Macher and Hansson 1987].

Impactors used for the collection of airborne microorganisms may have range from a single slit to more than 400 holes per stage. The particles impact onto growth medium with one or more bacterial or fungal colonies forming at some impaction sites. Multiple particles, each containing one or more organisms, passing through a single hole may be inaccurately counted as a single colony. As the number of organism-containing particles deposited onto the growth medium increases, the probability that the next organism-containing particle will impact a "clean" hole decreases. The basic formula for the coincidence correction follows:

$$P_r = N\left[\frac{1}{N} + \frac{1}{(N-1)} + \frac{1}{(N-2)} + \cdots + \frac{1}{(N-r+1)}\right]$$

Andersen [1958] and Leopold [1988] stated that P_r is the estimated culturable particle count given **r** culturable particles are observed on the sample plate, and **N** is the total number of holes per impactor stage. For example, if 75% of the holes have received one particle, the chance that the next particle will impact a "clean" hole is one in four (25%) [Andersen 1958; Andersen 1984; Leopold 1988; Macher 1989].

c. Filtration

Collection of particles from a nonbiological aerosol sample is most commonly achieved by filtration. Filter media are available in both fibrous (typically glass) and membranous forms. Deposition occurs when particles impact and are intercepted by the fibers or surface of filter membranes [Hinds 1982]. Thus, particles smaller than the pore size may be efficiently collected. Sampling filter media may have pore sizes of 0.01 to 10 µm. The efficiency of removing particles from the air depends on the face velocity (i.e., the cross sectional air velocity of the filter holder). For particles less than 1 µm, the overall efficiency decreases with increasing face velocity [Liu et al. 1983; Lippmann 1995]. For particles greater than approximately 1 µm, the filter collection efficiency is greater than 99%. The overall efficiency of membrane filters is approximately 100% for particles larger than the pore size [Lippmann 1995].

Membrane filters are manufactured in a variety of pore sizes from polymers such as cellulose ester, polyvinyl chloride, and polycarbonate. Polymeric membrane filters lack rigidity and must be used with a support pad. The choice of a filter medium depends on the contaminant of interest and the requirements of the analytical technique. For gravimetric analysis, nonhygroscopic materials such as glass fibers, silver, or polyvinyl chloride membranes are selected. For analysis by microscopy, cellulose ester or polycarbonate membranes are the usual choices.

Filters are often held in disposable plastic filter cassettes during bioaerosol sampling. The three-piece cassette may be used either in open- or closed-face modes. Open-face sampling is performed by removing the end plug and the plastic cover from the three-piece cassette and is used when the particulate must be uniformly deposited (i.e., for microscopic analysis). If a three-piece cassette is used in the open-face arrangement, the plastic cover is retained to protect the filter after sampling is concluded. All plastic cassettes are securely assembled and sealed with a cellulose shrink band or tape around the seams of the cassette to prevent leakage past the filter.

Membrane filters for use in sampling are usually supplied as disks of 37- or 47-mm diameter. Because the pressure drop across a filter increases with the air velocity

through the filter, the use of a larger (47-mm) filter results in a lower pressure drop for a given volumetric flow rate. The use of the smaller (37-mm) filter concentrates the deposit of the contaminant onto a smaller total area, thus increasing the density of particles per unit area of filter. This may be helpful for direct microscopic examination of low concentrations of organisms. In areas of high concentration, the microorganisms may have to be eluted, diluted, and then refiltered for microscopic analysis.

Filtration techniques are used for the collection of certain fungi and endospore-forming bacteria that are desiccation-resistant. The sampled organisms are washed from the surface of smooth-surface polycarbonate filters. The microorganisms in the wash solution are either cultured or refiltered to distribute the microorganisms uniformly on the membrane filter. In the latter case, the microorganisms are stained and examined microscopically [Wolf et al. 1959; Fields et al. 1974; Lundholm 1982; Palmgren et al. 1986a]. To culture the organisms, the membrane filter from each sampling cassette is washed with a 0.02% Tween™ 20 (J.T. Baker Chemical Co., Phillipsburg, NJ) in aqueous solution (three 2-mL washes), with agitation. Some of the recovered wash volume is serially diluted from full strength (1:10, 1:100, 1:1000) and 0.1 mL of each dilution is inoculated onto duplicate 100-mm x 15-mm petri dishes containing the appropriate medium. Residual culturable microorganisms on the membrane filter from each sampling cassette are counted by placing the filter on a medium in a Petri dish to allow the microorganisms to colonize. The Petri dishes are incubated and the colonies are identified and enumerated [Muilenberg et al. 1992]. This method of serial dilution allows flexibility in dealing with unpredictable levels of spores by permitting a count of the spores collected on the filter either directly or by serial dilution of the wash solution. An inherent weakness in this procedure is that high analytical dilutions can statistically exclude taxa present in the air sample at low concentrations. This dilution technique favors the predominant fungi populations at the expense of minor populations.

d. Impingement

The liquid impingers are a special type of impactor. Impingers are useful for the collection of culturable aerosols [White et al. 1975; Lembke et al. 1981; Henningson et al. 1988]. Impingers such as the Greenberg-Smith impinger or the AGI-30 use a liquid (e.g., a simple salt solution such as 0.3 mM phosphate-buffered dilution water) as the collection medium. Additives to the collection medium such as proteins, antifoam, or antifreeze aid in resuscitation of bacterial cells, prevent foaming and loss of the collection fluid, and minimize injury to the cells. The jet is positioned a set distance above the impinger base and consists of a short piece of capillary tube designed to reduce cell injury when the air is dispersed through the liquid and the particles are entrapped. The Greenberg-Smith and AGI-30 samplers operate by drawing aerosols at nominal flow rates of 28.3 and 12.5 L/min, respectively, through an inlet tube [Macher et al. 1995]. The d_{50} of these samplers is approximately 0.3 µm [Wolf et al. 1959; Cown et al. 1957]. The AGI-30 inlet tube is curved to simulate particle collection in the nasal passage [Cox 1987]. This makes it especially useful for studying infectious airborne microorganisms by

separating respirable (collection fluid) and nonrespirable (inlet tube) microorganisms. When the AGI-30 is used to recover total airborne organisms from the environment, the curved inlet tube is washed with a known amount of collecting fluid after sampling because larger particles (i.e., over 15 µm) are collected on the tube wall by inertial force. After sampling for the appropriate amount of time, 10 mL of the full-strength collection fluid is filtered through a 0.45-µm pore size membrane filter. In addition, serial dilutions of the remaining collection fluid are handled similarly [Greenberg et al. 1992]. The membrane filter is placed in a 100-mm by 15-mm sterile plastic petri plate filled with the appropriate medium and incubated for later identification and enumeration.

e. Characteristics of Several Bioaerosol Samplers

Once the purpose or the goal of bioaerosol sampling is determined, the appropriate sampling method(s) may be chosen. The selected bioaerosol sampler(s) must be capable of high efficiency particle collection within the physical and biological conditions required by the microorganism(s) to be sampled. Experimental, theoretical, and physical characteristics of several commonly used bioaerosol samplers are shown in Table I. The physical characteristics (flow rate, diameter of hole or width of slit, area of nozzle, and velocity of air through the nozzle) were used to calculate the theoretical cut-diameters of the listed samplers. The theoretical characteristics were discussed in the preceding subsections.

The particle size distribution of the bioaerosol is very important in the evaluation of the data obtained using the selected sampler. If the selected sampler does not provide particle size distribution data, then a cascade impactor such as the Andersen 6-stage sampler also should be used. For example, if an SAS-Compact sampler was the selected sampler for collection of culturable *Escherichia coli*, an Andersen 6-Stage sampler should be used to determine the particle size distribution at each location sampled. However, a membrane filter sampler is not appropriate for sampling culturable *E. coli* because the cells would desiccate and become either nonviable or viable but not culturable under these conditions [Jensen et al. 1992]. In another example, an impactor with a d_{50} of 4 µm should not be used to collect *Aspergillus niger* spores ($d_{ae} \approx$ 1-3 µm) because most spores would remain entrained in the air passing through the instrument.

General guidelines for matching the appropriate sampler with the bioaerosol of interest are shown in Table II. The bioaerosol of interest categories include culturable bioaerosol sampling, and nonculturable and nonviable bioaerosol sampling. Subcategories include free bacteria (i.e., mostly single cells), free fungi (i.e., mostly single spores), and clumped bacteria and fungi with MMAD $\geq$ 4 µm. Culturable bioaerosol sampling instruments must minimize injury during the collection process and maintain the culturability of the collected microorganisms. Free bacteria and fungi are the bioaerosols of interest in some environmental investigations, and the sampler must collect these small aerosols [Wright et al. 1969; Lee et al. 1973]. Often, however, the bioaerosols will be clumps of microorganisms or microorganisms attached to another particle such as a skin scale

or piece of lint. When using any culturable bioaerosol sampler, the investigator must select sampling time, considering estimated concentration, such that 30-100 colonies (up to 300 in some situations) develop per plate [Tortora et al. 1989]. The lower limit (30 colonies) is necessary to obtain sufficient statistical power for comparison purposes. However, when a clean room or other environment having extremely low levels of culturable bioaerosols is sampled, the lower limit of 30 colonies may not be achievable. In such a situation, a qualitative representation must be used without accommodation of statistical validity. The upper limit (100-300 colonies) is the maximum range in which one can easily count and differentiate colonies. When nonviable microorganisms are sampled or when culturability is not of concern, collection efficiency is the overriding concern. Table II is not an all inclusive listing of bioaerosol samplers. Investigators should take special note of the limitations listed at the bottom of the table.

Table I. Experimental, theoretical, and physical characteristics of several commonly used bioaerosol samplers.

Sampler	d_{50} True μm	d_{50} Theoretical μm	# holes	Q L/min	D_j or W_j mm	A_j mm^2	U_j m/s
Andersen 6-Stage [Andersen 1958, 1984]							
Stage 1	7.0	6.24	400	28.3	1.18	1.10	1.08
Stage 2	4.7	4.21	400	28.3	0.914	0.656	1.80
Stage 3	3.3	2.86	400	28.3	0.711	0.397	2.97
Stage 4	2.1	1.84	400	28.3	0.533	0.223	5.28
Stage 5	1.1	0.94	400	28.3	0.343	0.092	12.8
Stage 6	0.65	0.58	400	28.3	0.254	0.051	23.3
Andersen 2-Stage [Phillips 1990]							
Stage 0	8.0	6.28	200	28.3	1.50	1.77	1.33
Stage 1	0.95	0.83	200	28.3	0.400	0.126	18.8
Andersen 1-Stage [Andersen 1958; Phillips 1990]							
Stage N6	0.65	0.58	400	28.3	0.254	0.051	23.3
Mattson-Garvin Slit-to-Agar		0.53	1	28.3	0.152	6.23	75.7
Ace Glass All-Glass Impinger-30		0.30	1	12.5	1.00	0.785	265.
PBI Surface Air Sampler [Lach 1985]							
Compact	2.0	1.97	219	90	1.00	0.785	8.72
Standard	2.0	1.52	260	180	1.00	0.785	14.7
BIOTEST Reuter Centrifugal Sampler [BIOTEST undated; Macher and First 1983]							
Standard	3.8	7.5		280			
RCS-Plus							
Membrane Filter Samplers							
Burkard Spore Trap (1,7-Day)							
Standard Nozzle		3.70	1	10	2.00	28.0	5.95
High Efficiency Nozzle		2.17	1	10	2.00	10.0	16.7
Burkard (Personal) Sampler							
Slit			1	10			
Seive		4.18	100	20	1.00	0.785	1.94
Burkard May-Type Multi-Stage Impinger							
Stage 1	10		1	20			
Stage 2	4		1	20			
Stage 3			1	20			
Allergenco MK-2			1				

Where:

d_{50} = Cut-diameter or aerodynamic diameter above which the collection efficiency of the impactor approaches 100%, both the true and the theoretical d_{50}s are shown;
Q = Airflow rate;
D_j or W_j = Diameter of seive or hole *j*/Width of slit *j*;
A_j = Area of hole *j* or slit *j*; and
U_j = Velocity of air through hole *j* or slit *j*.

Table II. General guidelines for matching the appropriate sampler with the bioaerosol of interest.

Sampler Sampling	Culturable Bioaerosol Sampling			Non-Viable Bioaerosol	
	Free Bacteria MMAD < 4 μm	Free Fungi MMAD < 4 μm	Clumped MMAD ≥ 4 μm	Bioaerosols MMAD < 4 μm	Bioaerosols MMAD ≥ 4 μm
Andersen 6-Stage	✓ A	✓ A	✓ A		
Andersen 2-Stage	✓ A	✓ A	✓ A		
Andersen 1-Stage	✓ A	✓ A	✓ A,H		
Mattson-Garvin Slit-to-Agar	✓ A	✓ A	✓ A		
Ace Glass All-Glass Impinger-30		✓ C,D	✓ C,D	D,E	
PBI Surface Air System					
Compact	G	G	✓ B		
Standard	G	G	✓ B		
BIOTEST Reuter Centrifugal Sampler					
Standard			✓ B		
RCS-Plus			✓ B		
Membrane Filter Samplers	✓ C,F	✓ C	✓ C	✓ C	✓ C
Burkard Spore Trap (1,7-Day)					
Standard Nozzle					✓ I
High-Efficiency Nozzle				✓	✓
Burkard (Personal) Sampler					
Slit					✓
Seive			✓ B		
Burkard May-Type Multi-Stage Impinger	✓ C,D	✓ C,D	E		
Allergenco MK-2					✓

✓ = Satisfactory for specified application.

A = Concentrations greater than 5,000-7,000 CFU/m^3 will overload sample;

B = Concentrations greater than 1,000-2,000 CFU/m^3 will overload sample;

C = Good for very low to very high concentrations;

D = Bioaerosols may be reaerosolized and drawn out of the impingers during sampling, resulting in an underestimation of concentration and a decrease in precision;

E = May overestimate concentration due to breaking up of clumps;

F = For desiccation-resistant bacteria only;

G = May be acceptable with new sampling head being evaluated by PBI/Spiral Biotech;

H = May underestimate conc. of large bioaerosols (MMAD > 10 μm) due to impactor entry losses;

I = May underestimate concentration of small bioaerosols (MMAD ≤ 5 μm).

3. SAMPLING CONSIDERATIONS

a. Safety

Investigators should use appropriate personal protective equipment (PPE) and practice good personal hygiene when conducting indoor environmental quality, disease outbreaks, and agricultural health investigations that have resulted in medically diagnosed symptoms. PPE may include respiratory protection to prevent inhalation of microbes and microorganism-resistant clothing to prevent the transmission (bodily contact with microorganisms) to investigators. Good personal hygiene practices include washing exposed skin and clothing thoroughly and refraining from eating, drinking, or smoking in a contaminated area. These simple steps will help minimize the ingestion, inhalation, or uptake of microorganisms.

All samplers, culture plates, equipment, etc. should be handled aseptically to prevent contamination of the samplers and, more importantly, to prevent the spread of potential human pathogens to the worker or the work environment [CDC/NIH 1992; McKinney et al. 1991]. All surfaces, including washed hands, harbor microorganisms or spores unless they are specifically sterilized. Practically speaking, however, not all objects may be sterilized. While disinfection with an oxidizing chemical or alcohol destroys most vegetative cells, these agents do not destroy all spores. Samplers should be disinfected or, if possible, sterilized after each sample collection. Special care should be given to samplers with convoluted inlets or air pathways where microorganisms may accumulate.

b. Environmental Conditions

Temperature and relative humidity (RH) should be recorded over the sampling period. Airborne bacteria will dessicate (i.e., intracellular and extracellular water evaporate) when exposed to unstaurated air. The degree of cellular stress and rate of evaporation increase as relative humidity decreases and temperature increases [Marthi and Lighthart 1990]. In field experiments (greenhouse), survival of certain bacteria was 35- to 65-fold higher at 80% RH than at 40% [Walter et al. 1990]. In laboratory experiments, survival of certain bacteria was virtually complete at low RH but was reduced at RH values above 80% [Cox 1968]. Cox [1987] believes the potential for the movement of the solvent water is an important environmental criterion in assessing survivability of bacteria, viruses, and phages. Limited studies have been made of temperature effects. Temperature induces morphological changes in dimorphic fungi. For example, *Histoplasma capsulatum*, a pathogen, exists as a spore or mycelial form below 25 °C. However, higher temperatures have been shown to induce a transition from the mycelial form to the yeast form [Salvin 1949]. Like most particles, freshly generated microbial aerosols are nearly always electrostatically charged unless steps are taken to neutralize them. There is very little published information about electric charges on actual workplace aerosols, and even less on bioaerosols [Johnston et al. 1985]. In general, the effect of electrical charge has been overlooked, resulting in the possible bias of sampling

results. At RH values above 70% RH, electrostatic phenomena are minimal [Hinds 1982; Cox 1987].

Sampling locations should be selected to assist in evaluation of your hypothesis. If you are evaluating worker exposure, then the samplers should be placed in inhabited areas where worker exposures may be measured. If you are evaluating contamination of a ventilation system, then sampling in the system and at the ventilation louvers would be appropriate. Care must be exercised to ensure people do not tamper with the samplers and that you do not inadvertently aerosolize microorganisms on surfaces or in duct-work.

c. Flow Calibration

Accurate airflow rates are very important in calculating the concentration of microorganisms in the air. All samplers should be calibrated before and after sampling to ensure the flow rate is within the manufacturer's specifications and does not change from the initial calibration. Calibration may be performed using a primary standard such as a spirometer or bubble calibrator. Where it is not possible to calibrate using a primary standard, a secondary standard such as a dry gas meter may be used. The calibration of such a secondary standard should be traceable to a primary standard. See Chapter D. General Considerations for Sampling Airborne Contaminants of this manual for further details on calibration of airflow rates.

d. Culture Media

General detection and enumeration media are normally used in the collection of fungi, bacteria, and thermophilic *Actinomycetes*. Plates can be replicated on differential or selective media for identification after the organisms have been collected. In addition, it may be advisable to concurrently use more than one type of culture medium to collect aerosolized microorganisms, because of inherent biases caused by media selection. The following are some general guidelines for media:

(1) Fungi

Traditionally, malt extract agar (MEA) and rose bengal agar (RBA) have been recommended as broad spectrum media for the collection and enumeration of fungi [Morring et al. 1983; Burge et al. 1977; Smid et al. 1989]. MEA and RBA are generic terms and formulations vary from supplier to supplier and laboratory to laboratory. One MEA recipe is a less nutritious, unamended 2% MEA, which is reported to promote better sporulation than MEA amended with glucose and/or peptone [Hunter et al. 1988; Strachan et al. 1990]. With RBA, the colonies remain small; however, natural or artificial light may make the medium toxic to some fungi. In addition, pigmentation of the fungal growth on RBA complicates the identification process. Based on the work of researchers in Australia and Holland,

dichloran glycerol 18 agar (DG-18) is recommended for identification and enumeration of fungi [Hocking and Pitt 1980; Pitt et al. 1983; Verhoeff et al. 1990]. This medium is adequate for most fungi, including xerophilic fungi. DG-18 does not have the disadvantages of RBA. To inhibit the growth of bacteria, antibiotics, such as streptomycin, may be added to the RBA medium [DIFCO 1984].

(2) Bacteria

Tryptic soy agar (TSA), casein soy peptone agar (CSPA) and nutrient agar (NA) are broad spectrum media for the collection and enumeration of bacteria. Special purpose media (i.e., selective media) are often used to select for specific microorganisms of interest. As with the media for fungi, chemicals may be added to the media which restrict growth of selected fungi and bacteria [DIFCO 1984].

(3) Thermophilic *Actinomycetes*

Thermophilic *Actinomycetes* is a special class of bacteria that has been associated with indoor environmental quality problems [Nevalainen 1989]. CSPA, TSA, and tryptone glucose yeast agar (also known as standard methods agar [SMA] and standard plate count agar [SPCA]) are broad spectrum media for the collection and enumeration of thermophilic *Actinomycetes* [DIFCO 1984; Amner et al. 1989; ACGIH 1989, Bacteria].

(4) Additional Media

Other media for the detection and enumeration of fungi and bacteria may be used. To discriminate for a general class of microorganisms by inhibiting or eliminating other microorganisms, a selective medium containing an antibiotic or other growth-restricting chemical may be used. To distinguish among species, a differential media may be used. Differential media contain indicators that permit the recognition of microorganisms with particular metabolic activities. Different incubation times or temperatures can also be used to get differential growth on the same medium. When a specific medium (i.e., selective or differential) is needed, the investigator(s) should refer to the most recent Manual of Clinical Microbiology published by the American Society for Microbiology, DIFCO Manual: Dehydrated Culture Media and Reagents for Microbiology published by DIFCO Laboratories, or the various catalogues published by the American *Type Culture* Collection (ATCC) [DIFCO 1984; Murray et al. 1995; Gherna et al. 1992; Jong and Edwards 1991].

e. Blanks

(1) Laboratory Media Blanks

Laboratory media blanks are unexposed, fresh media samples. These samples are generally not taken into the field. Before using any batch of media, incubate at least three culture plates under the same conditions as planned for the field samples, in order to check for sterility of the media. Approximately five media blanks should be included with each sample set. If the samples are to be analyzed by an outside laboratory, consult the specific laboratory procedure for the number of blanks to be submitted.

(2) Field Blanks

Field blanks are simply unopened, fresh media samples that are handled in every way the same as field samples, including labeling, except that no air is drawn through the sampler. The recommended practice for the number of field blanks is to provide two field blanks for every 10 samples with a maximum of 10 field blanks for each sample set.

4. PREPARATION, IDENTIFICATION, AND ENUMERATION PROCEDURES FOR CULTURABLE BIOAEROSOLS

a. Sample Preparation

Inoculated agar plates are incubated at the appropriate temperature for times ranging from hours for a fast-growing bacterium to develop a microcolony; to days for a fungus to develop into a visible colony, and perhaps sporulate; to weeks for an organism such as drug resistant *Mycobacterium tuberculosis* to produce visible colonies [ATS 1990]. As a rule, plates are incubated at the temperatures shown in Table III [ACGIH 1989, Fungi and Bacteria; Baron and Finegold 1990].

Table III. Incubation temperatures and conditions for viable (culturable) microorganisms.

Fungi	25 °C or Room temperature with natural light
Bacteria, environmental	25 to 30 °C
Bacteria, human-source	35 to 37 °C
Bacteria, thermophilic *Actinomycetes*	50 to 56 °C

Laboratory media blanks and field media blanks must be handled in the same manner as samples.

b. Enumeration

(1) Total Concentration (Colony Forming Units Per Cubic Meter)

The total concentration of culturable microorganisms is calculated by dividing the volume of air sampled into the total number of colonies observed on the plate. A colony is a macroscopically visible growth of microorganisms on a solid culture medium. Concentrations of culturable bioaerosols normally are reported as colony forming units (CFU) per unit volume of air. CFU is the number of microorganisms that can replicate to form colonies, as determined by the number of colonies that develop.

(2) Adjusted Concentration (CFU/m^3)

Often, it is difficult to identify multiple colonies at one location on a plate because of the lack of differential colony morphology or because the chemicals secreted by one microorganism might inhibit the growth of other microorganisms at that same location [Burge et al. 1977]. In addition, some organisms produce large, spreading colonies while others produce microcolonies. Also, the morphology of the colony of one microorganism may completely obscure that of another, and a fast-grower might obscure a slow-grower. In these cases, a statistical adjustment of the observed number of colonies is needed to account for the probability that more than

one particle impacted the same site [Andersen 1958; Leopold 1988; Macher 1989]. The adjusted concentration of culturable microorganisms is calculated by dividing the volume of air sampled into the adjusted number of colonies observed on the plate (see section 2.b.).

(3) Limitations

Bioaerosol collection methods are "grab sample" techniques and, thus, represent only approximations of transient microbial concentrations in problematic atmospheres. Timely ascertainment of bioaerosol involvement is not possible, because of the time-dependent nature of the cultivation of samples and the subsequent enumeration of colonies.

The methods thus far pertain to culturable microorganisms. Microorganisms that are stressed or injured either by environmental conditions or bioaerosol sampling procedures may be viable, but not culturable [McFeters et al. 1982]. Certain species may be too fastidious to grow in laboratory culture. For instance, some bioaerosols (e.g., *Legionella pneumophila*, *Histoplasma capsulatum* or *Pneumocystis carinii*) are very difficult, if not impossible, to collect and culture [Ibach et al. 1954; Dennis 1990].

c. Identification of Culturable Bioaerosols

The science of classification, especially the classification of living forms, is called taxonomy. The objective of taxonomy is to classify living organisms to establish the relationship between one group of organisms and another, and to differentiate between them. Several criteria and methods for the classification of culturable microorganisms and the routine identification of some are discussed in the subsections that follow. Besides using these methods, the nonviable and nonculturable methods of identification discussed in Section 5 also may be used with culturable microorganisms.

(1) Classical or General Microbiology

Classical microbiology includes general methods for classifying or identifying microorganisms. The least specific of these is the observation of growth characteristics. Growth characteristics include the appearance of the microorganisms in liquid medium, colonial morphology on solid medium, and pigmentation.

On the cellular level of bacteria, cell shape, cell size, arrangement of cells, and presence (absence) of flagella, capsule, or endospores are characteristic of general classes of microorganisms. Simple and differential staining may be performed on bacteria. Simple staining is a method of staining microorganisms with a single basic dye that highlights cellular size, cellular shape, cellular arrangement, and presence (absence) of flagella, capsule, or endospore using a microscope. Stains such as methylene blue, carbolfuchsin, crystal violet, or safranin may be used for bacteria. A stain that distinguishes among structures or

microorganisms based on reactions to the staining procedure is called a differential stain. Two examples of differential stains are the Gram stain and the acid-fast stain. The mechanism of the Gram stain may be explained on the basis of physical differences in the cell walls of these two general groups of bacteria (Gram-positive and Gram-negative). The Gram-positive bacteria possess a cell wall composed of a relatively thick peptidoglycan layer and teichoic acids. Gram-negative bacteria possess a cell wall composed of a thin peptidoglycan layer and an outer membrane which consists of lipoproteins, lipopolysaccharides, and phospholipids [Tortora et al. 1989]. A few of the commercially available identification kits require a Gram-stain prescreening to assure that the correct reagents are used. Some species of bacteria, particularly those of the genus *Mycobacterium*, do not stain readily. In the acid-fast staining process, the application of heat facilitates the staining of the microorganism.

In general, fungi are classified by spore morphology or colonial morphology. Stains such as lactophenol cotton blue, periodic acid-Schiff stain, or potassium hydroxide (10% KOH) may be used.

Biochemical, physiological, and nutritional tests for bacteria evaluate cell wall constituents, pigment biochemicals, storage inclusions, antigens, temperature range and optimum, oxygen relationships, pH tolerance, osmotic tolerance, salt requirement and tolerance, antibiotic sensitivity, energy sources, carbon sources, nitrogen sources, fermentation products, and modes of metabolism (autotrophic, heterotrophic, fermentative, respiratory). As a rule, batteries of such tests, rather than any one individual test, are used to identify or classify microorganisms. A few commercially available test batteries are discussed in the following subsection.

Fungi are very difficult to classify [Smith 1990].

(2) Clinical and Environmental Microbiology

All identification systems should permit the efficient and reliable differentiation between microorganisms. Several modifications of classical biochemical procedures have been used in recent years to facilitate inoculation of media, to decrease the incubation time, to automate the procedure, and to systematize the determination of species based on reaction patterns. Historically, clinical microbiological techniques are used for analysis of environmental samples. However, clinical strains and environmental isolates may differ, requiring modification of clinically-based techniques.

(I) Biochemical Analyses

Several commercial multitest systems have been developed for identification of members of the family *Enterobacteriaceae* and other pathogenic microorganisms because of the high frequency of isolation of Gram-negative rods in clinical settings. These microorganisms are indistinguishable except for characteristics determined by detailed biochemical testing. These

systems require that a pure culture be examined and characterized. Following is a listing of commercially available identification kits: API® 20E (Analytab Products, Plainview, NY); Enterotube II and R/B Enteric (Roche Diagnostics Systems, Nutley, NJ; Hoffmann-La Roche & Co., AG, Basel, Switzerland); Micro-ID (Organon Teknika-Cappel, Durham, NC); Minitek and Sceptor (BBL Microbiology Systems, Cockeysville, MD); and MicroScan (American Microscan, Inc., Sacramento, CA). Automated identification systems include Quantum II (Abbott Laboratories, North Chicago, IL), Autobac IDX (General Diagnostics, Warner-Lambert Co., Morris Plains, NJ), and AutoMicrobic System (Vitek Systems, Inc., Hazelwood, MO). All ten of these multitest systems have documented accuracies greater than 90% in clinical settings [Baron and Finegold 1990; Koneman et al. 1988]. Biolog (Biolog, Inc., Hayward, CA) is one of the newest multitest systems on the market, but its application to environmental and clinical samples is not well documented [Amy et al. 1992; Miller and Rhoden 1991].

(ii) Cellular Fatty Acid Analysis

Cellular fatty acids (CFA) of bacteria are structural in nature, occurring in the cell membrane or cell wall of all bacteria. When the bacteria are grown under standardized growth conditions, the CFA profiles are reproducible within a genus, down to the subspecies or strain level in some microorganisms. The Microbial Identification System (MIS), developed by MIDI (Newark, DE), provides a chromatographic technique and software libraries capable of identifying various microorganisms based on their CFA composition [Sasser 1990a; Sasser 1990b]. The chromatographic technique is also known as gas chromatography fatty acid methyl ester analysis (GC-FAME). MIS has a database containing the analysis libraries for culturable Gram-negative and Gram-positive bacteria, and yeasts. In a comparison study [Amy et al. 1992], only 8 of 18 isolates, identified by either API multitest or MIDI MIS, were identified accurately using Biolog multitest. A prototype method for extracting and analyzing fungi is currently being distributed by MIDI.

d. Interpretation of Data

Generally speaking, the literature is divided on whether identification is necessary or recommended. If clinical or research aspects of the investigation would benefit by identification of the source of an etiologic agent, the following general guidelines are suggested:

Dose-response data are not available for most microorganism exposures. Indoor bioaerosol levels must be compared to outdoor levels or to an asymptomatic control area. In general, indoor levels are lower than outdoor levels, and the taxa are similar [ACGIH 1989, Step two, Fungi, and Bacteria; Solomon et al. 1980]. The Bioaerosol Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) states that outdoor airborne fungi concentration "**routinely** exceeds 1000 CFU/m^3 and

may average near 10,000 CFU/m^3 in summer months." No occupational exposure limit for bioaerosols has been promulgated by the Occupational Safety and Health Administration (OSHA). ACGIH [1989, Bacteria] also states that concentrations of less than 100 CFU/m^3 may be unhealthy to immunosuppressed people. However, the population of microorganisms must be evaluated for potential toxigenic microorganisms or microorganisms which emit volatile organic compounds. A low airborne concentration of microorganisms, in and of itself, does not indicate a clean and healthful environment.

Where local amplification and dissemination of bacteria have not occurred in an occupied, indoor environment, Gram-positive cocci (e.g., *Micrococcus* and *Staphylococcus*) are normally dominant [Morey et al. 1986]. ACGIH states that airborne human skin scales and respiratory secretions may contain Gram-positive cocci. Detection of high levels of these microorganisms are an indication of over-crowding and inadequate ventilation. Indoor air that tests high for Gram-negative bacteria indicates a need to identify and eliminate the source of contamination. Concentrations ranging from 4,500-10,000 CFU/m^3 have been suggested as the upper limit for ubiquitous bacterial aerosols [Nevalainen 1989; ACGIH 1989, Bacteria]. These exposure limits, however, do not apply to pathogenic microorganisms.

Actinomycetes (mesophilic and thermophilic) are commonly found in agricultural areas. Their presence in indoor environments is an indicator of contamination [ACGIH 1989, Bacteria; Banaszak et al. 1970; Lacey and Crook 1988]. Thermophilic *Actinomycetes* at concentrations above 70 CFU/m^3 in an affected person's work area have been regarded as the threshold for triggering remedial action [Otten et al. 1986].

5. ADDITIONAL IDENTIFICATION AND ENUMERATION PROCEDURES FOR NONVIABLE OR VIABLE BIOAEROSOLS

Classifying nonviable and nonculturable microorganisms cannot be performed using the methods described in the previous section. Identification of nonviable or nonculturable microorganisms or components of microorganisms can be performed using microscopy and molecular biology techniques. In addition, microscopy techniques may be used for enumeration of suspensions of viable and nonviable microorganisms [McCrone 1973].

a. Microscopy

(1) Bright-Field or Light

In bright-field or light microscopy, an ordinary microscope is used for simple observation or sizing. Visible light from an incandescent source is used for illumination and the specimen appears against a bright backfield. Objects smaller than 0.2 µm cannot be resolved. The image contrast (visibility) decreases as the refractive index of the substance/microorganism under observation and the mounting medium become similar. To maximize the contrast, the mounting medium should have the same refractive index as glass or the immersion oil. Membrane filters are often "cleared" by using the appropriate immersion oil. This

method is commonly used to observe various stained (killed) specimens and to count microorganisms. In addition, pollen grains and fungi spores are often identified and enumerated in this manner [Eduard et al. 1990].

(2) Phase Contrast

Phase-contrast microscopy is used when the microorganism under observation (e.g., *Escherichia coli*) is nearly invisible and an alternative mounting medium is not possible or permissible. A phase-contrast microscope uses a special condenser and diffraction plate to diffract light rays so that they are out of phase with one another. The specimen appears as different degrees of brightness and contrast. One cannot see an object exactly matching the refractive index of the mounting liquid; however, very slight differences produce visible images. This type of microscope is commonly used to provide detailed examination of the internal structures of living specimens; no staining is required.

(3) Fluorescence

Fluorescence microscopy uses ultraviolet or near-ultraviolet source of illumination that causes fluorescent compounds in a specimen to emit light. Fluorescence microscopy for the direct count of microorganisms has been described in a number of studies. Direct-count methods to enumerate microorganisms found in soil, aquatic, and food samples have been developed using acridine orange [Palmgren et al. 1986a, Palmgren et al. 1986b, Karlsson and Malmberg 1989]. More recently, this method was applied to airborne microorganisms and it was concluded that it is of the utmost importance to combine viable counts with total count enumeration in the study of microorganisms in work-related situations [Palmgren et al. 1986a].

(4) Electron

Electron microscopy uses a beam of electrons instead of light. Because of the shorter wavelength of electrons, structures smaller than 0.2 µm can be resolved. Scanning electron microscopy (SEM) is used to study the surface features of cells and viruses (usually magnified 1,000-10,000X); and the image produced appears three-dimensional. Also, SEM permits visualization of microorganisms and their structure (e.g., single spores or cells, clumps, chains, size, shape, or other morphological criteria). Viable microorganisms cannot be distinguished from nonviable microorganisms [Donham et al. 1986; Karlsson and Malmberg 1989]. Transmission electron microscopy is used to examine viruses or the internal ultrastructure in thin sections of cells (usually magnified 10,000-100,000X); and the image produced is not three dimensional.

b. Endotoxin Assay

A virulence factor possessed by all *Enterobacteriaceae* (as well as other Gram-negative bacteria) is the lipopolysaccharide, endotoxin, found in the outer membrane of the cell wall. Individuals may experience disseminated intravascular coagulopathy, respiratory

tract problems, cellular and tissue injury, fever, and other debilitating problems. Amebocytes are carried "within the blood-like circulating fluid" of the *Limulus polyphemus* (horseshoe crab). After exposure to the lysed amebocyte cells, a liquid suspension containing trace levels of endotoxin (lipopolysaccharides) will gel. This test is called the *Limulus* amebocyte lysate (LAL) assay. Clinical microbiology laboratories use this assay to test for contamination by Gram-negative bacteria [Baron and Finegold 1990]. Airborne endotoxin has been found in high concentrations in agricultural, industrial, and office environments [Milton et al. 1990; Rylander and Vesterlund 1982]. Endotoxin aerosol measurement techniques lack comparability between results obtained in different laboratories because of differing sampling, extraction, and analytical methods (generically called the *Limulus* method) [Rylander and Vesterlund 1982; Olenchock et al. 1983; Jacobs 1989; Milton et al. 1990]. Concentrations of endotoxin, a lipopolysaccharide found in the cell wall of Gram-negative bacteria, determined using the LAL assay method, have been correlated with patient symptoms in very few studies [Rylander and Vesterlund 1982; Milton et al. 1990].

c. Immunoassays

The immunoassay is an analytical technique for measuring a targeted antigen, which is also referred to as an analyte. A critical component of the immunoassay is the antibody, which binds a specific antigen. The binding of antibody and targeted antigen forms the basis for immunoassay, and numerous formats have been devised which permit visual or instrumental measurements of this reaction. Antibodies are commonly employed to detect organisms by binding to antigens, usually proteins or polysaccharides, on the surface or "coats" of organisms. The analysis is usually performed in a complex matrix without the need for extensive sample cleanup. Many immunoassays are now readily available from commercial sources, permitting laboratories to rapidly develop in-house immunochemical analytical capability without lengthy antibody preparation. Some of the more widely used formats are as follows:

(1) Radioimmunoassays (RIA)

Radiolabelled antigen is quantitatively added to antibody along with various concentrations of unlabeled antigen. The unlabeled antigen competes with the radiolabelled antigen for binding to the antibody. Thus, the higher the concentration of unlabeled antigen in the sample, the lower the level of radiolabelled antigen-antibody complexes. The unbound antigens are removed prior to determining the amount of radiolabelled antigen-antibody formed. A standard curve is then constructed showing the effect of known amount of unlabeled antigen on the amount of radiolabelled antigen-antibody formed. It is now possible to determine the amount of an unknown, unlabeled antigen present in a sample by determining where the value is located on the standard curve [Garvey 1977]. Alternatively, radiolabelled antibody is employed.

(2) Fluorescent Immunoassays (FIA)

Utilization of fluorescent-labeled antibodies to detect bacterial antigens was introduced by Coons et al. [1941 and 1942]. Various FIA techniques have now evolved. These are referred to as: (1) direct FIA, to detect antigen (cell-bound) using fluorescent antibody; (2) indirect FIA, to detect antigen (cell-bound) using antibody and fluorescent antigamma globulin antibody; and (3) indirect FIA, to detect serum antibody using antigen, serum, and fluorescent antibody. Various fluorescent dyes, such as fluorescein, fluorescein isothiocyanate, and rhodamine isothiocyanate, may be employed. A fluorescent microscope is used to evaluate the samples and to count the number of fluorescent organisms [Garvey et al. 1977]. FIA is used to detect viruses and microorganisms.

(3) Enzyme Immunoassays (EIA)

The binding of an antibody or antigen to an enzyme, such as horseradish peroxidase (HRP) or alkaline phosphatase (AP), is the basis of EIA techniques. Enzymatic activity, in the presence of a chromogen, results in a colored end-product. Quantitation is performed using a spectrophotometer [Monroe 1984]. Many, if not most, commercially available EIAs are enzyme-linked immunosorbent assays (ELISAs). In this competitive-binding EIA, the antibody is coated onto the surfaces of test tubes, or wells of a microtiter plate, and antigen-containing samples and enzyme-linked antigen are added, resulting in a color change. The more intense the color, the less antigen or analyte are present in the sample. ELISAs can be qualitative or quantitative. A standard curve must be generated if quantitative results are desired. ELISAs are now highly automated and efforts are underway to commercially develop well-standardized kits containing appropriate controls and materials.

d. Gene Probes

Diagnostic bacteriology, virology, and mycology are rapidly adapting molecular biology techniques in addition to classical identification methods to identify organisms. Thus, diagnostic assays utilizing nucleic acid or DNA probes have now been developed for the detection of numerous pathogenic organisms. Prior to employment of a DNA probe, it must first be demonstrated that the DNA probe is highly specific for the targeted organism. For example, a DNA probe for *Mycobacterium tuberculosis* (*Mtb*) should not detect other *Mycobacteria* species. However, it should detect all *Mtb* isolates. Described below are various types of DNA probes and formats used for the detection of organisms.

(1) Nick-translated DNA Probes

An isolated genomic DNA fragment is enzymatically disrupted and some of the DNA bases replaced with highly radioactive DNA bases [Sambrook et al. 1989]. The radioactive probe is now tested for its ability to bind (hybridize) the extracted DNA or RNA from the organism of interest. Prior to hybridization, the targeted DNA or RNA is either fixed to a membrane, microscope slide or resuspended in an aqueous buffer. After hybridization, the unbound DNA probe is then removed and the specimen DNA or RNA analyzed for bound DNA probe. Alternatively, nonradioactive labeling is often employed, but these probes, in general, are less sensitive than use of phosphorus-32 (^{32}P) labeled DNA [Goltz et al. 1990].

(2) Synthetic Oligomer DNA Probes

A short single-stranded DNA segment, usually 20-60 bases in length is designed and chemically synthesized. If the precise DNA sequence of the targeted organism is known, a complementary probe, representing a perfect match to the targeted DNA is designed. However, the precise sequence of the targeted DNA is often not known. Instead, the starting point for probe design is the amino acid sequence. In this situation, because of codon degeneracy, a single probe exhibiting exact complementarity cannot be designed. Thus, an educated guess, based on understanding the genetic code and codon usage, is used to design the probe. This type of probe usually exhibits a high degree of matching, although seldom is a perfect match achieved. Alternatively, a set or "family" of probes is synthesized. These are designed to cover all possible DNA sequences in the targeted organism. The probes are labeled, usually with ^{32}P, prior to hybridization experiments [Sambrook et al. 1989].

(3) Polymerase Chain Reaction (PCR)

First introduced in 1985, the PCR has revolutionized the way DNA analysis is conducted in clinical and research laboratories. Application of the PCR results in the amplification (the *in vitro* enzymatic synthesis of thousands of copies) of a targeted DNA [Saiki et al. 1985]. Two synthetic, single-stranded DNA segments, usually 18-25 bases in length, are bound to the targeted DNA. These serve as primers and permit the rapid enzymatic amplification of complementary DNA. The method is extremely sensitive and specific. Culturing of the targeted organism prior to DNA extraction is often not necessary. This approach has been successfully utilized to detect various organisms including *Mtb* [Brisson-Noel et al. 1989; Wren et al. 1990; Eisenach et al. 1991].

(4) Restriction Fragment Length Polymorphic (RFLP) Analysis

RFLP is widely utilized to distinguish genetic changes within a species. A pure clone of each of the organisms of interest must be generated using standard culturing techniques. The genomic DNA is isolated and cut with a series of restriction enzymes. Each of these enzymes cut double-stranded DNA at a

unique, short sequence of DNA bases, generating genomic DNA fragments of various sizes [Sambrook et al. 1989]. The DNA fragments are examined by sizing them on agarose gels. Eventually, the region(s) of altered DNA is detected. The fragment appears as a different size when compared to the other isolates. Confirmation may be accomplished by using gene probes as described above.

6. MANUFACTURERS

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Denville, NJ 07834
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7. REFERENCES

ACGIH [1989]. Step two: On-site investigation, pp. 1-8; Fungi, pp. 1-10; Bacteria, pp. 1-7. Committee on Bioaerosols, eds. In: Guidelines for the assessment of bioaerosols in the indoor environment. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

Amner W, Edwards C, McCarthy AJ [1989]. Improved medium for recovery and enumeration of the farmer's lung organism, *Saccharomonospora viridis*. Appl Environ Microbiol *55*(10):2669-2774.

Amy PS, Haldeman DL, Ringelberg D, Hall DH, Russell C [1992]. Comparison of identification systems for classification of bacteria isolated from water and endolithic habitats within the deep subsurface. Appl Environ Microbiol *58*(10):3367-3373.

Andersen AA [1958]. New sampler for the collection, sizing, and enumeration of viable airborne particles. J Bacteriol *76*:471-484.

Andersen Instruments, Inc. [1984]. Operating manual for Andersen sampler, Inc., viable (microbial) particle sizing sampler. Atlanta, GA: Andersen Instruments, Inc. (Currently Smyrna, GA: Graseby Andersen), TR# 76-00042, pp. 18-19.

American Thoracic Society (ATS) [1990]. Diagnostic standards and classification of tuberculosis. Am Rev Resp Dis *142*(3):725-735.

Banaszak EF, Thiede WH, Fink JN [1970]. Hypersensitivity pneumonitis due to contamination of an air conditioner. New Engl J Med *283*(6):271-276.

Baron EJ, Finegold SM [1990]. Bailey & Scott's diagnostic microbiology, 8th ed. St. Louis, MO: The C.V. Mosby Company, pp. 76, 79, 82, 100-126, 133.

Brisson-Noel A, Lecossier D, Nassif X, Gicquel B, Levy-Frebault V, Hance AJ [1989]. Rapid diagnosis of tuberculosis by amplification of mycobacterial DNA in clinical samples. Lancet *No. 8671*:1069-1071.

Burge HP, Boise JR, Rutherford JA, Solomon WR [1977]. Comparative recoveries of airborne fungus spores by viable and non-viable modes of volumetric collection. Mycopathologia *61*(1):27-33.

CDC/NIH [1993]. Biosafety in microbiological and biomedical laboratories, 3rd ed. Washington, DC: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control; National Institutes of Health. HHS Publication No. (CDC) 93-8395.

Coons AH, Creech HJ, Jones RN [1941]. Immunological properties of an antigen containing a fluorescent group. Proc Soc Exp Biol Med *47*:200-202.

Coons AH, Creech HJ, Jones RN, Berliner E [1942]. The demonstration of pneumococcal antigen in tissues by use of fluorescent antibody. J Immunol *45*:159-170.

Cown WB, Kethley TW, Fincher EL [1957]. The critical-orifice liquid impinger as a sampler for bacterial aerosols. Appl Microbiol *5*:119-124.

Cox CS [1968]. The aerosol survival of *Escherichia coli B* in nitrogen, argon and helium atmospheres and the influence of relative humidity. J Gen Microbiol *50*(1):139-147.

Cox CS [1987]. The aerobiological pathway of microorganisms. New York, NY: John Wiley & Sons Ltd., pp. 4, 56, 73, 172-205.

Dennis PJL [1990]. An unnecessary risk: Legionnaires' disease. In: Morey PR, Feeley JC, Otten JA, eds. Biological contaminants in indoor environments. Philadelphia, PA: ASTM, STP1071, pp. 84-89.

DIFCO Laboratories [1984]. DIFCO manual: dehydrated culture media and reagents for microbiology, 10th ed. Detroit, MI: DIFCO Laboratories, Inc, pp. 9, 75, 565-566, 679-680, 749-752.

Donham KJ, Popendorf W, Palmgren U, Larsson L [1986]. Characterization of dusts collected from swine confinement buildings. Am J Ind Med *10*(3):294-297.

Eduard W, Lacey J, Karlsson K, Palmgren U, Ström G, Blomquist G [1990]. Evaluation of methods for enumerating microorganisms in filter samples from highly contaminated occupational environments. Am Ind Hyg Assoc J *51*(8):427-436.

Eisenach KD, Cave MD, Bates JH, Crawford JT [1990]. Polymerase chain reaction amplification of a repetitive DNA sequence specific for *Mycobacterium tuberculosis*. J Infect Dis *161*:977-981.

Fields ND, Oxborrow GS, Puleo JR, Herring CM [1974]. Evaluation of membrane filter field monitors for microbiological air sampling. Appl Microbiol *27*(3):517-520.

Garvey JS, Cremer NE, Sussdorf DH [1977]. Methods in immunology, 3rd ed. Reading, MA: W.A. Benjamin, Inc., pp. 87, 301-312, 431-434.

Gherna R, Pienta P, Cote R, eds. [1992]. Catalogue of bacteria and phages, 18th ed. Rockville, MD: American *Type Culture* Collection.

Goltz SP, Donegan JJ, Yang H-L, Pollice M, Todd JA, Molina MM, Victor J, Kelker N [1990]. The use of nonradioactive DNA probes for rapid diagnosis of sexually transmitted bacterial infections. In: Macario AJL, de Macario EC, eds. Gene probes for bacteria. San Diego, CA: Academic Press, Inc., pp. 1-44.

Greenberg AE, Clesceri LS, Eaton AD, eds. [1992]. Standard methods for the examination of water and waste water. 18th ed. Washington, DC: American Public Health Association. pp. 9-38 - 9-39.

Henningson EW, Fängmark I, Larsson E, Wikström LE [1988]. Collection efficiency of liquid samplers for microbiological aerosols. J Aerosol Sci *19*:911-914.

Hinds WC [1982]. Aerosol technology. New York, NY: John Wiley & Sons, Ltd., pp. 78, 104-126, 165.

Hocking AD, Pitt JI [1980]. Dichloran-glycerol medium for enumeration of xerophilic fungi from low-moisture foods. Appl Environ Microbiol *39*:488-492.

Hunter CA, Grant C, Flannigan B, Bravery AF [1988]. Mould in buildings: the air spora of domestic dwellings. Int Biod *24*(2):81-101.

Ibach MJ, Larsh HW, Furcolow ML [1954]. Isolation of *Histoplasma capsulatum* from the air. Science *119*:71.

Jacobs RR [1989]. Airborne endotoxins: an association with occupational lung disease. Appl Ind Hyg *4*:50-56.

Jensen PA, Lighthart B, Mohr AJ, Shaffer BT [1994]. Instrumentation used with microbial bioaerosol. In: Lighthart B, Mohr AJ, eds. Atmospheric microbial aerosols: theory and applications. New York, NY: Chapman & Hall, pp. 226-284.

Jensen PA, Todd WF, Davis GN, Scarpino PV [1992]. Evaluation of eight bioaerosol samplers challenged with aerosols of free bacteria. Am Ind Hyg Assoc J *53*(10):660-667.

Johnston AM, Vincent JH, Jones AD [1985]. Measurements of electric charge for workplace aerosols. Ann Occup Hyg *29*(2):271-284.

Jong SC, Edwards MJ, eds. [1991]. Catalogue of filamentous fungi, 18th ed. Rockville, MD: American *Type Culture* Collection.

Karlsson K, Malmberg P [1989]. Characterization of exposure to molds and actinomycetes in agricultural dusts by scanning electron microscopy, fluorescence microscopy and the culture method. Scand J Work Environ Health *15*:353-359.

Koneman EW, Allen SD, Dowell VR, Janda WM, Sommers HM, Winn WC [1988]. Color atlas and textbook of diagnostic microbiology, 3rd ed. Philadelphia, PA: J.B. Lippincott Company, pp.136-143.

Lacey J, Crook B [1988]. Fungal and actinomycete spores as pollutants of the workplace and occupational allergens. Ann Occup Hyg *32*(4):515-533.

Lee RE, Harris K, Akland G [1973]. Relationship between viable bacteria and air pollution in an urban atmosphere. Am Ind Hyg Assoc J *34*(4):164-170.

Lembke LL, Kniseley RN, Nostrand RCV, Hale MD [1981]. Precision of the all-glass impinger and the Andersen microbial impactor for air sampling in solid-waste handling facilities. Appl Environ Microbiol *42*:222-225.

Leopold SS [1988]. "Positive hole" statistical adjustment for a two-stage, 200-hole-per-stage Andersen air sampler. Am Ind Hyg Assoc J *49*(2):A88-A90.

Lippmann M [1995]. Filters and filter holders. In: Cohen BS, Hering SV, eds. Air sampling instruments for evaluation of atmospheric contaminants, 8th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, Inc., pp. 247-279.

Liu BYH, Pui DYH, Rubow KL [1983]. Characteristics of air sampling filter media. In: Marple VA, Liu BYH, eds. Aerosols in the mining and industrial work environments, vol. 3, instrumentation. Ann Arbor, MI: Ann Arbor Science, pp. 989-1038.

Lundholm IM [1982]. Comparison of methods for quantitative determination of airborne bacteria and evaluation of total viable counts. Appl Environ Microbiol *44*:179-183.

Macher JM [1989]. Positive-hole correction of multiple-jet impactors for collecting viable microorganisms. Am Ind Hyg Assoc J *50*(11):561-568.

Macher JM, Chatigny MA, Burge HA [1995]. Sampling airborne microorganisms and aeroallergens. In: Cohen BS, Hering SV, eds. Air sampling instruments for evaluation of atmospheric contaminants, 8th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, Inc., pp. 589-617.

Macher JM, Hansson HC [1987]. Personal size-separating impactor for sampling microbiological aerosols. Am Ind Hyg Assoc J *48*(7):652-655.

Marple VA, Willeke K [1976]. Inertial impactors: theory, design and use. In: Liu BYH, ed. Fine particles: aerosol generation, measurement, sampling, and analysis. New York, NY: Academic Press, Inc., pp. 411-446.

Marthi B, Lighthart B [1990]. Effects of betaine on enumeration of airborne bacteria. Appl Environ Microbiol *56*(5):1286-1289.

McCrone WC, Delly JG [1973]. The particle atlas. Vol. II. 2nd ed. Ann Arbor, MI: Ann Arbor Science Publishers, pp. 342-345.

McFeters GA, Cameron SC, LeChevallier MW [1982]. Influence of diluents, media, and membrane filters on detection of injured waterborne coliform bacteria. Appl Environ Microbiol *43*(1):97-103.

McKinney RW, Barkley WE, Wedum AG [1991]. The hazard of infectious agents in microbiological laboratories. In: Block SS, ed. Disinfection, sterilization, and preservation, 4th ed. Philadelphia, PA: Lea and Febiger, pp. 749-756.

Miller JM, Rhoden DL [1991]. Preliminary evaluation of Biolog, a carbon source utilization method for bacterial identification. J Clin Microbiol *29*(6):1143-7.

Milton DK, Gere RJ, Feldman HA, Greaves IA [1990]. Endotoxin measurement: aerosol sampling and application of a new *Limulus* method. Am Ind Hyg Assoc J *51*(6):331-337.

Monroe D [1984]. Enzyme immunoassay. Anal Chem *56*(8):920A-931A.

Morey P, Otten J, Burge H, Chatigny M, Feeley J, LaForce FM, Peterson K [1986]. Airborne viable microorganisms in office environments: sampling protocol and analytical procedures. Appl Ind Hyg *1*:R19-R23.

Morring KL, Sorenson WG, Attfield MD [1983]. Sampling for airborne fungi: a statistical comparison of media. Am Ind Hyg Assoc J *44*(9):662-664.

Muilenberg ML, Sweet TM, Burge HA [1992]. A comparison of methods of estimating bacterial levels in machining oil mists (Abstract #20). In: Rogers C, Hall B, Ritchie J, eds. Aerobiology 1992. Toronto, Ontario, Canada: Symposium of the Pan-American Aerobiology Association.

Murray PR, Baron EJ, Pfaller MA, Tenover FC, Yolken RH, eds. [1995]. Manual of clinical microbiology, 6th ed. Washington, DC: American Society for Microbiology (ASM).

Nevalainen A [1989]. Bacterial aerosols in indoor air [dissertation]. Helsinki, Finland: National Public Health Institute, NPHI A3/1989, pp. 58, 66-69, 73.

Olenchock SA, Mull JC, Jones WG [1983]. Endotoxins in cotton: washing effects and size distribution. Am J Ind Med *4*:515-521.

Otten JA, Morey PR, Burge HA, Chatigny MA, Feeley JC, Peterson K [1986]. Airborne viable microorganisms in office environments: sampling protocol and analytical procedures. In: Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants, EPA Report No. 600/9-86-013. Raleigh, NC: U.S. EPA, Environmental Monitoring Systems Laboratory, Air Pollution Control Association, pp. 36-44.

Palmgren U, Ström G, Blomquist G, Malmberg P [1986a]. Collection of airborne micro-organisms on nuclepore filters, estimation and analysis - CAMNEA method. J Appl Bacteriol *61*:401-406.

Palmgren U, Ström G, Malmberg P, Blomquist G [1986b]. The nuclepore filter method: a technique for enumeration of viable and nonviable airborne microorganisms. Am J Ind Med *10*(3):325-327.

Pitt JI, Hocking AD, Glenn DR [1983]. An improved medium for the detection of *Aspergillus flavus* and *A. parasiticus*. J Appl Bacteriol *54*:109-114.

Rylander R, Vesterlund J [1982]. Airborne endotoxins in various occupational environments. In: Back N, Brewer GJ, Eijsvoogel VP, Grover R, Hirschhorn L, Kety SS, Udenfriend S, Uhr JW, series eds. Progress in clinical and biological research. Vol. 93. New York, NY: Alan R. Liss, Inc., pp. 399-409.

Saiki RK, Scharf S, Faloona F, Mullis KB, Horn GT, Erlich HA, Arnheim N [1985]. Enzymatic amplification of beta-globin genomic sequences and restriction site analysis for diagnosis of sickle cell anemia. Science *230*:1350-1354.

Salvin SB [1949]. Cysteine and related compounds in the growth of the yeastlike phase of *Histoplasma capsulatum.* J Infect Dis *84*:275-283.

Sambrook J, Fritsch EF, Maniatis T [1989]. Molecular cloning: a laboratory manual. 2nd ed. Cold Spring Harbor, NY: Cold Spring Harbor Laboratory Press, pp. 5.1-5.95, 10.1-10.70, 11.1-11.61, 14.1-14.35.

Sasser M [1990a]. Identification of bacteria through fatty acid analysis. In: Klement Z, Rudolph K, Sands DC, eds. Methods in phytobacteriology. Budapest, Hungary: Akadémiai Kiadó, pp. 199-204.

Sasser M [1990b]. Identification of bacteria by gas chromatography of cellular fatty acids. Newark, DE: Microbial Identification, Inc. (MIDI), Technical Note #101.

Smid T, Schokkin E, Boleij JSM, Heederik D [1989]. Enumeration of viable fungi in occupational environments: a comparison of samplers and media. Am Ind Hyg Assoc J *50*(5):235-239.

Solomon WR, Burge HP, Boise JR [1980]. Exclusion of particulate allergens by window air conditioners. J Allergy Clin Immunol *65*(4):305-308.

Smith EG [1990]. Sampling and identifying allergenic pollens and molds. San Antonio, TX: Blewstone Press, pp. 15, 41-49.

Strachan DP, Flannigan B, McCabe EM, McGarry F [1990]. Quantification of airborne moulds in the homes of children with and without wheeze. Thorax *45*(5):382-387.

Tortora GJ, Funke BR, Case CL [1989]. Microbiology - an introduction. 3rd ed. Redwood City, CA: The Benjamin/Cummings Publishing Company, Inc., pp. 72, 82-83, 162, 215-216.

Verhoeff AP, van Wijnen JH, Boleij JSM, Brunekreef B, van Reenen-Hoekstra ES, Samson RA [1990]. Enumeration and identification of airborne viable mould propagules in houses: a field comparison of selected techniques. Allergy *45*(4):275-284.

White LA, Hadley DJ, Davids DE, Naylor I [1975]. Improved large-volume sampler for the collection of bacterial cells from aerosol. Appl Microbiol *29*:335-339.

Wolf H, Skaliy P, Hall LB, Harris MM, Decker HM, Buchanan LM, Dahlgren CM [1959]. Public Health Monograph No. 60: sampling microbiological aerosols. U.S. Department of Health, Education, and Welfare, Public Health Service, pp. 2-3, 6, 18-19, 24.

Wren B, Clayton C, Tabaqchali S [1990]. Rapid identification of toxigenic *Clostridium difficile* by polymerase chain reaction (letters). Lancet *335*:423.

Walter MV, Marthi B, Fieland VP, Ganio LM [1990]. Effects of aerosolization on subsequent bacterial survival. Appl Environ Microbiol *56*(11):3468-3472.

Wright TJ, Greene VW, Paulus HJ [1969]. Viable microorganisms in an urban atmosphere. J Air Pollut Control Assoc *19*(5):337-341.

K. DETERMINATION OF AIRBORNE ISOCYANATE EXPOSURE

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1. INTRODUCTION

A variety of air sampling and analysis methods for determining workers' exposures to isocyanate-containing compounds have been published or are under development by NIOSH, OSHA, and others. The following chapter provides information on the health effects, exposure criteria, sampling considerations, and analytical considerations used at NIOSH to select isocyanate methods. The purpose is to provide information to the industrial hygienist, chemist, and client of laboratory services to make an informed decision on which isocyanate method is appropriate for a given exposure scenario. Summary tables of isocyanate exposure standards (Table I) and NIOSH and OSHA analytical methods for isocyanates (Table II) are included. Other discussions of air sampling methods and direct reading instruments have been published.[1,2,3,4]

Many material safety data sheets (MSDS) use isocyanate-related terms interchangeably. For the purpose of this discussion, terms are defined as follows.

Diisocyanates (Monomers): The difunctional isocyanate species from which polyisocyanates and polyurethanes are derived (Figure 1a). Common examples of monomeric isocyanates include 1,6-hexamethylene diisocyanate (HDI), 2,4- and/or 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), methylene bis(4-cyclohexylisocyanate (HMDI), isophorone diisocyanate (IPDI), and 1,5-naphthalene diisocyanate (NDI). Commercial-grade TDI is an 80:20 mixture of the 2,4- and 2,6-isomers of TDI, respectively.

Polyisocyanates: Species possessing free isocyanate groups and derived from monomeric isocyanates either by directly linking these monomeric units (a homopolymer) or by reacting these monomers with di- or polyfunctional alcohols or amines (a copolymer). Figure 1b shows the structure of a TDI-based polyisocyanate.

Prepolymers: Species possessing free isocyanate groups, prepared from the reaction of a polyol with an excess of di- or polyisocyanate (Figure 1c).[5] Commercially available isocyanate products frequently contain prepolymers in lieu of more volatile isocyanate monomers.

Oligomeric Isocyanates (Oligomers): Relatively low molecular weight polyisocyanates.

Intermediates: Species possessing free isocyanate groups, formed during use of an isocyanate product by partial reaction of the isocyanate species with a polyol.

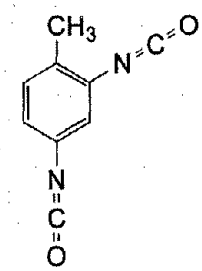
This discussion covers isocyanate-containing compounds, except monofunctional isocyanates, because monofunctional isocyanates have different industrial applications, such as the manufacture of pesticides, and have very different toxicities.

2. BACKGROUND

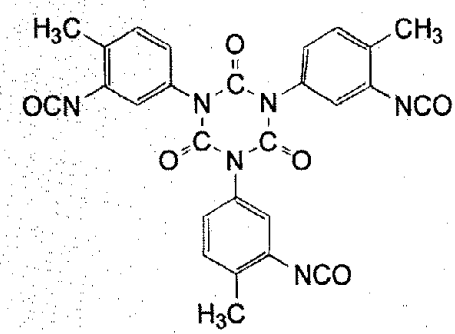
The feature common to all diisocyanates (monomers) is the presence of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound. These compounds are widely used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants.

In general, the types of exposures encountered during the use of isocyanates (*i.e.*, monomers, prepolymers, polyisocyanates, and oligomers) in the workplace are related to the vapor pressures of the individual compounds. The lower molecular weight isocyanates tend to volatilize at room temperature, creating a vapor inhalation hazard. Conversely, the higher molecular weight isocyanates do not readily volatilize at ambient temperatures, but are still an inhalation hazard if aerosolized or heated in the work environment. The latter is important since many reactions involving isocyanates are exothermic in nature, thus providing the heat for volatilization. As exposure limits decrease, the volatility of solid materials becomes an issue. To reduce the vapor hazards associated with the lower molecular weight diisocyanates, prepolymer and polyisocyanate forms of these diisocyanates were developed and have replaced the monomers in many product formulations. An example is the biuret of HDI, which consists of three molecules of HDI monomer joined together to form a higher molecular weight oligomer having similar characteristics to those found in the monomer. Also, many MDI product formulations consist of a combination of MDI monomer and a MDI-based polyisocyanate (such as polymethylene polyphenyl isocyanate). Many prepolymer and polyisocyanate formulations contain a small fraction (usually less than 1%) of unreacted monomer.

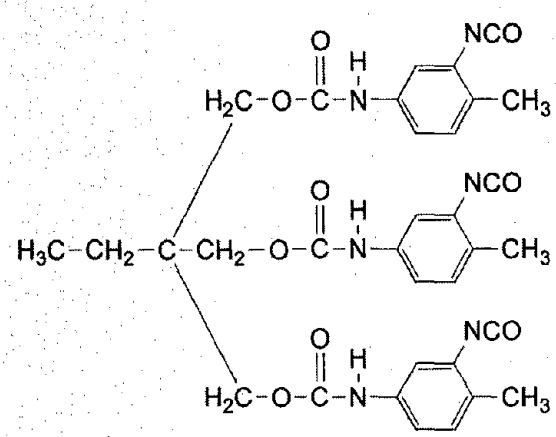
Isocyanates exist in many different physical forms in the workplace. Not only are workers potentially exposed to the unreacted monomer, prepolymer, polyisocyanate, and/or oligomer species found in a given product formulation, they can also be exposed to partially reacted



a. 2,4-TDI monomer.



b. Polyisocyanate of TDI.



c. Prepolymer adduct of TDI and trimethylol propane.

Figure 1. Examples of isocyanate structures.

isocyanate-containing intermediates formed during polyurethane production. In addition, isocyanate-containing mixtures of vapors and aerosols can be generated during the thermal degradation of polyurethane coatings and plastics. The capability to measure all isocyanate-containing substances in air, whether they are in monomer, prepolymer, polyisocyanate, oligomer, and/or intermediate forms, is important when assessing a worker's total airborne isocyanate exposure.

3. ISOCYANATE EXPOSURE RELATED HEALTH EFFECTS

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract.[6,7] The most common adverse health outcome associated with isocyanate exposure is asthma due to sensitization; less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP).[7,8,9] Contact dermatitis can result in symptoms such as rash, itching, hives, and swelling of the extremities.[6,9] A worker suspected of having isocyanate-induced asthma/sensitization will exhibit the traditional symptoms of acute airway obstruction, *e.g.*, coughing, wheezing, shortness of breath, tightness in the chest, and nocturnal awakening.[6,8] An isocyanate-exposed worker may first develop an asthmatic condition (*i.e.*, become sensitized) after a single (acute) exposure, but sensitization usually takes a few months to several years of exposure.[6,8,10,11,12] The asthmatic reaction may occur minutes after exposure (immediate), several hours after exposure (late), or a combination of both immediate and late components after exposure (dual).[8,11] The late asthmatic reaction is the most common, occurring in approximately 40% of isocyanate sensitized workers.[13] After sensitization, any exposure, even to levels below an occupational exposure limit or standard, can produce an asthmatic response which may be life threatening. Experience with isocyanates has shown that monomeric, prepolymeric and polyisocyanate species are capable of producing respiratory sensitization in exposed workers.[14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30] Since the intermediates may be chemically similar to these compounds, it is reasonable to assume that they may also produce this condition. Prevalence estimates for isocyanate-induced asthma in exposed worker populations vary considerably: from 5% to 10% in diisocyanate production facilities[10,31] to 25% in polyurethane production plants[31,32] and 30% in polyurethane seatcover operations.[33] The scientific literature contains a limited amount of animal data suggesting that dermal exposure to diisocyanates may produce respiratory sensitization.[34,35,36,37] This finding has not been tested in dermally exposed workers.

Hypersensitivity pneumonitis (HP) also has been described in workers exposed to isocyanates.[38,39,40,41] Currently, the prevalence of isocyanate-induced HP in the worker population is unknown, and is considered to be rare when compared to the prevalence rates for isocyanate-induced asthma.[9] Whereas asthma is an obstructive respiratory disease usually affecting the bronchi, HP is a restrictive respiratory disease affecting the lung parenchyma (bronchioles and alveoli). The initial symptoms associated with isocyanate-induced HP are flu-like, including shortness of breath, non-productive cough, fever, chills, sweats, malaise, and nausea.[8,9] After the onset of HP, prolonged and/or repeated exposures may lead to an irreversible decline in pulmonary function and lung compliance, and to the development of diffuse interstitial fibrosis.[8,9] Early diagnosis is difficult since many aspects of HP, *i.e.*, the flu-like symptoms and the changes in pulmonary function, are manifestations common to many other respiratory diseases and conditions.

The only effective intervention for workers with isocyanate-induced sensitization (asthma) or HP is cessation of all isocyanate exposure. This can be accomplished by removing the worker from the work environment where isocyanate exposure occurs, or by providing the worker with supplied-air respiratory protection and preventing any dermal exposures.

4. EXPOSURE CRITERIA FOR DIISOCYANATES

The primary sources of exposure criteria for workplace inhalation exposures are the following: (1) NIOSH recommended exposure limits (RELs),[42] (2) the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®),[43] and (3) the U.S. Department of Labor, OSHA permissible exposure limits (PELs).[44] These exposure criteria are for diisocyanate monomers. In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs can have lower limits. Table 1 contains a comparison of the respective NIOSH RELs, ACGIH TLVs, OSHA PELs, and United Kingdom Health and Safety Executive (UK-HSE) exposure criteria for the isocyanates. The UK-HSE has taken a different approach, *i.e.*, developing a non-specific standard based on the total number of reactive isocyanate groups (TRIG) in a volume of air.[45] The standards and limits listed in Table 1 are based on a general standard that isocyanate exposures should not exceed an 8-hour time-weighted average (TWA) exposure of 5 parts per billion (ppb), or a short term or ceiling exposure of 20 ppb.

Table 1: NIOSH, ACGIH, OSHA, and UK-HSE Exposure Criteria for Isocyanates

Isocyanate Species	*Exposure Criteria - Full-shift TWAs Micrograms per cubic meter of air*			*Exposure Criteria - Short Term or Ceiling Limits Micrograms per cubic meter of air*			
	NIOSH REL	ACGIH TLV	UK-HSE	NIOSH REL Ceiling	ACGIH TLV-STEL	UK-HSE Ceiling	OSHA PEL Ceiling
TDI	CA-LFC[1]	36	None	None	140	None	140
MDI	50	51	None	200	None	None	200
HDI	35	34	None	140	None	None	None
HMDI	None	54	None	210	None	None	None
IPDI	45	45	None	180	None	None	None
NDI	40	None	None	170	None	None	None
TRIG[2]	None	None	20	None	None	70	None

[1] NIOSH considers TDI to be an occupational carcinogen (CA) and recommends that exposures be reduced to the lowest feasible concentration (LFC).
[2] TRIG - total reactive isocyanate group.

Table II. Comparison of NIOSH and OSHA Isocyanate Methods

	NIOSH 5521	NIOSH 5522	NIOSH 2535	OSHA 42/47	PROPOSED NEW NIOSH[1]
Isocyanate					
a) Monomers	TDI, MDI, HDI, NDI, HMDI[2]	TDI, MDI, HDI, NDI, HMDI,[2] IPDI [2]	TDI, HDI	42 TDI, HDI 47 MDI	TDI, HDI, MDI, NDI,[2] HMDI,[2] IPDI [2]
b) Oligomers	HDI	TDI, MDI, HDI	None	None	HDI, MDI,[2] TDI[2]
Sampler	impinger	impinger	coated glass wool/opaque tube	coated GFF	impinger; GFF; impinger + GFF
Reagent	MOPP in toluene	tryptamine in DMSO	nitro reagent	1-2PP	MAP in butyl benzoate
Shelf Life	7d 0 °C	6 mo 25°C in dark	7d 25°C in dark	42 0.1 mg; 47 1 mg 6 mo 0°C sealed	unknown
Sampling Rate **Volume**	1 L/min 5-500 L	1-2 L/min 15-360 L	0.2-1 L/min 2-170 L	1 L/min 15 L	1-2 L/min 1-500 L
Personal	No	No	Yes	Yes	Yes
Vapor	Yes	Yes	Yes	Yes	Yes
Particles ≤ 2 µm	No	No	No	Yes	impinger: No filter: Yes
Particles ≥2 µm					
a) Slow-cure	Yes	Yes	No	No[3]	impinger: Yes filter: No[3]
b) Fast-cure[4]	Yes	Yes	No	No	impinger: Yes filter: No
Sample Stability	7d 25°C: 78% 7d 4°C: 88%	28d 25°C in dark: 95-104%	14d 25°C: 91%	15d 22°C: 42 80-86%; 47 94.8%	unknown
Laboratory Sample Preparation	impinger: evap/ redissolve in methanol	none	ultrasonic extraction in methanol	extraction in ACN/ DMSO, 9 /1	impinger: SPE filter: extract or SPE
Technique	HPLC/RP, isocratic	HPLC/RP, gradient	HPLC/RP, isocratic	HPLC/RP, isocratic	HPLC/RP, gradient
Detector 1	UV @ 242 nm/ PDA	FL ex 275 nm em 320 nm	UV @ 254 nm	FL ex 240 nm em 370 nm	UV @ 253 nm
LOD[5]:					
a) amount injected	14 pmol	0.7 pmol	14 pmol	0.2 - 1 pmol	0.5 pmol
b) 15 L air conc.	1.2 ppb	0.9 ppb	0.9 ppb	0.06 - 0.1 ppb	0.08 ppb
Detector 2	EC (+ 0.8V)	EC (+ 0.8V)	None	UV @ 254 nm	FL ex 250 nm em 409 nm
LOD[5]:					
a) amount injected	0.5 pmol				est. ~ 5 fmol
b) 15 L air conc	0.04 ppb				est. ~ 0.8 ppt
Identification	Monomer: Retention Time Aliphatic oligomers: PDA	Monomer: FL Retention Time Other isocyanate: EC confirmation	Retention Time	Retention Time	Monomer: Retention Time Other isocyanate: UV/FL ratio

[1] This method is under development; procedures may change somewhat pending validation.
[2] Determination possible; lacks validation data.
[3] Usually underestimates concentration.
[4] Half-life under several minutes.
[5] Instrumental limit of detection

Abbreviations: ACN = acetonitrile; conc = concentration; d = days; DMSO = dimethyl sulfoxide; EC = electrochemical detector; em = emission; evap = evaporate; ex = excitation; FL = fluorescence detector; GFF = glass fiber filter; HPLC = high performance liquid chromatography; LOD = limit of detection; MAP = 1-(9-anthracenylmethyl)piperazine; mo = months; MOPP = 1-(2-methoxyphenyl)piperazine; nitro reagent = *N*-[(4-nitrophenyl) methyl] propylamine; PDA = photodiode array detector; 1-2PP = 1-(2-pyridyl)piperazine; RP = reversed phase; SPE = solid phase extraction; UV = ultraviolet detector

The NIOSH REL is for TWA diisocyanate exposures up to 10-hours per workday, and the ACGIH TLV is an 8-hour TWA exposure. The NIOSH RELs-ceiling limits and ACGIH short term exposure limits (STELs) are based on 10- and 15-minute TWA exposures, respectively; and should not be exceeded during the work shift. The OSHA ceiling limit is a concentration that should never be exceeded during a workday. OSHA does not have a full shift, TWA PEL for any of the diisocyanate species. The State of Oregon OSHA has promulgated occupational exposure standards for HDI-based polyisocyanates of 0.5 mg/m^3 as an 8-hour TWA, and a ceiling limit of 1.0 mg/m.[46]

5. AIR SAMPLING AND ANALYTICAL ISSUES

The measurement of isocyanates in air is a challenging sampling and analytical problem for several reasons. Isocyanates can exist in air as vapor, or as aerosol having a wide range of particle sizes. Isocyanates are very reactive, hence, unstable. There are many different chemical species, even in the same air sample, that need to be quantified. Pure analytical standards are not available for the vast majority of isocyanate species, and qualitative standards (bulk products) do not account for isocyanate species generated during polyurethane formation or breakdown. Finally, to measure isocyanates at levels corresponding to current monomer exposure limits, analytical methods must be very sensitive.

Because of the complex problems associated with accurate sampling and analysis of total isocyanate group in air, existing methods have limitations. To assess these limitations and to make rational decisions in choosing methodologies or making improvements to existing methodologies, it is useful to break down the sampling and analysis process, chronologically, into discrete steps. Each of these steps can be examined individually for the likelihood of isocyanate losses or the introduction of errors.

The sampling and analysis of isocyanates can be logically divided into six steps: collection, derivatization, sample preparation, separation, identification, and quantification. Each of these can result in losses of isocyanate or the introduction of other errors. In addition to the issue of accuracy, options for these steps differ in terms of convenience, simplicity, and speed. All of these have to be considered in choosing sampling and analytical methodology. Table II summarizes current OSHA and NIOSH sampling and analytical methods and lists the factors involved in selecting the most appropriate method for a given workplace environment.

a. Collection

Collection is the removal of the isocyanate species from the air sample into a portion of the sampler amenable to subsequent analysis. A generalized isocyanate sampler would have to be able to collect both vapor and aerosol of widely varying particle sizes. Mechanisms of collection of isocyanate vapors include dissolution into a solvent (*e.g.*, impingers) or adsorption onto a sorbent. In some cases, successful collection of isocyanate vapors may depend on reaction with a derivatizing reagent to create a nonvolatile derivative. The aspects of the sampler governing collection efficiency of particulate isocyanates are, of course, independent of the fact that these particles contain isocyanate groups.

Collection errors can be divided into three types:

(1) Aspiration errors: The efficiency with which particles enter the sampler inlet is the aspiration efficiency. The concentration of particles entering the sampler may be biased relative to the concentration outside the sampler or relative to human inhalation efficiency.

(2) Internal wall losses: There can be deposition of the isocyanate species on the internal walls of the sampler where it is not available for subsequent analysis.

(3) Transmission losses: Losses can occur from isocyanate species passing completely through the sampler.

The relative importance of these problems depends on the particle size, the sampler and inlet geometries, the sampling rate, and the collection mechanism of the sampler.

Samplers have been evaluated for aspiration efficiencies and internal losses.[47] A number of samplers have been designed with the intent to collect particles with efficiencies that match human inhalation efficiency.[48] One of these, the UK Institute of Occupational Medicine (IOM) personal inhalable sampler, has been recommended for isocyanate sampling.[49] Problems with poor aspiration efficiency and internal losses may be very important factors in the overall accuracy of the method. A recent study by the International Isocyanate Institute (III) on collection of MDI aerosol by filters and impingers found high variability in the aspiration efficiencies of particles with diameters in the 5 to 30 micrometers (μm) range.[50] This high variability is not inconsistent with what is often found in the sampling of large particles.[48] The III study also found that for large particles, a substantial percentage of the aerosol collected by filter samplers was deposited on the filter holder. It has also been shown that losses of relatively large particles can occur on the walls of both the inlet and the nozzle of the impingers.[47,51]

Assessments of collection efficiencies in isocyanate sampling have often been limited to measuring the relative amount of isocyanate species passing through the sampler. Based on this criterion, reagent-coated glass fiber filters (GFFs) appear to prevent the passage of isocyanate vapors and particles of widely varying sizes.[52,53] Recent studies have investigated the mechanisms by which particles pass through impingers.[54,55] Impingers have been found to prevent passage of vapors and particles greater than 2 μm in diameter, but allow substantial penetration of particles smaller than 2 μm.[50,56,57] Particles smaller than 2 μm include condensation aerosol (*e.g.*, environments where MDI is heated) and aerosol generated from combustion processes.

Two methods have been developed that segregate isocyanate species on collection according to their physical states. Being able to differentiate vapor and aerosol exposures is desirable because vapor and aerosol differ in their extent of penetration and deposition in the respiratory tract. These different types of exposures can result in different health consequences. One method uses a dual filter system, where aerosols are collected on a reagentless front filter and vapors collected on a reagent-coated back filter.[58,59] One potential problem with this system is the loss of isocyanate species in the aerosol fraction due to curing reactions occurring between the times of collection and post-sampling derivatization. This problem would be

expected to be greater the longer the sampling time and the more reactive the isocyanate system. Another potential problem is the misclassification of semivolatile species, such as monomers, either by adsorption of vapor on the front filter or volatilization of species originally collected as aerosol. Another sampler used for isocyanates that separates vapor and aerosol consists of an annular denuder for vapor collection, followed by a reagent-coated GFF for aerosol collection.[60] A limitation of this system is that it is too large for personal sampling.

b. Derivatization

Once the isocyanate species have been collected, they must be efficiently derivatized. Derivatization of isocyanate species accomplishes two things. First, it stabilizes the isocyanate, which would otherwise be lost to reaction with polyols or water. Second, it improves detection of the isocyanate by increasing sensitivity and selectivity.

The two most important factors in achieving efficient derivatization are the inherent reactivity of the reagent and the ability of the collection medium to dissolve or disperse collected particles or droplets and/or make derivatizing reagent accessible to the isocyanate groups. Derivatizing reagents in use today are most commonly primary or secondary aliphatic amines and their inherent reactivities with isocyanates typically differ by less than a factor of five.[61,62] This difference is probably not very important. Probably of greater importance is the efficiency of mixing the collected particles and derivatizing reagent.

Aerosols generated from spray applications of isocyanate products typically contain a mixture of isocyanate and polyol. If the polyol and isocyanate are not separated and the derivatizing reagent is not accessible to the isocyanate group at the time of collection, the isocyanate will be lost to reaction with the polyols within the droplet.[2,63] This would appear to be a significant problem for collection of droplets on reagent-coated GFFs. Micrographs of spray paint droplets on GFFs show that droplets typically make only minimal contact with the fibers.[51] This is not conducive to dispersal of the droplet or mixing of the reagent coated on the fiber with the isocyanate species. The larger the droplet, the greater the problem is likely to be because of the greater potential deficiency of reagent at or near the sites of contact with the fibers. Derivatization of isocyanate species present in particles or droplets is expected to be more efficient using impinger collection. The solvent not only serves to disperse or dissolve the droplet or particle, thereby interfering with the curing reaction but also provides a means for bringing the reagent and the isocyanate species together.

Two practices have been investigated that appear to improve the performance of reagent-coated GFFs when sampling aerosols. One is the presence of a small amount of nonvolatile solvent, such as diethyl phthalate or diphenylmethane, on the filter.[64,65,66,67] Another is the desorption of the filter in a solution of derivatizing reagent immediately after sampling.[66]

c. Sampling: Collection plus Derivatization

Reagent-coated GFFs and sorbents, impingers, and bubblers have all been investigated as samplers for isocyanates. Some sampler comparisons have been conducted under laboratory conditions and others in the field. The majority of comparisons have found that solventless samplers give higher results than impingers or bubblers in laboratory evaluations and impingers

and bubblers give higher results in the field.[2] A likely explanation is that collection efficiency is most important in laboratory evaluations, under which conditions the polyols that compete with derivatizing reagent are generally not present. Under conditions where derivatization kinetics are relatively unimportant, reagent-coated GFFs may give higher results than impingers because the GFFs collect small particles more efficiently. In the field, where derivatization rate is clearly important, impingers and bubblers tend to give higher results than solventless samplers. Evidence for this is especially strong in environments where rapidly curing MDI-based products are sprayed.[67,68,69,70] The literature is more ambiguous concerning environments where less reactive HDI-based products are used.[71,72,73,74]

Table II gives recommendations for sampler use based on the size and cure rate of the isocyanate aerosol. The cure rate of isocyanate systems depends on the nature of the isocyanate, the nature of the co-reactant (typically polyols), the type of catalysis (if any), and the temperature. The half-lives of isocyanate species in reactive systems (*i.e.*, the time it takes for half of the isocyanate groups to undergo a curing reaction) can vary from a few seconds to many hours. For the purposes of this document, isocyanate systems having half lives of a few minutes or less are considered fast cure. The faster the product cures, the more strongly an impinger is recommended for sampling. Also, the larger the particle size, the more strongly an impinger is recommended. An impinger is recommended for all aerosols having particle diameters greater than 2 μm because it is believed that the poor mixing on filters results in poor derivatization efficiency. Based on the thin-walled sampler model of Vincent,[75] estimation of the aspiration efficiency of the impinger indicates reasonably close agreement with the inhalability convention for particles smaller than 20 μm when ambient wind speed is low (as is typical for indoor workplace environments[76]). For larger particle sizes and relatively high wind speeds, the impinger is expected to undersample relative to the inhalability convention. Filters are recommended for sampling particles smaller than 2 μm because these particles are known to be collected inefficiently by impingers and because smaller particles, by requiring much less reagent than large particles, are less susceptible to local depletion of reagent. For environments that are likely to have isocyanate species present as both large and small particles, a sampling train consisting of an impinger followed by a reagent-coated filter is recommended.[2,49]

There are other factors in addition to accuracy that must be considered in choosing a sampler. The use of an impinger is considerably less convenient than use of a filter. Impingers may even be deemed inappropriate for personal sampling. NIOSH Method 5521[77] (which is adapted from United Kingdom Health and Safety Executive Method MDHS 25[78]) uses an impinger containing a solution of reagent in toluene. Because the toluene vaporizes extensively during sampling, NIOSH does not recommend this method for personal sampling. NIOSH Method 5522[79] uses an impinger containing a solution of dimethyl sulfoxide (DMSO). Because DMSO is readily absorbed through the skin, NIOSH recommends that DMSO impingers be used for area air sampling only. The new NIOSH method under development uses impingers containing a solution of reagent in butyl benzoate. Since butyl benzoate is a non-volatile solvent, sampling with it generates minimal vapor. It does not elicit the same concern as DMSO in terms of dermal absorption.

d. Sample Handling and Preparation

Sample handling and preparation include those steps taken to stabilize the sample or make the sample more compatible with the analytical procedure. Sample handling considerations actually begin before sample collection. Some reagents and sampling media have limited shelf lives and require special storage conditions. For example, the nitro reagent and 9-(methylaminomethyl)-anthracene (MAMA) are known to be light sensitive.[4,80] It has also been found that filters coated with 1-(2-pyridyl)piperazine show substantial reagent loss to the back-up pad during storage.[81] This loss is greatly reduced by storing the reagent-coated filters in the freezer before use. Users of methods need to be aware of such problems and follow the method's guidelines for storage of sampling media.

All filter methods require extraction of the filter with a suitable solvent prior to analysis by high performance liquid chromatography (HPLC). The Iso-Chek™ method,[58,59] which utilizes a reagentless filter, requires that extraction with a derivatization solution be done immediately after sampling. It has been reported that extraction in the field, preferably with a reagent solution, is beneficial for reagent-coated filters as well.[66] Typically, reagent-coated filters are transported to the laboratory, where extraction takes place prior to analysis. It may be desirable to filter the extraction solution prior to analysis by HPLC.[49]

Impinger methods frequently require the impinger solvent to be exchanged to a more HPLC-compatible solvent prior to analysis. This is generally achieved by evaporation of the impinger solvent to dryness and the redissolution of the sample in a solvent more compatible with HPLC analysis. Toluene impingers are typically treated in this manner.[77,78] If the volume of solvent used for redissolution is relatively small (or the redissolution solvent is easily concentrated), this step can also serve to concentrate the sample and improve the LOD of the method. Losses can conceivably occur because of incomplete redissolution of the sample components. Ultrasonication of the reconstituted solution may be done to facilitate redissolution.[77] Evaporation/redissolution requires that the impinger solvent be somewhat volatile. Unfortunately, a volatile solvent is undesirable during sampling because of the potential for vapor exposures as well as fire hazards.

If a method uses a non-volatile, HPLC-incompatible impinger solvent, solvent exchange can be accomplished by solid-phase extraction (SPE). This is the procedure used to remove the butyl benzoate in the NIOSH method currently under development. SPE has the advantage of being readily automated. Also, it may enable removal of excess reagent and impurities prior to HPLC analysis. A drawback is the potential for incomplete elution of isocyanate species.

If the derivatizing reagent is not removed prior to HPLC analysis (*e.g.*, by SPE), methods frequently recommend acetylation of the excess reagent with acetic anhydride prior to sample injection.[49,77,82] Excess reagent typically gives a large, tailing peak near the beginning of the HPLC chromatogram. This tail may interfere with the quantification of analytes. Also, repeated injection of large amounts of amine reagent can degrade the analytical column. The acetylated reagent does not tail appreciably and its presence in the sample does not degrade the analytical column.

In cases where a method uses an impinger solvent compatible with HPLC analysis, pre-analysis sample preparation may not be necessary. In NIOSH Method 5522,[79] an aliquot of the DMSO impinger solution is injected directly into the HPLC. This is simple, saves time, and avoids losses of isocyanate that can result from sample manipulation.

e. Separation

The first step in the analysis of a solution containing derivatized isocyanates is the separation. The separation technique isolates individual compounds from a complex mixture to enable correct identification and accurate quantification of each component. A total isocyanate method will be biased low if the separation technique does not deliver all the derivatized isocyanate species to the detector(s) as identifiable and quantifiable peaks.

Reversed-phase HPLC has been the dominant separation technique in isocyanate analysis.[1,3,4] A reversed-phase HPLC analysis can be isocratic, *i.e.*, having a constant mobile phase strength, or gradient, *i.e.*, having the mobile phase strength increasing during the course of the analysis. Isocyanate samples frequently contain compounds of greatly varied molecular weight, which translates to greatly varied retention in an isocratic analysis. Such an analysis is necessarily long, with late eluting peaks that are broad and difficult to detect and quantify accurately.

Gradient elution is frequently used when compounds of widely differing retention need to be determined in the same analysis. Weakly retained compounds are eluted early in the chromatogram with a relatively weak mobile phase. Then the mobile phase is strengthened to accelerate the elution of more highly retained compounds. Not only do these compounds elute faster than in an isocratic analysis, resulting in shorter analysis times, but also the peaks are taller and narrower, improving the LOD and facilitating peak integration.

Several total isocyanate methods have been evaluated for recovery of derivatized oligomeric isocyanate species. An evaluation of MDHS 25 found an average recovery of 105% for three isocyanate prepolymers.[83] In contrast, two separate investigations of prepolymers using NIOSH 5521 (which is very similar to MDHS 25) found 58% and 60% recoveries, respectively.[84,85] An evaluation of NIOSH 5522 found average recoveries for five prepolymer products of 62%.[85] MDHS 25 and NIOSH 5521 are isocratic methods, whereas NIOSH 5522 increases the strength of the mobile phase slightly during the analysis. These evaluations did not distinguish between actual physical losses of isocyanate and apparent losses resulting from prepolymers having lower detector response factors than the monomers used for calibration. However, the similarities in recoveries, comparing NIOSH 5521 and NIOSH 5522, suggest that physical losses are likely. If this is the case, a method using a stronger gradient may improve recoveries. This contrasts with the experience of the developers of MDHS 25/2 who have found no additional isocyanate-derived peaks even after using a gradient ending and holding at 100% acetonitrile.[86]

Gradient elution most frequently involves increasing the percent of organic modifier in the mobile phase. There are several disadvantages to this approach relative to isocratic analyses. It requires preparation of at least two mobile phases. Although the analytes elute faster, there may be considerable time required between analyses to allow for the system to reequilibrate

to the initial conditions.[87] The baseline of the chromatogram is likely to change during the gradient, making it more difficult to integrate small peaks. Finally, artifact peaks can elute as the mobile phase is strengthened.[88] There are also some disadvantages of gradient elution of particular importance in isocyanate analysis. Several methods for total isocyanate (MDHS 25,[78] NIOSH 5522,[79] and the Ontario Ministry of Labour tryptamine method[82]) use electrochemical (EC) detectors. Unfortunately, EC detectors are somewhat incompatible with gradient elution because they are especially sensitive to changes in mobile phase. Also, HPLC-based total isocyanate methods quantify isocyanate species for which analytical standards are not available by assuming the detector response per isocyanate group is the same as that of a derivatized monomer standard. Even if the responses are the same in the same mobile phase, the response of a late-eluting isocyanate species may be quite different than that of the derivatized monomer if the two are eluting in substantially different mobile phases. Therefore, there is a potential for quantification errors.

The method under development at NIOSH uses a pH gradient to accelerate the elution of highly retained compounds, rather than the more common organic modifier gradient. This is made possible because isocyanate derivatives of 1-(9-anthracenylmethyl)piperazine[62,89,90] (MAP) contain a highly basic tertiary amine group that is easily protonated. The degree of protonation, which is controlled by the mobile phase pH, has a very large effect on the retention of MAP derivatives, especially those containing multiple derivatized isocyanate groups. Several disadvantages associated with organic modifier gradients are minimized or eliminated with the pH gradient. Reequilibration time between runs is very short, baseline changes during the gradient are relatively small, and elution of artifacts originating from the mobile phase solvents is less likely because the gradient selectively accelerates compounds with amine functionalities. Similarly, if a MAP-isocyanate derivative should co-elute with a non-amine interferant, a small change in pH gradient will move the MAP derivative away from the interferant. With a nonselective organic modifier gradient, the separation of an analyte from a co-eluting interferant is not so straightforward since both compounds will respond to a change in the gradient. The UV response of MAP-derivatized isocyanates is only minimally affected by the changing pH. The fluorescence (FL) response of MAP derivatives is greatly affected by mobile phase pH, but this is readily corrected by lowering the pH with post column addition of acid. Disadvantages of pH gradients are that they are limited to ionizable compounds and these ionizable compounds are more prone to problems associated with adsorption in the chromatographic system. These problems may include tailing peaks, reduced peak heights and areas, and carry-over. Special procedures or equipment (such as inert fluid paths in the HPLC or base-deactivated analytical columns) are necessary to avoid adsorption problems.

Another type of gradient that has been used for total isocyanate analysis is a mobile phase flow gradient.[91] Instead of changing mobile phase composition, the flow rate is increased to reduce the retention time of late-eluting compounds. The advantages of this procedure are that only one mobile phase is required, there is minimal disturbance of the baseline, and no mobile-phase related artifacts are eluted. One of the disadvantages is that, although peaks are narrower, UV or FL detector responses decrease with increasing flow rate. Also, since the acceleration of the analytes is directly proportional to the flow rate increase, pressure limitations make the accelerating power of this gradient modest compared to organic modifier or pH gradients.

Capillary-zone electrophoresis (CZE) has been investigated for isocyanate analysis.[92] It has several advantages relative to HPLC — low solvent consumption, relatively short analysis time, higher resolution, and a greater certainty that all analytes will reach the detector. Moreover, there is a degree of selectivity associated with the technique because only charged analytes migrate to the detector. The major disadvantage of CZE is the relatively poor concentration sensitivity owing to the extremely small injection volumes used. Both 1-(2-methoxyphenyl)piperazine (MOPP) and MAP have been found to be useful derivatizing reagents for CZE analysis.[93] One advantage that MAP derivatives possess is that they are more basic than MOPP derivatives. As a result, they are protonated in the solutions of relatively high organic content needed for dissolving oligomeric isocyanate species.

f. Identification

In typical chromatographic analyses of environmental contaminants, analytical standards exist for the analyte of interest. The analyte is identified as such in a real sample if its chromatographic retention time matches that of the analytical standard. However, for isocyanate species, pure analytical standards generally exist only for derivatized monomers. Moreover, in many environments, monomers contribute very little to the total isocyanate group present. The analysis of a derivatized bulk of prepolymeric isocyanate product can be very useful in identifying non-monomeric isocyanate species in real samples collected during use of that product. There are limitations to using such products as analytical standards for identification and quantification. Not all isocyanate species to which a worker may be exposed are present in the product. When isocyanate products are being used, the components are typically undergoing curing reactions with polyols, so new species containing isocyanate groups are being generated. Isocyanate-containing species are also generated during thermal breakdown of polyurethane. Chromatographic retention times are not available to identify these new species. In order to identify all isocyanate species — monomers or oligomers, those present in the bulk product and those newly generated — a means of identification other than chromatographic retention time is necessary.

Correct identification of unknown isocyanate species requires that the detection scheme be selective or provide some qualitative information about the species in question. Isocyanate methods generally utilize derivatizing reagents that are responsible for the detectability of the reagent/isocyanate derivative. Total isocyanate methods generally seek to identify all compounds labeled with the derivatizing reagent. Knowledge of the work environment is required to discount any nonisocyanate species that may react with the derivatizing reagent and give a signal in the sample chromatogram. Once these compounds are accounted for, it is assumed that all other compounds in the chromatogram that contain the reagent label are derivatized isocyanates.

A single non-selective detector (such as a UV detector) is insufficient for total isocyanate analysis because it provides little qualitative information about the chromatographic peaks. However, two detectors in series provide a considerable amount of qualitative information. The reason for this is that when the responses for each detector are in the detectors' linear operating range, the ratio of detector responses is a constant (*i.e.*, independent of concentration) for any given compound. Therefore, a compound can be identified by that ratio. If the detector responses of derivatized isocyanates are derived primarily from the reagent

label, then it is conceivable that all derivatized isocyanates would have similar detector response ratios and could be identified on the basis of those ratios. Several total isocyanate methods operate by this strategy.[78,79,82,84]

A widely used method for total isocyanate group is MDHS 25.[78] It identifies isocyanates derivatized with MOPP based on the ratio of EC and UV detector (242 nm) responses. The EC detector is sensitive and fairly selective,[94] but it also has been found to be relatively unstable.[82,95] UV absorbance at 242 nm is not selective and not especially strong for MOPP-derivatized isocyanates.[62] As a result, a substantial portion of the absorbance of MOPP-derivatized aromatic isocyanates comes from the aromatic portion of the isocyanates rather than from the MOPP-derivatized isocyanate group. Under these circumstances, an oligomeric aromatic isocyanate compound containing more aromatic rings per isocyanate group than the derivatized monomer will have a substantially higher UV response per isocyanate group than the derivatized monomer. This could adversely affect the identification of unknown isocyanate species. This problem was demonstrated in a study involving 2,4-TDI-based urethane oligomers.[96] This same study found that the EC detector response for these compounds is not directly proportional to the number of derivatized isocyanate groups. It was concluded that MOPP-derivatized oligomeric isocyanates, particularly oligomeric aromatic isocyanates, are likely to give EC/UV ratios substantially different from the EC/UV ratio of the MOPP-derivatized monomer and therefore not recognizable as isocyanates.

Methods based on tryptamine derivatization, including NIOSH 5522[79] and the method developed by the Ontario Ministry of Labour,[82] use FL and EC detection in series for identification. Estimations of the compound-to-compound variabilities of detector responses, as indicated by their relative standard deviations (S_r), vary in different studies (FL S_r 13-26% and EC S_r 18-71%).[62,82,97] Not only is the compound-to-compound response variability relatively small for FL detection of tryptamine derivatives, but the selectivities of FL and EC detection are much greater than that of UV detection. Overall, FL/EC detection of tryptamine derivatives would appear to give more reliable identification than EC/UV of MOPP derivatives.

A total isocyanate method based on derivatization with MAMA and either FL/UV or UV/UV detection has been developed.[91,98] MAMA absorbs very strongly in the UV at 256 nm. Even though this is not a particularly selective wavelength, the intensity of the absorbance is so great that nearly all the absorbance of a MAMA-derivatized isocyanate at 256 nm comes from the MAMA group. This results in very small compound-to-compound variability of UV responses (S_r 7-14%)[62,98], which facilitates identification. Secondary absorbances (such as 366 nm) are relatively weak but highly selective, so that UV/UV ratios are very constant and diagnostic (S_r 3-8%).[62,98] FL compound-to-compound variability is relatively high (S_r 55-59%).[62,98] But, as in the case of tryptamine, the inherent selectivity of FL detection makes FL/UV identification attractive, especially given the substantially better sensitivity than a method relying on UV/UV identification.

The NIOSH method under development using the MAP reagent relies on FL/UV detection for identification. Like MAMA, MAP contains an anthracene group as the chromophore/fluorophore so that the absorbance and fluorescence characteristics of the two reagents are very similar. MAP derivatives appear to have somewhat lower compound-to-

compound variabilities in both UV (S_r 3.5%) and FL (S_r 33%) responses than the corresponding MAMA derivatives.[62]

Instead of using two one-dimensional detectors in series, some methods utilize multidimensional detectors for identification. It has been found that photodiode array (PDA) detection, which provides an entire UV spectrum of a chromatographic peak, is useful in identifying MOPP-derivatized isocyanates.[95] The developers of MDHS 25/2 now advocate the use of the PDA detector to strengthen identification.[86] The disadvantage of the PDA is that it is somewhat less sensitive than standard UV detectors. Several researchers have investigated the mass spectrometer (MS) as a detector for derivatized isocyanates.[99,100,101,102] The MS has the potential to go beyond simply identifying a compound as a derivatized isocyanate. It can provide considerable information about the structure of the compound and serves as an important research tool. The primary disadvantages of using HPLC/MS for typical sample sets are the expense of the instrument and the expense and nonroutine nature of its operation.

g. Quantification

Once a chromatographic peak has been correctly identified as being isocyanate-derived, it must be quantified. For methods used to determine monomeric isocyanates only, identification is generally based on retention time and analytical standards exist that enable direct construction of a calibration curve for quantification. The major factor in choosing a derivatizing reagent/detector combination is LOD. The LODs for reagent/detector combinations used in NIOSH and OSHA methods are given in Table II. With regard to NIOSH and OSHA methods limited to measuring monomer, NIOSH 2535[103] uses the nitro reagent with UV detection to determine TDI and HDI. This reagent/detector combination provides relatively poor sensitivity. OSHA 42[104] and OSHA 47[105] use 1-(2-pyridyl)piperazine (PP) to derivatize TDI, HDI, and MDI with detection by either FL or UV. FL detection of PP derivatives provides fairly good sensitivity.

Methods for quantifying non-monomeric isocyanate species can be divided into those that use the bulk product for calibration, such as Miles (Bayer) Method 1.4.3,[106] and those that quantify every isocyanate derivative in the chromatogram based on the response of the derivatized monomer (*e.g.*, MDHS 25/2[49] and NIOSH Method 5522[79]). Miles Method 1.4.3 uses known amounts of derivatized bulk isocyanate product to construct a calibration curve.[106] The areas of the largest peak or several largest peaks in the chromatogram are plotted against the concentration of the product injected. Using this calibration curve, the peak areas in real samples can be correlated with a quantity of bulk isocyanate product. Taking this a step further, the total isocyanate concentration in the sample can be calculated using the known or measured isocyanate content of the bulk product. There are several advantages to this approach. It requires the integration of at most a few peaks in the sample chromatogram. Since identification is based on retention time, only a single detector is needed. Finally, it does not depend on all isocyanate species in the sample eluting from the HPLC as identifiable peaks. The disadvantage of this approach is that it does not enable accurate quantification of total isocyanate group in all environments. For example, this approach cannot be used to quantify the isocyanate species produced by thermal decomposition of polyurethane. Also, even when an isocyanate product is being used, this approach cannot take into account newly formed

isocyanate species that are not present in the product. The approach assumes that the major components in the bulk are the major components to which exposure occurs. This is probably a reasonable assumption for spraying relatively slow-curing isocyanate products. The more reactive the product and the greater the time between initiation of curing reactions and exposure, the more likely that the composition of the isocyanate species to which exposure occurs will differ significantly from the composition in the bulk product.

Total isocyanate methods that attempt to quantify every isocyanate species in a chromatogram typically use two detectors for identification; only one detector is required for quantification. Nevertheless, the method LOD is generally limited by the LOD of the less sensitive detector, since below that LOD a compound cannot be properly identified. A possible exception to this is for isocyanate compounds that are present in the bulk product. Analysis of a relatively high concentration of the derivatized bulk product enables evaluation of each chromatographic peak using both detectors. Derivatized isocyanates can then be identified in real samples if their retention times match those of compounds identified as isocyanates in the bulk product, even when the levels are below the LOD of the less sensitive detector.

In addition to LOD considerations, an important aspect of quantification of total isocyanates is accuracy. To quantify compounds for which analytical standards are not available, the detector response factor for the unknown derivatized isocyanate species must be the same as that of the derivatized monomer. This is achieved by choosing a derivatizing reagent/detector combination such that nearly all the detector response is attributable to the derivatization reagent label and that response does not change from compound to compound. Whereas a certain amount of compound-to-compound variability in detector response is tolerable for compound identification, especially when dealing with very selective detectors, compound-to-compound response variability in the detector used for quantification translates directly to errors in quantification.

For MDHS 25,[78] which quantifies MOPP-derivatized isocyanates by EC, two studies have found compound-to-compound variability of the EC response for model compounds to be S_r of 26%[97] and 28%[62], respectively. Also, a study of MOPP-derivatized urethane oligomers found that the EC response is not proportional to the number of derivatized isocyanate groups. Instead, it was found that the EC response increased as the size of the oligomer increased.[96] Methods employing the tryptamine reagent use FL and EC detection; FL is recommended for quantification. Studies have found the compound-to-compound variabilities by FL in the range of S_r 13-26%.[62,82,97] The sensitivity for detection of tryptamine-derivatized isocyanates by FL is fairly good.

Methods employing the MAMA and MAP reagents use UV and FL detection. The very small compound-to-compound variability in UV response for MAMA- and MAP-derivatized isocyanates, coupled with the fairly good sensitivity for UV detection around 256 nm, makes quantification of MAMA and MAP derivatives by UV arguably superior to other reagent/detector combinations. The sensitivities of detection for MAMA and MAP derivatives by FL are better than any other reagent/detector combination in common use for isocyanate determination. Unfortunately, the compound-to-compound variability is unacceptably high for quantification of derivatized isocyanates for which standards are unavailable. Fluorescence detection can be used to quantify monomers. It may also be suitable for quantification of

other isocyanate species present below the UV LOD if their UV/FL ratios have been previously determined in a sample containing levels above the UV LOD.

Excellent limits of detection have been reported for HPLC/MS, comparable to or better than those of MAMA and MAP derivatives by FL.[99,100] A limitation of MS in quantifying isocyanate species for which analytical standards are not available is that compound-to-compound variability in response is likely to be very high. This is because the kinetics of the processes that produce ions for quantification in the MS are greatly influenced by the molecular structures of the compounds. As a result, quantification of non-monomeric isocyanate species based on the monomer response is likely to be very inaccurate.

6. CONCLUSIONS

The ability to measure isocyanate-containing substances in air, whether they are in monomer, prepolymer, polyisocyanate, and/or oligomer forms, is important when assessing a worker's isocyanate exposure. Adverse health outcomes from isocyanate exposure include irritation to the skin, mucous membranes, eyes, and respiratory tract; contact and allergic dermatitis; hypersensitivity pneumonitis; and respiratory sensitization (asthma). Respiratory sensitization (an asthma-like response) is the most common of these health outcomes with a prevalence ranging from 5 to 30% of workers in a variety of industrial processes. Experience has shown that monomeric, prepolymer, polyisocyanate, and oligomeric isocyanate species are capable of producing respiratory sensitization in exposed workers. After sensitization, any exposure, even to levels below existing occupational exposure limits or standards, can produce an asthma-like response that may be life threatening.

Accurate and sensitive determination of isocyanates is complex and difficult. The advantages and disadvantages of the various methods must be understood, in order to choose the most appropriate sampling and analytical method for a particular workplace environment. Isocyanates may be in the form of vapors or aerosols of various particle size; the species of interest are reactive and unstable; few pure analytical standards exist; and high analytical sensitivity is needed. In addition, there are numerous points in the sampling and analytical procedures where errors can be introduced. The selection of the most appropriate isocyanate method for a given workplace environment is based upon an evaluation of measurement accuracy, specificity, sensitivity, convenience, simplicity, and speed. These factors must be considered for the entire analytical measurement process including collection, derivatization, sample preparation, separation, identification, and quantification. Unfortunately, the need to measure highly reactive isocyanate species at low levels is many times in conflict with the desire of industrial hygienists and chemists to choose methods that are convenient to use in the field and are easy to run in the laboratory.

Table I summarizes NIOSH, OSHA, ACGIH, and United Kingdom HSE isocyanate exposure standards. Table II summarizes NIOSH and OSHA isocyanate methods and method selection for a given workplace environment. The selection of the most appropriate isocyanate method depends upon the isocyanate species, its physical state, its cure rate, the sensitivity required and other factors shown in Table II. This information, which is used to select methods for NIOSH research studies and health hazard evaluations, is provided when employers, industrial hygienists, or laboratories request NIOSH technical assistance on isocyanate methods.

In closing, more research is needed to resolve the limitations of current sampling and analytical methods. Such research is ongoing at NIOSH and elsewhere in government, in academia, and in the private sector. Therefore, this guidance is subject to revision as isocyanate exposure standards change and as new or improved isocyanate analytical methods are published.

REFERENCES

1. Purnell CJ, Walker RF [1985]. Methods for the determination of atmospheric organic isocyanates: a review. *Analyst 110*: 893-905.

2. Streicher RP, Kennedy ER, Lorberau CD [1994]. Strategies for the simultaneous collection of vapours and aerosols with emphasis on isocyanate sampling. *Analyst 119*: 89-97.

3. Levine SP, Hillig KJD, Dharmarajan V, Spence MW, Baker MD [1995]. Critical review of methods of sampling, analysis, and monitoring for TDI and MDI. *American Industrial Hygiene Association Journal 56*: 581-589.

4. Dharmarajan V, Lingg RD, Booth KS, Hackathorne DR [1987]. Recent developments in the sampling and analysis of isocyanates in air. In *Sampling and Calibration for Atmospheric Instruments*, JK Taylor, ed. [ASTM Special Technical Publication No. 957]. Philadelphia, PA: American Society for Testing and Materials.

5. Woods G [1987]. *The ICI Polyurethanes Book*. New York, NY: ICI Polyurethanes and John Wiley & Sons. Inc.

6. NIOSH [1978]. Criteria for a recommended standard: occupational exposure to diisocyanates. DHEW (NIOSH) Publication No. 78-215. Cincinnati, OH: U.S. Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH.

7. NIOSH [1990]. Pocket guide to chemical hazards. DHHS (NIOSH) Publication No. 90-117. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH.

8. NIOSH [1986]. Occupational respiratory diseases. DHHS (NIOSH) Publication No. 86-102. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH.

9. Levy BS, Wegman DH (editors) [1988]. *Occupational Health: Recognizing and Preventing Work-Related Diseases*. Second Edition. Boston/Toronto: Little, Brown and Company.

10. Porter CV, Higgins RL, Scheel LD [1975]. A retrospective study of clinical, physiologic, and immunologic changes in workers exposed to toluene diisocyanate. *American Industrial Hygiene Association Journal 36*: 159-168.

11. Chan Yeung M, Lam S [1986]. Occupational asthma. *American Review of Respiratory Disease 133*: 686-703.

12. NIOSH [1981]. Technical report: respiratory and immunologic evaluation of isocyanate exposure in a new manufacturing plant. DHHS (NIOSH) Publication No. 81-125. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH.

13. McKay RT, Brooks SM [1981]. Toluene diisocyanate (TDI): biochemical and physiologic studies. *American Review of Respiratory Disease 123*: 132.

14. Harries M, Burge S, Samson M, Taylor A, Pepys J [1979]. Isocyanate asthma: respiratory symptoms due to 1,5-naphthylene di-isocyanate. *Thorax 34*: 762-766.

15. Woolrich PF [1982]. Toxicology, industrial hygiene and medical control of TDI, MDI, and PMPPI. *American Industrial Hygiene Association Journal 43*: 89-98.

16. Mobay Corporation [1983]. Health & safety information for MDI, diphenylmethane diisocyanate, monomeric, polymeric, modified. Pittsburgh, PA: Mobay Corporation.

17. Berlin L, Hjortsberg U, Wass U [1981]. Life-threatening pulmonary reaction to car paint containing a prepolymerized isocyanate. *Scandinavian Journal of Work, Environment and Health 7*: 310-312.

18. Zammit-Tabona M, Sherkin M, Kijek K, Chan H, Chan-Yeung M [1983]. Asthma caused by diphenylmethane diisocyanate in foundry workers. *American Review of Respiratory Disease 128*: 226-230.

19. Chang KC, Karol MH [1984]. Diphenylmethane diisocyanate (MDI)-induced asthma: evaluation of immunologic responses and application of an animal model of isocyanate sensitivity. *Clinical Allergy 14*: 329-339.

20. Seguin P, Allard A, Cartier A, Malo JL [1987]. Prevalence of occupational asthma in spray painters exposed to several types of isocyanates, including polymethylene polyphenyl isocyanate. *Journal of Occupational Medicine 29*: 340-344.

21. Nielsen J, Sungo C, Winroth G, Hallberg T, Skerfving S [1985]. Systemic reactions associated with polyisocyanate exposure. *Scandinavian Journal of Work, Environment and Health 11*: 51-54.

22. Alexandersson R, Gustafsson P, Hedenstierna G, Rosen G [1986]. Exposure to naphthalene-diisocyanate in a rubber plant: symptoms and lung function. *Archives of Environmental Health 41*: 85-89.

23. Mapp CE, Chiesura-Corona P, DeMarzo N, Fabbri L [1988]. Persistent asthma due to isocyanates. *American Review of Respiratory Disease 137*: 1326-1329.

24. Liss GM, Bernstein DI, Moller DR, Gallagher JS, Stephenson RL, Bernstein IL [1988]. Pulmonary and immunologic evaluation of foundry workers exposed to methylene diphenyldiisocyanate (MDI). *Journal of Allergy and Clinical Immunology 82*: 55-61.

25. Keskinen H, Tupasela O, Tiikkainen U, Nordman H [1988]. Experiences of specific IgE in asthma due to diisocyanates. *Clinical Allergy 18*: 597-604.

26. Cartier A, Grammar L, Malo JL, Lagier F, Ghezzo H, Harris K, Patterson R [1989]. Specific serum antibodies against isocyanates: association with occupational asthma. *Journal of Allergy and Clinical Immunology 84*: 507-514.

27. Mobay Corporation [1991]. Hexamethylene diisocyanate based polyisocyanates, health and safety information. Pittsburgh, PA: Mobay Corporation.

28. Vandenplas O, Cartier A, Lesage J, Perrault G, Grammar LC, Malo JL [1992]. Occupational asthma caused by a prepolymer but not the monomer of toluene diisocyanate (TDI). *Journal of Allergy and Clinical Immunology 89*: 1183-1188.

29. Vandenplas O, Cartier A, Lesage J, Cloutier Y, Perrault G, Grammar LC, Shaughnessy MA, Malo JL [1992]. Prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. *Journal of Allergy and Clinical Immunology 91*: 850-861.

30. Baur X, Marek W, Ammon J, Czuppon AB, Marczynski B, Raulf-Heimsoth M, Roemmelt H, Fruhmann G [1994]. Respiratory and other hazards of isocyanates. *International Archives of Occupational and Environmental Health 66*: 141-152.

31. Weill H [1979]. Epidemiologic and medical-legal aspects of occupational asthma. *The Journal of Allergy and Clinical Immunology 64*: 662-664.

32. Adams WGF [1975]. Long-term effects on the health of men engaged in the manufacture of tolylene diisocyanate. *British Journal of Industrial Medicine 32*: 72-78.

33. White WG, Sugden E, Morris MJ, Zapata E [1980]. Isocyanate-induced asthma in a car factory. *Lancet i*: 756-760.

34. Karol MH, Hauth BA, Riley EJ, Magreni CM [1981]. Dermal contact with toluene diisocyanate (TDI) produces respiratory tract hypersensitivity in guinea pigs. *Toxicology and Applied Pharmacology 58*: 221-230.

35. Erjefalt I, Persson CGA [1992]. Increased sensitivity to toluene diisocyanate (TDI) in airways previously exposed to low doses of TDI. *Clinical and Experimental Allergy 22*: 854-862.

36. Rattray NJ, Bothman PA, Hext PM, Woodcock DR, Fielding I, Dearman RJ, Kimber I [1994]. Induction of respiratory hypersensitivity to diphenylmethane-4,4'-diisocyanate (MDI) in guinea pigs. Influence of route of exposure. *Toxicology 88*: 15-30.

37. Bickis U [1994]. Investigation of dermally induced airway hyperreactivity to toluene diisocyanate in guinea pigs. Ph.D. Dissertation, Department of Pharmacology and Toxicology, Queens University, Kingston, Ontario, Canada.

38. Baur X, Dewair M, Rommelt H [1984]. Acute airway obstruction followed by hypersensitivity pneumonitis in an isocyanate (MDI) worker. *Journal of Occupational Medicine 26*: 285-287.

39. Yoshizawa Y, Ohtsuka M, Noguchi K, Uchida Y, Suko M, Hasegawa S [1989]. Hypersensitivity pneumonitis induced by toluene diisocyanate: sequelae of continuous exposure. *Annals of Internal Medicine 110*: 31-34.

40. Selden AI, Belin L, Wass U [1989]. Isocyanate exposure and hypersensitivity pneumonitis - report of a probable case and prevalence of specific immunoglobulin G antibodies among exposed individuals. *Scandinavian Journal of Work, Environment and Health 15*: 234-237.

41. Vanderplas O, Malo JL, Dugas M, Cartier A, Desjardins A, Levesque J, Shaughnessy MA, Grammar LC [1993]. Hypersensitivity pneumonitis-like reaction among workers exposed to diphenylmethane diisocyanate (MDI). *American Review of Respiratory Disease 147*: 338-346.

42. NIOSH [1992]. Recommendations for occupational safety and health, compendium of policy documents and statements. DHHS (NIOSH) Publication No. 92-100. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.

43. ACGIH [1996]. 1996 threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

44. Code of Federal Regulations [1989]. 29 CFR 1910.1000. Washington, DC: U.S. Government Printing Office, Federal Register.

45. Silk SJ, Hardy HL [1983]. Control limits for isocyanates. *Annals of Occupational Hygiene 27*: 333-339.

46. Janko M, McCarthy K, Fajer M, van Raalte J [1992]. Occupational exposure to 1,6-hexamethylene diisocyanate-based polyisocyanates in the State of Oregon, 1980-1990. *American Industrial Hygiene Association Journal 53*: 331-338.

47. Brockman JE [1993]: Sampling and Transport of Aerosols. In *Aerosol Measurement: Principles, Techniques, and Applications*, K Willeke and P Baron, eds. New York, NY:Van Nostrand Reinhold.

48. Kenny LC, Aitken R, Chalmers C, Fabriès JF, Gonzalez-Fernandez E, Kromhout H, Lidén G, Mark D, Riediger G, Prodi V [1997]. A collaborative European study of personal inhalable aerosol sampler performance. *Annals of Occupational Hygiene 41*: 135-153.

49. Health and Safety Executive [1994]. MDHS 25/2, methods for the determination of hazardous substances: organic isocyanates in air. Sheffield, U.K.: Occupational Medicine and Hygiene Laboratory, Health and Safety Executive.

50. Hext PM [1996]. A comparison of the sampling efficiencies of a range of atmospheric samplers when collecting polymeric MDI aerosols. International Isocyanate Institute, Reference 11232.

51. Bell JL [1994]. Evaluation of the OSHA 42 and NIOSH 5521 methods in determining the free isocyanate concentration in aerosols and vapor phases during application of two component 1,6-hexamethylene diisocyanate paints. Masters Thesis, Texas A&M University, College Station, TX.

52. Dharmarajan V [1979]. Occupational exposures to methylene bisphenylisocyanate (MDI): gaseous or aerosol? *Journal of Environmental Pathology and Toxicology 2*: 1-8.

53. Tucker SP, Arnold JE [1982]. Sampling and determination of 2,4-bis(carbonylamino)toluene and 4,4'-bis(carbonylamino)diphenylmethane in air. *Analytical Chemistry 54*: 1137-1141.

54. Lin X, Willeke K, Ulevicius V, Grinshpun SA [1997]. Effect of sampling time on the collection efficiency of all-glass impingers. *American Industrial Hygiene Association Journal 58*: 480-488.

55. Grinshpun SA, Willeke K, Ulevicius V, Juozaitis A, Terzieva S, Donnelly J, Stelma GN, Brenner, KP [1997]. Effect of impaction, bounce and reaerosolization on the collection efficiency of impingers. *Aerosol Science and Technology*, 26: 326-342.

56. Murphy CH [1989]. *Handbook of Particle Sampling and Analysis Methods*. New York, NY: Verlag Chemie International.

57. Cadle RD [1975]. *The Measurement of Airborne Particles*. New York, NY: Wiley.

58. Omega Specialty [1996]. ISO-CHEK isocyanate sampling cassette for 2,4-TDI, 2,6-TDI, 1,6-HDI, and MDI. Chelmsford, MA: Omega Specialty.

59. Lesage J, Goyer N, Desjardins F, Vincent J-Y, Perrault G [1992]. Workers' exposure to isocyanates. *American Industrial Hygiene Association Journal 53*: 146-153.

60. Rando RJ, Poovey HG [1994]. Dichotomous sampling of vapor and aerosol of methylene-bis-(phenylisocyanate) [MDI] with an annular diffusional denuder. *American Industrial Hygiene Association Journal 55*: 716-721.

61. Wu WS, Stoyanoff RE, Gaind VS [1991]. Application of tryptamine as a derivatizing agent for airborne isocyanate determination: Part 4. Evaluation of major high-performance liquid chromatographic methods regarding airborne isocyanate determination with specific investigation of the competitive rate of derivatization. *Analyst 116*: 21-25.

62. Streicher RP, Arnold JE, Ernst MK, Cooper CV [1996]. Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. *American Industrial Hygiene Association Journal 57*: 905-913.

63. Hardy HL [1984]. Appropriate sampling methodologies for isocyanate-containing aerosols: contrasting conclusions in recent AIHA journal papers. *American Industrial Hygiene Association Journal 45*: B-30-32.

64. Brenner KS, Bosscher F [1995]. TDI-and MDI-analysis during fire simulation tests - filter- and high-volume impinger-sampling. *Fresenius Journal of Analytical Chemistry 351*: 216-220.

65. Miles [1992]. Miles Corporate Industrial Hygiene Laboratory Method 1.7.5: determination of airborne methylene bis(phenylisocyanate) by sampling on a diethylphthalate/1-(2-pyridyl)piperazine-coated glass-fiber filter and analysis by high performance liquid chromatography. Pittsburgh, PA: Miles

66. Coyne LB [1989]. Monitoring of MDI vapors/aerosols in the workplace. International Isocyanate Institute, Reference 27123.

67. Seymour MJ [1987]. Evaluation of a coated sampling method for the determination of isocyanate concentrations in air. NTIS Publication No. 87-205001, National Technical Information Service.

68. Andersson K, Gudehn A, Levin J-O, Nilsson C-A [1984]. A comparative study of solvent and solvent-free sampling methods for airborne 4,4'-diphenylmethane diisocyanate (MDI) generated in polyurethane production. *American Industrial Hygiene Association Journal 44*: 802-808.

69. NIOSH [1984]. Hazard Evaluation and Technical Assistance Report, NIOSH Ridge Road, Cincinnati, OH. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, NIOSH Report No. 84-405-1717.

70. Key-Schwartz RJ [1995]. Comparison of filter and impinger sampling of MDI sprayed in a mine (unpublished data). Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.

71. Maître A, Leplay A, Perdrix A, Ohl G, Boinay P, Romazini S, Aubrun JC [1996]. Comparison between solid sampler and impinger for evaluation of occupational exposure to 1,6-hexamethylene diisocyanate polyisocyanates during spray painting. *American Industrial Hygiene Association Journal 57*: 153-160.

72. Huynh CK, Vu-Duc T, Savolainen H [1992]. Design and evaluation of a solid sampler for the monitoring of airborne 1,6-hexamethylene diisocyanate (HDI) and its prepolymers in two-component spray painting. *American Industrial Hygiene Association Journal 53*: 157-162.

73. Rosenberg C, Tuomi T [1984]. Airborne isocyanates in polyurethane spray painting: determination and respirator efficiency. *American Industrial Hygiene Association Journal 45*: 117-121.

74. Rudzinski WE, Dahlquist B, Svejda SA, Richardson A, Thomas T [1995]. Sampling and analysis of isocyanates in spray-painting operations. *American Industrial Hygiene Association Journal 56*: 284-289.

75. Vincent JH [1989]. *Aerosol Sampling*. Chichester, U.K.: John Wiley & Sons.

76. Baldwin PEJ, Maynard AD [1997]. Measurement of wind speeds in indoor workplaces. In *Aerosols, Their Generation, Behaviour, and Applications*, Proceedings of the Aerosol Society, 11th Annual Conference.

77. NIOSH [1994]. Method 5521, isocyanates, monomeric. Issue 2. In: Eller PM, Cassinelli ME, eds. *NIOSH Manual of Analytical Methods*, 4th ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

78. Health and Safety Executive [1987]. MDHS 25, methods for the determination of hazardous substances: organic isocyanates in air. London, U.K.: Occupational Safety and Hygiene Laboratory, Health and Safety Executive.

79. NIOSH [1994]: Method 5522, isocyanates. In: Eller PM, Cassinelli ME, eds. *NIOSH Manual of Analytical Methods*, 4th ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

80. Sangö C, Zimerson E [1980]. A new reagent for determination of isocyanates in working atmospheres by HPLC using UV or fluorescence detection. *Journal of Liquid Chromatography 3*: 971-990.

81. Meyer P, Czarnecki B [1996]. 1-(2-pyridyl)piperazine stability on coated glass fiber filters. Presented at the American Industrial Hygiene Conference and Exhibition, May 20-24, 1996, Washington, D.C.

82. Wu WS, Stoyanoff RE, Szklar RS, Gaind VS [1990]. Application of tryptamine as a derivatizing agent for airborne isocyanate determination: part 3. Evaluation of total isocyanates analysis by high-performance liquid chromatography with fluorescence and

amperometric detection. *Analyst 115*: 801-807.

83. Bagon DA, Warwick CJ, Brown RH [1984]. Evaluation of total isocyanate-in-air method using 1-(2-methoxyphenyl)piperazine and HPLC. *American Industrial Hygiene Association Journal 45*: 39-43.

84. NIOSH [1989]: Method 5521, isocyanates. In: Eller PM, ed. *NIOSH Manual of Analytical Methods*, 3rd ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

85. Key-Schwartz RJ [1994]. Evaluation of recoveries of several prepolymeric isocyanate products using NIOSH Methods 5521 and 5522 (unpublished data). Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.

86. White J, Evans S, Patel S, Brown RH [1997]. Development of MDHS 25/2: organic isocyanates in air. Sheffield, U.K.: Health and Safety Executive.

87. Southern DL, Dolan JW [1996]. Solvent changeover and column equilibration. *LC•GC 14*: 860-864.

88. Dolan JW, Kern JR, Culley T [1996]. Water problems - a case study. *LC•GC 14*: 202-208.

89. Streicher RP [1994]. *Method of detecting isocyanates.* U.S. Patent no. 5,354,689, October 11, 1994.

90. Rudzinski WE, Norman, S, Dahlquist B, Greebon KW, Richardson A, Locke K, Thomas T [1996]. Evaluation of 1-(9-anthracenylmethyl)piperazine for the analysis of isocyanates in spray-painting operations. *American Industrial Hygiene Association Journal 57*: 914-917.

91. Rando RJ, Poovey HG, Gibson RA [1995]. Evaluation of 9-methylaminomethylanthracene as a chemical label for total reactive isocyanate group: application to isocyanate oligomers, polyurethane precursors, and phosgene. *Journal of Liquid Chromatography 18*: 2743-2763.

92. Rudzinski WE, Pin L, Sutcliffe R, Richardson A, Thomas T [1994]. Determination of hexamethylene diisocyanate in spray-painting operations using capillary zone electrophoresis. *Analytical Chemistry 66*: 1664-1666.

93. Rudzinski WE, Yin J, Johnson C, Perez G [1997]. A comparison of sampling and analysis methods for HDI monomer and oligomer. Presented at the 1997 Plenary Meeting, ISO TC 146, Sept. 7-12, 1997, Maui, HI.

94. Warwick CJ, Bagon DA, Purnell CJ [1981]. Application of electrochemical detection to the measurement of free monomeric aromatic and aliphatic isocyanates in air by

high-performance liquid chromatography. *Analyst 106*: 676-685.

95. Key-Schwartz RJ [1995]. Analytical problems encountered with NIOSH method 5521 for total isocyanates. *American Industrial Hygiene Association Journal 56*: 474-479.

96. Streicher RP, Arnold JE, Cooper CV, Fischbach TJ [1995]. Investigation of the ability of MDHS method 25 to determine urethane-bound isocyanate groups. *American Industrial Hygiene Association Journal 56*: 437-442.

97. Rando RJ, Lefante JJ, Poovey HG [1995]. A dichotomous sampler for TRIG aerosol and vapor. Final report submitted to the National Institute for Occupational Safety and Health, Grant no. 5 R01 OH02664-02, Tulane University, New Orleans, LA.

98. Rando RJ, Poovey HG, Lefante JJ, Esmundo FR [1993]. Evaluation of 9-methylaminomethylanthracene as a chemical label for total reactive isocyanate group: a comparison of mono- and di-isocyanate monomers. *Journal of Liquid Chromatography 16*: 3977-3996.

99. Tinnerberg H, Spanne M, Dalene M, Skarping G [1996]. Determination of complex mixtures of airborne isocyanates and amines: part 2. Toluene diisocyanate and aminoisocyanate and toluenediamine after thermal degradation of a toluene diisocyanate-polyurethane. *Analyst 121*: 1101-1106.

100. Lesage J, Ostiguy C, René L, Gaudette F, Nguyen P, Tra HV [1997]. New analytical method for determination of ppt levels of isocyanates in the workplace by triple quadrupole mass spectrometry. Presented at the American Industrial Hygiene Conference and Exhibition, May 19-23, Dallas, TX.

101. Tinnerberg H, Spanne M, Dalene M, Skarping G [1997]. Determination of complex mixtures of airborne isocyanates and amines: part 3. Methylenediphenyl diisocyanate, methylenediphenylamino isocyanate, and methylenediphenyldiamine and structural analogues after thermal degradation of polyurethane. *Analyst 122*: 275-278.

102. Karlsson A, Spanne M, Dalene M, Skarping G [1997]. Determination of complex mixtures of airborne isocyanates and amines: part 4. Determination of aliphatic isocyanates as dibutylamine derivatives using liquid chromatography and mass spectrometry. *Analyst* (submitted for publication).

103. NIOSH [1994]. Method 2535: toluene-2,4-diisocyanate, issue 2. In: Eller PM, Cassinelli ME, eds. *NIOSH Manual of Analytical Methods*, 4th ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

104. OSHA [1983]. Method 42: diisocyanates. Salt Lake City, UT: U.S. Dept. Of Labor, Occupational Safety and Health Administration.

105. OSHA [1985]. Method 47: methylene bisphenyl isocyanate (MDI). Salt Lake City, UT: U.S. Dept. Of Labor, Occupational Safety and Health Administration.

106. Miles [1992]. Miles Corporate Industrial Hygiene Laboratory Method 1.4.3: determination of isocyanates in spray mist environments by sampling in an impinger with N-4-nitrobenzyl-n-propylamine in toluene and analysis by high performance liquid chromatography. Pittsburgh, PA: Miles, Inc.

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, $\hat{S}_{rT}$, 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.
GFAAS	Graphite furnace atomic absorption spectrophotometry
GPO	U.S. Government Printing Office, Washington, DC 20402.
Hemolysis	Rupture of red blood cells due to improper collection and handling of whole blood.
HYAAS	Hydride generation 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, $\hat{S}_r$, 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 $\hat{S}_r = 0.1$.
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_r (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 international dust sampling convention. 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 *1998 TLVs® and BEIs®, Threshold Limit Values for Chemical Substances and Physical Agents and Biological Indices* (American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1998).
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," or *Guidelines for Air Sampling and Analytical Method Development and Evaluation* (NIOSH Technical Report).
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 THIRD AND FOURTH EDITION METHOD NUMBERS

XX = Discontinued Method

0500 PARTICULATES NOT OTHERWISE REGULATED, TOTAL (Grav)
0600 PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE (Grav)
0700 see 9100
0800 BIOAEROSOL SAMPLING (Indoor Air)
0801 AEROBIC BACTERIA BY GC-FAME
0900 MYCOBACTERIUM TUBERCULOSIS, AIRBORNE
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, CHLORODIFLUOROMETHANE (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
1302 *N*-METHYL-2-PYRROLIDINONE
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)
1455 XX- Triphenyl phosphate
1456 see 5037
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)
1552 TERPENES
- limonene
- α-pinene
- β-pinene
- 3-carene

1600 CARBON DISULFIDE (GC)
1601 1,1-DICHLORO-1-NITROETHANE (GC)
1602 DIOXANE (GC)
1603 ACETIC ACID (GC)
1604 ACRYLONITRILE (GC)
1605 XX Ethers I
1606 ACETONITRILE (GC)
1607 XX Ethylene Oxide - see 1614
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)
2001 XX Cresol - see 2546
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 NITROAROMATIC COMPOUNDS (GC)
- 4-chloronitrobenzene
- nitrobenzene
- nitrotoluene

2007 AMINOETHANOL COMPOUNDS I (GC)
- 2-aminoethanol
- 2-dibutylaminoethanol
- 2-diethylaminoethanol

2008 CHLOROACETIC ACID (IC)
2009 XX - see 2540
2010 AMINES, ALIPHATIC (GC)
- diethylamine
- dimethylamine

2011 FORMIC ACID (IC)
2012 *n*-BUTYLAMINE (GC)
2013 PHENYL ETHER & DIPHENYL (GC)
2014 *p*-CHLOROPHENOL (HPLC)
2015 CHLOROACETALDEHYDE
2016 FORMALDEHYDE
2017 ANILINE, *o*-TOLUIDINE, AND NITROBENZENE
2500 METHYL ETHYL KETONE (GC)
2501 ACROLEIN (GC)
2502 XX Formaldehyde
2503 XX Mevinphos - see 5600
2504 TETRAETHYL PYROPHOSPHATE (TEPP) (GC)
2505 FURFURYL ALCOHOL (GC)
2506 ACETONE CYANOHYDRIN (GC)
2507 NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE (GC)
2508 ISOPHORONE (GC)
2509 XX Hydrazine
2510 1-OCTANETHIOL (GC)

2511 XX - see 2545
2512 XX Hexachlorobutadiene
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)
2520 METHYL BROMIDE
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)
2531 XX Glutaraldehyde (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)
2549 VOLATILE ORGANIC CPDS (SCREENING) (GC/MS)
2550 BENZOTHIAZOLE IN ASPHALT FUME
2551 NICOTINE
3500 FORMALDEHYDE (chromotropic acid)(VIS)
3501 XX Formaldehyde (Girard T)
3502 XX Phenol - see 2546
3503 HYDRAZINE (VIS)
3504 XX Hydrazine (color)
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 XX Methylene chloride (portable GC)
3704 PERCHLOROETHYLENE (portable GC) in exhaled breath and air
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)
5015 XX Xanthanates
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/GFAAS)
p-aminophenyl arsonic acid
dimethyl arsenic acid
methylarsonic acid
5023 XX Coal Tar Pitch Volatiles
5024 XX Tetryl
5025 CHLORINATED DIPHENYL ETHER (GC)
5026 OIL MIST, MINERAL (IR)

5027 RIBAVARIN (HPLC)
5028 XX Picric acid
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)
5040 ELEMENTAL CARBON (DIESEL EXHAUST) (EGA)
5041 CAPSAICIN & DIHYDROCAPSAICIN (HPLC/FL)
5042 BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)
5043 *p*-TOLUENESULFONIC ACID
5500 XX Ethylene glycol - see 5523
5501 XX 4-dimethylaminoazobenzene
5502 ALDRIN & LINDANE (GC)
5503 POLYCHLOROBIPHENYLS (GC)
5504 ORGANOTIN COMPOUNDS, as Sn (HPLC/GFAAS)
bibutyltin bis(isooctyl mercaptoacetate)
tetrabutyltin
tributyltin chloride
tricyclohexyltin hydroxide
5505 XX Isocyanates
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
5507 XX Glutaraldehyde - see 2532
5508 KEPONE (GC/ECD)
5509 BENZIDINE and 3,3'-DICHLOROBENZIDINE (HPLC)
5510 CHLORDANE (GC)
5511 XX Ronnel - see 5600
5512 PENTACHLOROPHENOL (HPLC)
5513 XX Hexachloronaphthalene
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)
5520 XX Dinitrobenzene & dinitrotoluene
5521 ISOCYANATES, MONOMERIC (HPLC)
5522 ISOCYANATES (HPLC/FL)
5523 GLYCOLS (GC)
ethylene glycol
1,3-butylene glycol
triethylene glycol
propylene glycol
diethylene glycol
tetraethylene glycol
5600 ORGANOPHOSPHOROUS PESTICIDES (GC/FPD)
Azinphos methyl
Chlorpyrifos
Diazinon
Dicrotophos
Disulfoton
Ethion
Ethoprop
Fenamiphos
Fonofos
Malathion
Methamidophos
Methyl parathion
Mevinphos (E)

Mevinphos (E&Z)
Monocrotophos (E)
Monocrotophos (Z)
Parathion
Phorate
Ronnel
Sulprophos
Terbufos

5601 ORGANONITROGEN PESTICIDES
aldicarb
benomyl
captan
carbaryl
carbendazim
carbofuran
chlorpropham
diuron
formetanate.HCl
methiocarb
methonyl
oxamyl
propham
propoxur
thiobencarb

5602 CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING)
alachlor
atrazine
cyanazine
2,4-D acid
2,4-D, 2-butoxyethyl ester
2,4-D, 2-ethylhexyl ester
metolachlor
simazine

5603 ALACHLOR in Air
5700 FORMALDEHYDE ON DUST/FIBERS (HPLC)
5701 RESORCINOL
5800 POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs)
6000 XX Mercury - see 6009
6001 ARSINE (GFAAS)
6002 PHOSPHINE (UV/VIS)
6003 XX Tellurium fluoride
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 XX Hydrogen sulfide (IC)
6014 NITRIC OXIDE/NITROGEN DIOXIDE (VIS)
6015 AMMONIA (VIS)
6016 AMMONIA by IC
6400 XX Hydrogen sulfide
6401 XX Phosphorus pentachloride
6402 PHOSPHORUS TRICHLORIDE (VIS)
6600 NITROUS OXIDE (portable IR)
6601 OXYGEN (EC sensor)
6602 SULFUR HEXAFLUORIDE (portable GC)
6603 CARBON DIOXIDE (portable GC)
6604 CARBON MONOXIDE (EC sensor)
6700 NITROGEN DIOXIDE
6701 XX Ammonia (pass)
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 XX Vanadium, sol/insol (ICP)
7102 BERYLLIUM (GFAAS)
7103 XX Rhodium - see 7300
7104 XX Platinum - see 7300
7105 LEAD (GFAAS)
7300 ELEMENTS (ICP)
7400 ASBESTOS and other FIBERS by PCM
7401 ALKALINE DUST (titration)
7402 ASBESTOS by TEM
7403 see 9002
7500 SILICA (XRD)
7501 SILICA, AMORPHOUS (XRD)
7502 ZINC OXIDE (XRD)
7503 XX Talc
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)
7700 LEAD by Chemical Spot Test
7701 LEAD BY ULTRASOND/ASV
7702 LEAD BY FIELD PORTABLE XRF
7900 ARSENIC (HYDRIDE AAS)
7901 ARSENIC TRIOXIDE (GFAAS)
7902 FLUORIDES by ISE
7903 ACIDS,INORGANIC (IC)
Hydrobromic acid
Hydrochloric acid
Hydrofluoric acid
Nitric acid
Phosphoric acid

Sulfuric acid
7904 CYANIDES (ISE)
7905 PHOSPHORUS (GC)
7906 FLUORIDES by IC
8000 XX Alad in blood
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)
antimony
cadmium
chromium
cobalt
copper
iron
lanthanum
lead
manganese
molybdenum
nickel
platinum
silver
strontium
tin
titanium
zinc
8300 HIPPURIC ACID in urine (VIS)
8301 HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC)
8302 MBOCA in urine
8303 PENTACHLOROPHENOL in urine
8304 XX Benzidine in urine (TLC)
8305 PHENOL & *p*-CRESOL in urine
8306 BENZIDINE in urine (GC)
8307 XX Arsenic in urine
8308 FLUORIDE in urine
8309 XX Mercury in urine
8310 METALS in urine (ICP)
aluminum
lead
silver
barium
manganese
strontium
cadmium
molybdenum
tin
chromium
nickel
titanium
copper
platinum
zinc
iron
9000 ASBESTOS, CHRYSOTILE by XRD
9002 ASBESTOS (bulk) by PLM
9100 LEAD in surface wipe samples
9101 CHROMIUM (VI) in settled dust (Test Kit)
9200 CHLORINATED and ORGANONITROGEN HERBICIDES (HAND WASH)
9201 CHLORINATED and ORGANONITROGEN HERBICIDES (DERMAL PATCH)

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 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]; NITROGEN DIOXIDE [6700]
	109	1	Silica (XRD)	SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)	SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide	NRNR; see CARBON MONOXIDE [6604]
	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 [2016, 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]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	127	1	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
	127	1	Xylene	HYDROCARBONS, AROMATIC [1501]
	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, 5522]
	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; 7701; 7702]; 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

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P&CAM	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	ELEMENTS by ICP [7300]
	173	1,5	Tellurium	ELEMENTS by ICP [7300]
	173	1,5	Thallium	ELEMENTS by ICP [7300]
	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	ELEMENTS by ICP [7300]
	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]

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P&CAM	205	1	Ammonia	NRIU; see AMMONIA [6015, 6016]
	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	FLUORIDES [7902, 7906]; ACIDS, INORGANIC [7903]
	213	1	*bis*-(Chloromethyl)ether	NRIU
	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	NRIU; see 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]

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P&CAM	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
	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
	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]; ELEMENTS BY ICP [7300]
	272	4	2-Nitropropane	2-NITROPROPANE [2528]
	273	4	4-Nitrobiphenyl	NRIU
	276	4	Ethylenediamine	DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & 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	α-Chloroacetophenone	NRIU

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P&CAM	294	5	Cyclopentadiene	1,3-CYCLOPENTADIENE [2523]
	295	5	Dichlorovos	NRIU
	296	6	Hydrogen sulfide	NRIU
	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	NRIU
	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]
	317	6	Diethylcarbamoyl chloride	NRIU
	318	6	Formaldehyde	FORMALDEHYDE [2541, 3500, 5700]
	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, 5522]
	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-TEPP [2504]
	337	7	*p*-Chlorophenol	β-CHLOROPHENOL [2014]
	338	7	Ethylene glycol	NRNR; see GLYCOLS [5523]
	339	7	Inorganic acids	ACIDS, INORGANIC [7903]

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P&CAM	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, 5522]
	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 [2016; 2541, 3500, 5700]
	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]
	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]

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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	α-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]
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 [1400]
S65	2	Isopropyl alcohol	ALCOHOLS I [1400]
S66	2	*n*-Butyl alcohol	ALCOHOLS II [1401]
S67	2	Chlorinated camphene	CHLORINATED CAMPHENE [5039]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
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]
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]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
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
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

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
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	ELEMENTS BY ICP [7300]
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	ELEMENTS BY ICP [7300]
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
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
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]; CHLORINATED AND ORGANONITROGEN PESTICIDES [5602]
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]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S291	5	Methyl formate	NRIU
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]
S293	3	Nicotine	NRIU; see NICOTINE [2544; 2551]
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]; NITROGEN DIOXIDE [6700]
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, 5700]
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; see CARBON MONOXIDE [6604]
S341	3,7	Lead	LEAD [7082, 7701, 7702]; ELEMENTS BY ICP [7300]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S342	6	Mercury, organo	NRIU
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
S345	5	Acetaldehyde	ACETALDEHYDE [3507]
S346	4	Allyl glycidyl ether	ALLYL GLYCIDYL ETHER [2545]
S347	5	Ammonia	see AMMONIA BY VIS [6015, 6016]
S348	5	Ammonium sulfamate	NRIU
S349	3	Boron oxide	PARTICULATES NOT OTHERWISE REGULATED, TOTAL [0500]
S350	4	*n*-Butyl mercaptan	*n*-BUTYL MERCAPTAN [2525]; 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	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]

V. C. INDEX OF NAMES AND SYNONYMS

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, 5506 (HPLC); 5515 (GC)
Acenaphthylene, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
ACETALDEHYDE, 2538 (GC), 3507 (HPLC), see ALDEHYDES, SCREENING, 2539
ACETIC ACID, 1603
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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
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Acetic ether, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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Acetylene dichloride, see HYDROCARBONS, HALOGENATED, 1003
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Acetylene tetrachloride, see 1,1,2,2-TETRACHLOROETHANE, 1019
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ALCOHOLS IV, 1403
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ALDRIN and LINDANE, 5502
Alkali, see ALKALINE DUSTS, 7401
ALKALINE DUSTS, 7401
Allyl alcohol, see ALCOHOLS III, 1402
ALLYL CHLORIDE, 1000
ALLYL GLYCIDYL ETHER, 2545
Allyl trichloride, see HYDROCARBONS, HALOGENATED, 1003
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2-Aminoanisole, see ANISIDINE, 2514
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p-Aminonitrobenzene, see *p*-NITROANILINE, 5033
2-Aminoethanol, see AMINOETHANOL COMPOUNDS I, 2007; AMINOETHANOL COMPOUNDS II, 3509
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1,2-Dichloropropane, see PROPYLENE DICHLORIDE, 1013
1,2-Dichloropropane, see HYDROCARBONS, HALOGENATED, 1003
1,2-Dichlorotetrafluoroethane, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE, 1018
Dicrotophos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Diesel exhaust, see ELEMENTAL CARBON (DIESEL EXHAST), 5040
Diethanolamine, see AMINOETHANOL COMPOUNDS II, 3509
Diethylamine, see AMINES, ALIPHATIC, 2010
2-Diethylaminoethanol, see AMINOETHANOL COMPOUNDS I, 2007
Diethyl ether, see ETHYL ETHER, 1610
1,4-Diethylene dioxide, see DIOXANE, 1602
Diethylene ether, see DIOXANE, 1602
Diethylene glycol, see GLYCOLS, 5523
Diethylene glycol ethyl ether, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Diethylene oxide, see TETRAHYDROFURAN, 1609
DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE, 2540
Di(2-ethylhexyl) phthalate, see DIBUTYLPHTHALATE and DI(2-ETHYLHEXYL)PHTHALATE, 5020
DIFLUORODIBROMOMETHANE, 1012
Difluorodichloromethane, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE, 1018
Dihydrocapsaicin, see CAPSAICIN and DIHYDROCAPSAICIN, 5041
Diisobutyl ketone, see KETONES I, 1300
Diisopropyl ether, see ISOPROPYL ETHER, 1618
Diisopropyl oxide, see ISOPROPYL ETHER, 1618
Dimazine, see 1,1-DIMETHYLHYDRAZINE, 3515
1,1-DIMETHYLHYDRAZINE, 3515
Dimethoxymethane, see METHYLAL, 1611
[(Dimethoxyphosphinothioyl)thio] butanedioic acid diethyl ester, see EPN, 5012
DIMETHYLACETAMIDE, and DIMETHYLFORMAMIDE, 2004
N,N-Dimethylacetamide, see DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE, 2004
Dimethylamine, see AMINES, ALIPHATIC, 2010
p-Dimethylaminotoluene, see AMINES, AROMATIC, 2002
N,N-Dimethylaniline, see AMINES, AROMATIC, 2002
2,4-Dimethylaniline, see AMINES, AROMATIC, 2002

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
Diuron, see ORGANONITROGEN, 5601
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
ELEMENTAL CARBON (DIESEL EXHAUST), 5040
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
Ethanediol, see GLYCOLS. 5523
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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
ETHYLENE DIBROMIDE, 1008
Ethylene dichloride, see HYDROCARBONS, HALOGENATED, 1003
Ethylene dinitrate, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
Ethylene glycol, see GLYCOLS, 5523
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 (DNPH cartridge), 2016
FORMALDEHYDE (2-HMP), 2541; see ALDEHYDES, SCREENING, 2539
FORMALDEHYDE (chromotropic acid); 3500, see ALDEHYDES, SCREENING, 2539
FORMALDEHYDE ON DUST, 5700
Formetanate.HCl, see ORGANONITROGEN PESTICIDES, 5601
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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
GLYCOLS, 5523
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, MONOMER, 5521; ISOCYANATES, 5522
Heat-treating oils, see OIL MIST, MINERAL, 5026
Heptanal, see ALDEHYDES, SCREENING, 2539
n-Heptane, see HYDROCARBONS, BP 36-126 °C, 1500; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
1,7-Heptanedicarboxylic acid, see AZELAIC ACID, 5019
2-Heptanone, see KETONES II, 1301
3-Heptanone, see KETONES II, 1301
HEXACHLOROBUTADIENE, 2543
γ-Hexachlorocyclohexane, see ALDRIN and LINDANE, 5502
HEXACHLORO-1,3-CYCLOPENTADIENE, 2518
Hexachloroethane, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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, MONOMER, 5521; ISOCYANATES, 5522
Hexanal, see ALDEHYDES SCREENING, 2539; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
n-Hexane, see HYDROCARBONS, BP 36-126 °C, 1500; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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)
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
2-Hydroxyethyl ether, see GLYCOLS, 5523
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, 5506 (HPLC); 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, MONOMER, 5521; see ISOCYANATES, 5522; 2,4-TOLUENEDIISOCYANATE, 2535
ISOCYANATES, 5522
Isocyanuric acid, see CYANURIC ACID, 5030
Isodiprene, see TERPENES, 1552
ISOPHORONE, 2508
Isopropenylbenzene, see HYDROCARBONS, AROMATIC, 1501
ISOPROPYL ACETATE, 1454
Isopropyl alcohol, see ALCOHOLS I, 1400; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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 BY ULTRASOUND/ASV, 7701
LEAD BY FIELD PORTABLE XRF, 7702
LEAD, 7082 (FAAS); 7105 (GFAAS);(Spot test), 7700; (ULTRASOUND/ASV), 7701; (Portable XRF), 7702; (Surface wipes), 9100; ELEMENTS by ICP, 7300; LEAD in blood and urine, 8003
LEAD in Air by chemical spot test, 7700
LEAD in surface wipe samples, 9100
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
Limonene, see TERPENES, 1552; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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, MONOMER, 5521; ISOCYANATES, 5522
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-Mercaptobutane, see *n*-BUTYL MERCAPTAN, 2525; MERCAPTANS, Methyl, Ethyl, *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 (DNPH cartridge), 2016; 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; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Methiocarb, see ORGANONITROGEN PESTICIDES, 5601
Methomyl, see ORGANONITROGEN PESTICIDES, 5601
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
4-methylbenzenesulfonic acid, see *p*-TOLUENESULFONIC ACID, 5043
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
METHYL BROMIDE, 2520
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
4,4'-METHYLENEDIANILINE, 5029
4,4'-Methylenediphenyldiisocyanate (MDI), see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
(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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
2-Methyllactonitrile, see ACETONE CYANOHYDRIN, 2506

METHYL METHACRYLATE, 2537
Methyl parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
m-Methylnitrobenzene, see NITROAROMATIC COMPOUNDS, 2005
o-Methylnitrobenzene, see, NITROAROMATIC COMPOUNDS, 2005
p-Methylnitrobenzene, see NITROAROMATIC COMPOUNDS, 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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
3-Methylphenol, see CRESOLS and PHENOL, 2546; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
4-Methylphenol, see CRESOLS and PHENOL, 2546; PHENOL and *p*-CRESOL in urine, 8305; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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
α-Methylstyrene, see HYDROCARBONS, AROMATIC, 1501
Methylvinylbenzene, see HYDROCARBONS, AROMATIC, 1501
Methyl viologen, see PARAQUAT, 5003
Metolachlor, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
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
Monobromethane, see METHYL BROMIDE, 2520
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
Mycobacterium, see MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900; AEROBIC BACTERIA by GC-FAME, 0801
MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900
Naphthalene, see HYDROCARBONS, AROMATIC, 1501; POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 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
α-Naphthylamine, see NAPHTHYLAMINES, 5518
β-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
NICOTINE, 2551
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
NITROAROMATIC COMPOUNDS, 2005
Nitrobenzol, SEE ANILINE, *o*-TOLUIDINE, AND NITROBENZENE, 2017; NITROAROMATIC COMPOUNDS, 2005
Nitrocarbol, see NITROMETHANE, 2527
p-Nitrochlorobenzene, see NITROAROMATIC COMPOUNDS, 2005
NITROETHANE, 2526
Nitrogen dioxide, see NITROGEN DIOXIDE (passive), 6700; NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen monoxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen peroxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014; NITROGEN DIOXIDE(passive), 6700
NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
NITROMETHANE, 2527
2-NITROPROPANE, 2528
NITROSAMINES, 2522
N-METHYL-2-PYRROLIDINONE, 1302
N-methyl-y-butyrolactone, see N-METHYL-2-PYRROLIDINONE, 1302
NMP, see *N*-METHYL-2-PYRROLIDINONE, 1302
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 NITROAROMATIC COMPOUNDS, 2005
NITROUS OXIDE, 6600
Nonanal, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Octachlor, see CHLORDANE, 5510
Octamethylcyclotetrasiloxane, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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
ORGANONITROGEN PESTICIDES, 5601
ORGANOPHOSPHORUS PESTICIDES, 5600
ORGANOTIN COMPOUNDS, 5504
ortho-Phosphoric acid, see ACIDS, INORGANIC, 7903
Oxamyl, see ORGANONITROGEN, 5601
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
2,2'-Oxydiethanol, see GLYCOLS, 5523
OXYGEN, 6601

PAC, see POLYCYCLIC AROMATI C COMPOUNDS, TOTAL (PACs), 5800; POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
PAH, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
PARAQUAT, 5003
Parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
Pb, see LEAD, 7082 (FAAS); 7105 (GFAAS);(Spot test), 7700; (ULTRASOUND/ASV, 7701; (Portable XRF), 7702; (Surface wipes), 9100; 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
Pelargonic aldehyde, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
PERCHLOROETHYLENE (portable GC) in exhaled breath and air, 3704
Petroleum ether, see NAPHTHAS, 1550
Petroleum naphtha, see NAPHTHAS, 1550
Phenanthrene, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
Phenol, see CRESOLS and PHENOL, 2546; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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; TERPENES 1552; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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, 5506 (HPLC); 5515 (GC)
POLYCHLORINATED BIPHENYLS in serum, 8004
POLYCHLOROBENZENES, 5517
POLYCHLOROBIPHENYLS, 5503
Polychloroterphenyl, see CHLORINATED TERPHENYL, 5014
POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs), 5800
POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 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-Propanediol, see GLYCOLS, 5523
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
Propham, see ORGANONITROGEN PESTICIDES, 5601
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 glycol, see GLYCOLS, 5523
Propoxur, see ORGANONITROGEN PESTICIDES, 5601
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
RESORCINOL, 5701
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
Simazine, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200;
(DERMAL PATCH), 9201
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
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
TB, see MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900
TC, 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,MONOMER, 5521; ISOCYANATES, 5522

2,6-TDI, see ISOCYANATES,MONOMER, 5521; ISOCYANATES, 5522
TEA, see AMINOETHANOL COMPOUNDS II, 3509
TeBT, see ORGANOTIN COMPOUNDS, 5504
TEG, see GLYCOLS, 5523
TEL, see TETRAETHYL LEAD (as Pb), 2534
Tellurium, see ELEMENTS by ICP, 7300
TEPP, see TETRAETHYL PYROPHOSPHATE, 2504
Terbufos, see ORGANOPHOSPHORUS PESTICIDES, 5600
TERPENES, 1552
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
Tetrachloroethylene; perc, see PERCHLOROETHYLENE (portable GC) in exhaled breath and air, 3704
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, 5506 (HPLC); 5515 (GC)
Thallium, see ELEMENTS, 7300; ELEMENTS in blood or tissue, 8005
THF, see TETRAHYDROFURAN, 1609
Thiobencarb, see ORGANONITROGEN PESTICIDES, 5601
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
p-TOLUENESULFONIC ACID, 5043
TOLUENE, 4000; see HYDROCARBONS, BP 36-126 °C, 1500; HYDROCARBONS, AROMATIC, 1501; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
2,4- AND 2,6-TOLUENEDIAMINE, 5516
TOLUENE-2,4-DIISOCYANATE, 2535; see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
Toluene 2,6-TDI, see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
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; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
1,2,4-Trichlorobenzene, see POLYCHLOROBENZENES, 5517

1,1,1-Trichloroethane, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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
Triethylene glycol, see GLYCOLS, 5523
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
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VANADIUM OXIDES, 7504
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Vanadium sesquioxide, see VANADIUM OXIDES, 7504
Vanadium trioxide, see VANADIUM OXIDES, 7504
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VINYL BROMIDE, 1009
VINYL CHLORIDE, 1007
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ZINC OXIDE, 7502; see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; ZINC (FAAS), 7030
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Zinc white, see ZINC OXIDE (XRD), 7502
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CAS #206-44-0, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS #207-08-9, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS #208-96-8, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS #218-01-9, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS #280-57-9, see TRIETHYLENETETRAMINE, 2540
CAS #298-03-3, see DEMETON, 5514
CAS #299-84-3, see ORGANOPHOSPHORUS PESTICIDES, 5600
CAS #302-01-2, see HYDRAZINE, 3503
CAS #309-00-2, see ALDRIN and LINDANE, 5502
CAS #330-54-1, see ORGANONITROGEN PESTICIDES, 5601
CAS #334-88-3, see DIAZOMETHANE, 2515
CAS #404-86-4, see CAPSAICIN and DIHYDROCAPSAICIN, 5041
CAS #495-69-2, see HIPPURIC ACID in urine, 8300; HIPPURIC and METHYL HIPPURIC ACIDS in urine, 8301
CAS #540-59-0, see HYDROCARBONS, HALOGENATED, 1003
CAS #540-88-5, see ESTERS I, 1450
CAS #542-92-7, see 1,3-CYCLOPENTADIENE, 2523
CAS #552-30-7, see TRIMELLITIC ANHYDRIDE, 5036
CAS #556-52-5, see GLYCIDOL, 1608
CAS #556-67-2, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #573-58-0, see DYES, 5013
CAS #583-60-8, see METHYLCYCLOHEXANONE, 2521
CAS #584-84-9, see TOLUENE-2,4-DIISOCYANATE (HPLC-UV), 2535; ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
CAS #589-92-4, see METHYLCYCLOHEXANONE, 2521
CAS #590-86-3, see ALDEHYDES, SCREENING, 2539
CAS #591-24-2, see METHYLCYCLOHEXANONE, 2521
CAS #591-78-6, see KETONES I, 1300
CAS #593-60-2, see VINYL BROMIDE, 1009
CAS #594-72-9, see 1,1-DICHLORO-1-NITROETHANE, 1601
CAS #608-93-5, see POLYCHLOROBENZENES, 5517
CAS #621-64-7, see NITROSAMINES, 2522
CAS #626-38-0, see ESTERS I, 1450
CAS #628-63-7, see ESTERS I, 1450; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #628-96-6, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
CAS #630-08-0, see CARBON MONOXIDE, 6604
CAS #822-06-0, see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
CAS #823-40-5, see 2,6-TOLUENEDIAMINE, 5516
CAS #872-50-4, see *N*-METHYL-2-PYRROLIDINONE, 1302
CAS #924-16-3, see NITROSAMINES, 2522
CAS #930-55-2, see NITROSAMINES, 2522

CAS #992-59-6, see DYES, 5013
CAS #1303-86-2, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500; RESPIRABLE, 0600
CAS #1305-62-0, see CALCIUM, 7020; ELEMENTS by ICP, 7300
CAS #1305-78-8, see CALCIUM, 7020; ELEMENTS by ICP, 7300
CAS #1306-19-0, see CADMIUM, 7048; ELEMENTS by ICP, 7300
CAS #1307-96-6, see COBALT, 7027; ELEMENTS by ICP, 7300
CAS #1308-38-9, see CHROMIUM, 7024; ELEMENTS by ICP, 7300
CAS #1310-58-3, see ALKALINE DUSTS, 7401
CAS #1310-65-2, see ALKALINE DUSTS, 7401
CAS #1310-73-2, see ALKALINE DUSTS, 7401
CAS #1314-13-2, see ZINC, 7030; ZINC OXIDE, 7502
CAS #1314-34-7, see VANADIUM OXIDES, 7504
CAS #1314-62-1, see VANADIUM OXIDES, 7504
CAS #1314-87-0, see LEAD SULFIDE, 7505
CAS #1317-36-8, see LEAD, 7082 (FAAS); 7105 (GFAAS); ELEMENTS by ICP, 7300; LEAD (Spot test), 7700; LEAD (ULTRASOUND/ASV), 7701; LEAD (Portable XRF), 7702; LEAD (Surface wipes), 9100
CAS #1317-38-0, see COPPER, 7029
CAS #1317-39-1, see COPPER, 7029; ELEMENTS by ICP, 7300
CAS #1317-65-3, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020; ELEMENTS by ICP, 7300
CAS #1319-77-3, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #1327-53-3, see ARSENIC TRIOXIDE, 7901
CAS #1330-20-7, see HYDROCARBONS, AROMATIC, 1501; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #1331-22-2, see METHYLCYCLOHEXANONE, 2521
CAS #1332-21-4, see ASBESTOS and OTHER FIBERS by PCM, 7400
CAS #1333-82-0, see CHROMIUM, HEXAVALENT, 7600 (VIS), 7609 (IC), 9101 (in settled dust samples)
CAS #1333-86-4, see CARBON BLACK, 5000
CAS #1336-36-3, see POLYCHLOROBIPHENYLS, 5503
CAS #1338-23-4, see METHYL ETHYL KETONE PEROXIDE, 3508
CAS #1344-28-1, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; ALUMINUM, 7013
CAS #1461-22-9, see ORGANOTIN COMPOUNDS, 5504
CAS #1461-25-2, see ORGANOTIN COMPOUNDS, 5504
CAS #1480-60-7, see QUARTZ in coal mine dust, RESPIRABLE, 7603
CAS #1563-66-2, see ORGANONITROGEN PESTICIDES, 5601
CAS #1634-04-4, see METHYL *tert*-BUTYL ETHER, 1615
CAS #1689-84-5, see BROMOXYNIL and BROMOXYNIL OCTANOATE, 5010
CAS #1689-99-2, see BROMOXYNIL and BROMOXYNIL OCTANOATE, 5010
CAS #1910-42-5, see PARAQUAT, 5003
CAS #1912-24-9, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #1928-38-7, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #1928-43-4, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #1929-73-3, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #1937-37-7, see DYES, 5013
CAS #2032-65-7, see ORGANONITROGEN PESTICIDES, 5601
CAS #2074-50-2, see PARAQUAT, 5003
CAS #2104-64-5, see EPN, 5012
CAS #2426-08-6, see *n*-BUTYL GLYCIDYL ETHER, 1616
CAS #2429-71-2, see DYES, 5013
CAS #2551-62-4, see SULFUR HEXAFLUORIDE, 6602
CAS #2602-46-2, see DYES, 5013
CAS #2699-79-8, see SULFURYL FLUORIDE, 6012

CAS #2782-91-4, see TETRAMETHYL THIOUREA, 3505
CAS #4016-14-2, see ISOPROPYL GLYCIDYL ETHER, 1620
CAS #4170-30-3, see ALDEHYDES, SCREENING, 2539; CROTONALDEHYDE, 3516
CAS #5989-27-5, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #7429-90-5, see ALUMINUM, 7013; ELEMENTS by ICP, 7300
CAS #7439-92-1, see LEAD, 7082 (FAAS), 7105 (GFAAS); ELEMENTS by ICP, 7300; LEAD in blood and urine, 8003; LEAD (Spot test), 7700; LEAD (ULTRASOUND/ASV), 7701; LEAD (Portable XRF), 7702; LEAD (Surface wipes), 9100
CAS #7439-97-6, see MERCURY, 6009
CAS #7440-33-7, see TUNGSTEN, 7074
CAS #7440-38-2, see ARSENIC, 7900
CAS #7440-39-3, see BARIUM, soluble compounds, 7056
CAS #7440-41-7, see BERYLLIUM, 7102; ELEMENTS by ICP, 7300
CAS #7440-43-9, see CADMIUM, 7048; ELEMENTS by ICP, 7300
CAS #7440-47-3, see CHROMIUM, 7024; ELEMENTS by ICP, 7300
CAS #7440-48-4, see COBALT, 7027; ELEMENTS by ICP, 7300
CAS #7440-50-8, see COPPER, 7029; ELEMENTS by ICP, 7300
CAS #7440-66-6, see ZINC, 7030; ELEMENTS by ICP, 7300
CAS #7446-09-5, see SULFUR DIOXIDE, 6004
CAS #7553-56-2, see IODINE, 6005
CAS #7631-86-9, see SILICA, AMORPHOUS, 7501
CAS #7647-01-0, see ACIDS, INORGANIC, 7903
CAS #7664-38-2, see ACIDS, INORGANIC, 7903
CAS #7664-39-3, see FLUORIDES, 7902 (ISE), 7906 (IC); ACIDS, INORGANIC, 7903
CAS #7664-41-7, see AMMONIA, 6015; AMMONIA by IC, 6016
CAS #7664-93-9, see ACIDS, INORGANIC, 7903
CAS #7681-49-4, see FLUORIDES, 7902 (ISE), 7906 (IC); ACIDS, INORGANIC, 7903
CAS #7697-37-2, see ACIDS, INORGANIC, 7903
CAS #7719-12-2, see PHOSPHORUS TRICHLORIDE, 6402
CAS #7723-14-0, see PHOSPHORUS, 7905
CAS #7726-95-6, see CHLORINE and BROMINE, 6011
CAS #7782-44-7, see OXYGEN, 6601
CAS #7782-50-5, see CHLORINE and BROMINE, 6011
CAS #7783-06-4, see HYDROGEN SULFIDE, 6013
CAS #7784-42-1, see ARSINE, 6001
CAS #7786-34-7, see ORGANOPHOSPHORUS PESTICIDES, 5600
CAS #7803-51-2, see PHOSPHINE, 6002
CAS #7803-52-3, see STIBINE, 6008
CAS #8001-35-2, see CHLORINATED CAMPHENE, 5039
CAS #8003-34-7, see PYRETHRUM, 5008
CAS #8006-64-2, see TURPENTINE, 1551; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS #8007-45-2, see BENZENE-SOLUBLE FRACTION and TOTAL PARTICULATE (ASPHALT FUME), 5042
CAS #8012-95-1, see OIL MISTS, MINERAL, 5026
CAS #8030-30-6, see NAPHTHAS, 1550
CAS #8052-41-3, see NAPHTHAS, 1550
CAS #8065-48-3, see DEMETON, 5514
CAS #9004-34-6, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600;
CAS #10024-97-2, see NITROUS OXIDE, 6600
CAS #10035-10-6, see ACIDS, INORGANIC, 7903
CAS #10102-43-9, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014; NITROGEN DIOXIDE (Diffusive), 6700
CAS #10102-44-0, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
CAS #10605-21-7, see ORGANONITROGEN PESTICIDES, 5601
CAS #11097-69-1, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
CAS #11126-42-4, see CHLORINATED TERPHENYL, 5014
CAS #12001-28-4, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
CAS #12001-29-5, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402;

ASBESTOS, CHRYSOTILE (bulk) by XRD, 9000; ASBESTOS (bulk) by PLM, 9002
CAS #12069-32-8, see BORON CARBIDE, 7506
CAS #12172-73-5, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
CAS #13121-70-5, see ORGANOTIN COMPOUNDS, 5504
CAS #13463-39-3, see NICKEL CARBONYL, 6007
CAS #13466-78-9, see TERPENES,1552
CAS #13768-00-8, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
CAS #13775-53-6, see FLUORIDES, 7902 (ISE), 7906 (IC)
CAS #14464-46-1, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR)
CAS #14567-73-8, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
CAS #14808-60-7, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IC)
CAS #15468-32-3, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IC)
CAS #15972-60-8, see ALACHLOR, 5603; CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #16071-86-6, see DYES, 5013
CAS #16752-77-5, see ORGANONITROGEN PESTICIDES, 5601
CAS #17068-78-9, see ASBESTOS and OTHER FIBERS by PCM, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
CAS #17804-35-2, see ORGANONITROGEN PESTICIDES, 5601
CAS #18540-29-9, see CHROMIUM, HEXAVALENT, in settled dust samples, 9101
CAS #19287-45-7, see DIBORANE, 6006
CAS #19408-84-5, see CAPSAICIN and DIHYDROCAPSAICIN, 5041
CAS #21725-46-2, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #22839-47-0, see ASPARTAME, 5031
CAS #23135-22-0, see ORGANONITROGEN PESTICIDES, 5601
CAS #23422-53-9, see ORGANONITROGEN PESTICIDES, 5601
CAS #25013-15-4, see HYDROCARBONS, AROMATIC, 1501
CAS #25168-24-5, see ORGANOTIN COMPOUNDS, 5504
CAS #25639-42-3, see METHYLCYCLOHEXANOL, 1404
CAS #27323-18-8, see POLYCHLOROBIPHENYLS, 5503
CAS #28249-77-6, see ORGANONITROGEN PESTICIDES, 5601
CAS #29191-52-4, see ANISIDINE, 2514
CAS #36791-04-5, see RIBAVIRIN, 5027
CAS #51218-45-2, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
CAS #53469-21-9, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
CAS #55720-99-5, see CHLORINATED DIPHENYL ETHER, 5025

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

METHOD: 1606, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 January 1998

OSHA : 40 ppm
NIOSH: 20 ppm
ACGIH: 40 ppm; STEL 60 ppm
(1 ppm = 1.68 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.783 g/mL @ 20 °C; BP 82 °C; VP 12 kPa (89 mm Hg) @ 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, 400/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 40 ppm
-MAX: 25 L

SHIPMENT: keep cold; pack securely for shipment.

SAMPLE STABILITY: at least 30 days at 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 39.2 to 275 mg/m³ [1]

BIAS: 4.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [1,2]

ACCURACY: ± 16.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acetonitrile

DESORPTION: 2 mL methylene chloride/methanol (85:15); ultrasonic bath for 45 minutes.

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C, hold 4 min; 12 °C/min to 150 °C

CARRIER GAS: He, 2.4 mL/min

COLUMN: capillary, fused silica, 30 m x 0.32-mm ID, 1-µm film, crossbonded PEG, Stabilwax® or equivalent

CALIBRATION: solutions of acetonitrile in methylene chloride/methanol (85:15)

RANGE: 2.6 to 2000 µg per sample [1, 2]

ESTIMATED LOD: 0.8 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.015

APPLICABILITY: The working range is 0.06 to 7.4 ppm (0.1 to 12.5 mg/m³) for a 25-L air sample [1]. Large (400 mg/200 mg) charcoal tubes are required for analyte collection, since breakthrough volume is lower with smaller charcoal tubes [2]. Analyte capacity of the large charcoal tubes has not been determined under conditions of high relative humidity [3].

INTERFERENCES: Samples containing greater than 15% methanol or other alcohols.

OTHER METHODS: This method revises NMAM 1606 (dated 8/15/94) and is based on Method S165 [4]. In this method, a capillary GC column has replaced the original packed column. Improvements include but are not limited to the following: new and less hazardous desorption solvent, smaller volume of desorption solvent required, improved desorption efficiency (DE), and lower LOD/LOQ. A storage stability study was completed and was found acceptable at 98.5% after 30 days at 5 °C.

REAGENTS:

1. Acetonitrile (ACN), reagent grade (99.9+%)*.
2. Methylene chloride, HPLC grade*.
3. Methanol, HPLC grade*.
4. Helium, purified.
5. Hydrogen, purified.
6. Air, prefiltered and purified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated coconut shell charcoal (front = 400 mg, back = 200 mg), separated by a 3-mm section of polyurethane foam. A silanized glass wool plug precedes the front section and a 3-mm polyurethane plug follows the back section. Tubes are commercially available (SKC # 226-09, Supelco ORBO-32, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator, and Stabilwax® fused silica capillary column, or equivalent (page 1606-1).
4. Vials, glass, 4-mL, PTFE-lined screw caps.
5. Syringes, 10-µL to 1-mL.
6. Volumetric flasks, 10-mL.
7. Pipets, various sizes.
8. Refrigerant packs.

SPECIAL PRECAUTIONS: Acetonitrile is toxic and flammable. Methylene chloride is a potential carcinogen. Methanol is moderately toxic and flammable. Perform all work in a chemical hood and wear appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sample tube in line.
2. Break open the ends of the sample tube immediately prior to sampling. Attach sample tube 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 both ends of the sample tubes with plastic caps and pack securely for shipment. Ship with refrigerant packs to keep samples cold.

SAMPLE PREPARATION:

5. Place the initial glass wool plug and front sorbent section of the sample tube in a 4-mL glass screw cap vial. Place the back sorbent section of the sample tube in separate 4-mL vial. Discard the polyurethane foam plugs.
6. Add 2.0 mL of methylene chloride/methanol (85:15) to each 4-mL vial and cap securely.
7. Place each vial in an ultrasonic bath for 45 minutes.
8. Transfer 1.0-mL aliquots of each sample to autosampler vials and analyze (steps 11 and 12).

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working calibration standards over the range of interest.
   a. Add known amounts of calibration stock solution (prepare in concentration range of samples; 1 µL ACN = 78.3 µg) to methylene chloride/methanol (85:15) 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 acetonitrile).

10. Determine the desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
    a. Remove the back sorbent section of the sampler.
    b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each charcoal tube.
    c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with standards and blanks (steps 11 and 12).
    e. Prepare a graph of DE vs. µg acetonitrile recovered.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1606-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with methylene chloride/methanol (85:15), reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for 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):

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method development was based upon NMAM user requests to update and improve problematic gas chromatography methods. After determining that a methylene chloride/methanol (85:15) solution was the best desorption solvent (improved DE recovery and less hazardous than benzene), the desorption efficiency was determined for acetonitrile at 5 levels ranging from 39 µg to 275 µg. The average DE for acetonitrile was determined to be 1.019. The LOD was determined to be 0.8 µg per sample. The precision, as determined from the pooled relative standard deviation (S_r), was determined to be 0.015 [1]. Acetonitrile storage stability at 0.25 x REL and 5 °C, was acceptable after 30 days with an average recovery of 98.5%.

REFERENCES:

[1] Pendergrass SM [1997]. Acetonitrile Backup Data Report, unpublished data, NIOSH/DPSE.
[2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S165, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. No. 77-185.
[3] NIOSH [1981]. Health Hazard Evaluation Report, HHE 81-359-1058.
[4] NIOSH [1977]. Acetonitrile: Method S165. In: Taylor, DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., V. 3, U.S. Department of Health, Education, and Welfare (NIOSH) Publication No. 77-157C.

METHOD WRITTEN BY: Stephanie M. Pendergrass, NIOSH/DPSE

AEROBIC BACTERIA by GC-FAME 0801

METHOD: 0801, Issue 1 **EVALUATION:** N/A **Issue 1:** 15 January 1998

PROPERTIES: viable and culturable, requires oxygen

SYNONYMS: Gram positive (+) bacteria, gram negative (-) bacteria, mycobacterium species (sp)

SAMPLING

SAMPLER: ANDERSEN IMPACTOR (15 x 100-mm culture plates containing TSBA media)

FLOW RATE: 28.3 L/min [1]

VOL-MIN: 50 L
-MAX: 300 L

SHIPMENT: keep cold, ship overnight.

SAMPLE STABILITY: transfer bacteria to fresh culture media weekly.

BLANKS: not applicable

ACCURACY

RANGE STUDIED: not applicable

BIAS: not applicable

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

ACCURACY: not applicable

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: fatty acid methyl esters (FAME) of aerobic bacteria or *Mycobacterium* sp

DESORPTION: 1 mL hexane/MTBE (1:1)

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 170°C to 270°C (5°C/min)

CARRIER GAS: Helium, 2.4 mL/min

COLUMN: capillary, fused silica, 25 m, 0.20-mm ID, 0.33-µm film, Ultra-2 [2]

CALIBRATION: MIDI fatty acid methyl ester calibration mix (Containing various C9-C20 fatty acids)

IDENTIFICATION: comparison with profile library

ACCEPTABLE GENUS IDENTIFICATION: similarity index (SI) > 0.30

ACCEPTABLE SPECIES IDENTIFICATION: SI > 0.50

APPLICABILITY: This method is applicable to all viable and culturable bacteria containing C9-C20 fatty acids. The method is applicable to bulk solid and liquid samples containing culturable bacteria, as well as air samples.

INTERFERENCES: No specific interferences were identified. However, any fungi, yeasts, or other source of fatty acid materials will affect identification of bacteria. Additionally, any organic contaminants will interfere with the identification process.

OTHER METHODS: Method 0800, Bioaerosol Sampling, is a general procedure for sampling bioaerosols in air.

REAGENTS:

1. Sodium hydroxide pellets (NaOH), reagent grade.
2. Methanol, GC/HPLC grade.
3. Hydrochloric acid (HCl), 6*N*.
4. Sodium chloride (NaCl), reagent grade.
5. Hexane, GC/HPLC grade.
6. Methyl-t-butyl ether (MTBE), GC/HPLC grade.
7. Sodium sulfate, ultrapure grade.
8. TSA nutrient agar.
9. Granulated agar.
10. TSBA agar. Dissolve 30 g trypticase soy broth and 15 g granulated agar to 1 L deionized water.
11. Saponification reagent. Dissolve 45 g NaOH in 150 mL methanol and 150 mL deionized water.
12. Methylation reagent. Mix 325 mL 6*N* HCl with 275 mL methanol.
13. Extraction reagent. Mix 200 mL hexane with 200 mL methyl-t-butyl ether.
14. Basic wash solution. Dissolve 10.8 g NaOH in 900 mL deionized water.
15. Saturated NaCl solution.
16. MIDI FAME calibration solution (MIDI, Inc., Newark, DE)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Andersen impactor, 15 x 100-mm culture plates containing TSBA culture media.
2. Sampling pump, 28.3 L/min, with flexible tubing.
3. Gas chromatograph, flame ionization detector, Ultra-2 capillary column, and microbial identification system (MIS) (Page 0801-1).
4. Water baths, 80 °C, 100 °C, and room temperature.
5. Ice bath.
6. Vortex mixer, test tube .
7. Hematology mixer.
8. Test tubes, screw cap, 13-mm x 100 mm.
9. Incubator with humidity adjustment (100%), set at 28 ± 1 °C
10. Glass beads, 3-mm.
11. Glass pipettes, disposable.
12. Dispensette bottles, 4.
13. Platinum innoculating loop, 4-mm.
14. Autoclave.
15. Autoclave biohazard bags.
16. Bactoincinerator.
17. Refrigerant packs.

SPECIAL PRECAUTIONS: Sodium hydroxide is caustic and may cause burns. Hydrochloric acid causes severe burns. Methanol, hexane, and methyl-t-butyl ether are flammable. Methanol is toxic by ingestion. Handle all bacterial cultures in approved biosafety cabinet, level II minimum. Wear appropriate eye protection, rubber gloves, and lab coat/apron.

SAMPLING:

1. Calibrate each pump with a representative sampler in line.
2. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate at 28.3 L/min for a total sample size of 50 to 300 L.
4. Remove culture plates from sampler, cover, and pack securely for shipment (media side up).
   NOTE: Keep samples cool, but protect from freezing.

SAMPLE PREPARATION:

5. Isolate individual bacteria by pure culture technique.
   NOTE: See APPENDIX for *Mycobacterium* conditions.
6. Select a single pure colony from unknown field samples and innoculate the method specific TSBA agar using the quadrant streaking technique.
   NOTE: Identification with the clinical library of the FAME system requires incubation on Blood/Chocolate agar plates at 35 °C.
   a. Incubate at 28 °C for 24 to 48 hours.
   b. Harvest approximately 40 mg (either by weighing into test tube or harvesting an amount about the

size of a half moon on the platinum loop) of the pure cultured bacteria from the 3rd quadrant (or quadrant with confluent growth).

c. Place into a 13-mm x 100 mm test tube and cap.

NOTE: A harvest of 40 mg should ideally correspond to approximately a total area count of 300,000 as measured on the GC chromatogram.

7. To each test tube, add 1 mL of saponification reagent and tightly cap.
   a. Vortex 30 seconds, then place in a 100 °C water bath for 5 min.
   b. Remove from water bath, vortex for 30 seconds, and replace in the water bath for 25 min to complete the saponification process.
8. Cool test tubes in a water bath (room temperature).
   a. Add 2 mL of methylation reagent and cap tightly.
   b. Vortex for 30 seconds and place an 80 °C water bath for exactly 10 min.
9. Cool the test tubes in an ice bath for several minutes.
   a. Add 1.25 mL of extraction reagent and cap tightly.
   b. Place the test tubes in the hematology mixer and mix end over end for 10 min.
   c. Remove the bottom layer by pipetting and add 3 mL of basic wash mixture. Mix end over end for 5 min.
10. Remove the top layer (except for *Mycobacterium* analyses) by pipetting, transfer to an autosampler vial, and attach a crimp cap.

NOTE: If no definitive separation occurs, add several drops of saturated sodium chloride solution and agitate to facilitate separation.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with a fresh solution of the MIDI FAME calibration standard. The system automatically recalibrates after every ten injections.
12. Use *Xanthomonas maltophilia* as a positive QC culture (SI > 0.90). Other bacterial cultures suchas *Bacillus subtilus*, *Pseudomonas aeruginosa*, *Micrococcus roseus*, and *Mycobacterium smegmatis* (SI>0.80) serve as suitable blind QC cultures.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 0801-1. Inject a 2-µL sample aliquot with an autosampler.
14. The FAME profile generated for each unknown bacteria analyzed is electronically compared to a computer generated library containing the fatty acid profiles of over 5,000 bacteria. Bacterial identifications are generated for each sample and ranked in order based upon similarity indices.

NOTE: Identification is based on comparison with a profile library; therefore, sample identification is not definitive. The similarity index (SI) indicates how closely the sample compares to known bacteria in the library collection.

EVALUATION OF METHOD:

Approximately 500 analyses of bacterial cultures comprising 40 different genus and 80 plus species were completed in the evaluation of this method [3,4]. Overall accuracy of the GC-FAME-MIS in this evaluation was > 98%. Correct identification of *Mycobacterium* cultures was highly dependent upon the addition glycerol to the Middlebrook 7H10 culture media.

REFERENCES:

[1] Jensen PA, Scarpino P [1992]. Evaluation of eight bioaerosol samplers with bacteria. Am Ind Hyg Assoc J 53(10):660-667.

[2] Sasser M [1990]. Identification of bacteria by gas chromatography of cellular fatty acids. MIDI Technical Note # 101.
[3] Pendergrass SM, Jensen PA [1997]. Application of the gas chromatography-fatty acid methyl ester (GC-FAME) system for the identification of environmental and clinical isolates of the family *Micrococcaceae*. Appl Occup Environ Hyg *12*(8):543-546.
[4] Schafer M, Pendergrass SM [in preparation]. Identification and differentiation of selected members of the genus *Mycobacterium* by gas chromatography-fatty acid methyl ester (GC-FAME) analysis. J Applied and Environmental Microbiology.

METHOD WRITTEN BY: Stephanie M. Pendergrass, DPSE, NIOSH

APPENDIX. MYCOBACTERIUM CONDITIONS AND CULTURE MEDIA.

For the analysis of *Mycobacteria*, follow the method as written with exception of the following steps.

Step 6. Culture media: Middlebrook 7H10 culture media containing Middlebrook OADC Enrichment (with 0.5% glycerol).
Incubation: 35 °C in the presence of 5 to 10% CO_2 for 2 to 14 days; slow growing cultures like *Mycobacterium tuberculosis* may require up to six weeks.
Step 7. Vortex mixing: Add 3 to 5 glass beads to the mixture prior to vortexing.
Step 9. Extraction: For *Mycobacterium* analyses remove the top layer and add approximately 10 mg of sodium sulfate to remove any water from the FAME solution.
Step 10. Transfer: The FAME solution is pipetted to a new autosampler vial. Take care not to carry over any sodium sulfate, and attach crimp cap.
Step 12. Quality control: Use *Mycobacterium smegmatis* as a positive QC culture (SI > 0.80) for *Mycobacterium* analyses.

ALACHLOR in Air 5603

$C_{14}H_{20}O_2NCl$ MW: 269.6 CAS: 15972-60-8 RTECS: AE1225000

METHOD: 5603, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: colorless crystalline solid; d 1.133 g/mL @ 25 °C; MP 39.5 to 41.5 °C; VP 0.0029 Pa (2.2×10^{-5} mm Hg) @ 25 °C; solubility in water 242 mg/L @ 25 °C.

SYNONYMS: 2-Chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide; Lasso; Alanex; Alanox; Chimiclor

SAMPLING

SAMPLER: SOLID PHASE EXTRACTION (SPE) DISK (Styrene divinyl benzene [SDB]-xc disk)

FLOW RATE: 1 L/min

VOL-MIN: 70 L
-MAX: 1750 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days at 25 °C
at least 21 days at 4 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.24 to 120 µg per sample

BIAS: 0.0368

OVERALL PRECISION ($\hat{S}_{rT}$): 0.078 (12 µg to 48 µg) [1]

ACCURACY: ± 17.4%

MEASUREMENT

TECHNIQUE: ENZYME LINKED IMMUNOSORBENT ASSAY (ELISA)

ANALYTE: Alachlor

EXTRACTION: 2 mL methanol

WAVELENGTH: 450 nm

CALIBRATION: standard solutions of alachlor in ≤1% methanol in water

RANGE: 20 to 500 ng per sample [1]

ESTIMATED LOD: 9 ng per sample [1]

PRECISION ($\hat{S}_r$): 0.072 [1]

APPLICABILITY: This method provides a quantitative evaluation of alachlor in air utilizing ELISA technology designed to determine the concentration of alachlor in water. The limit of quantitation for the overall method is 20 ng/sample because of the need to negate the interferences of methanol in the ELISA. The assay is simple and adaptable enough that it may be used on site in the field as a screening method.

INTERFERENCES: 2-[(2,6-diethyl-phenyl)(methoxymethyl)amino]-2-oxoethane sulfonic acid (ESA) cross reacts with alachlor in the ELISA. ESA is not detected by standard HPLC or GC [2]. Alachlor related acetanilides may interfere with the determination of alachlor, such as acetochlor, metolachlor, and metalaxyl. The ELISA is also sensitive to the concentration of organic solvent remaining in the assay from solid phase extraction.

OTHER METHODS: Other ELISA kits may be used in a similar manner. Alachlor also is included in Method 5602, Chlorinated and Organonitrogen Herbicides in Air by GC/ECD [3].

REAGENTS:

1. Alachlor*
2. Methanol*, pesticide analytical grade
3. Deionized water
4. Alachlor plate kit, EnviroGard™, or equivalent (e.g., Ohmicron RaPID Assay® or Ensys RIS®).
5. Alachlor stock solution, 1000 µg/mL. Add 10 mg pure alachlor in 10 mL of pesticide free methanol. Store in freezer.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Solid phase extraction (SPE) disk, 25-mm, SDB-xc (3M Empore™, or equivalent), cellulose backup pad in 3-piece cassette with 50-mm extension.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. Microtiter plate reader, 450 nm, 650 nm backup.
4. Glass bottles, wide-mouth, ~1-oz. (diameter large enough to lay 25-mm disk flat), with PTFE-lined caps.
5. Vials , glass, 4-mL, with PTFE-lined caps.
6. Platform orbital shaker.
7. Timer.
8. Microtiter plate washer/shaker (optional).
9. Pipettor, positive displacement.
10. Pipettor, varichannel, multiwell with tips, 40- and 80-µL (80- and 120-µL volume for larger sample numbers).
11. Aerosol resistant tips (optional).
12. Disposable reagent reservoir..
13. Forceps
14. Protective gloves.
15. Laboratory towels.
16. Parafilm

SPECIAL PRECAUTIONS: NIOSH researchers have classified alachlor as a Group I compound, which is indicative of its adverse acute health effects from exposure to low concentrations. Handle carefully. Wear gloves and protective clothing. Methanol is flammable and moderately toxic by ingestion and inhalation.

SAMPLING:

1. Assemble each sampler in a clean environment.
2. Calibrate each personal sampling pump with a representative sampler in line.
3. Sample at an accurately known flow rate of ~1 L/min. The sampling period depends on suspected concentration.
4. Seal both ends of the sampler with plugs and pack securely for shipment, including the appropriate number of blanks.

SAMPLE PREPARATION:

5. Using forceps, remove the SDB disk from the sampler and place in a glass bottle with an ID large enough to allow the filter to lie flat.
   a. Add 2.0 mL of pesticide free methanol to the SDB disk, cap, and shake on a platform orbital shaker for 15 minutes.
   b. Transfer the methanol solution to a 4-mL sample vial with a PTFE-lined cap.
   c. Using a positive displacement pipettor or syringe, remove an aliquot of the sample and dilute it a minimum of 1:100 with deionized water.
      NOTE: If concentrations are higher than 0.5 µg/sample, further dilutions are needed to meet the target range of the assay. Multiple dilutions may be done if the concentration range is

unknown.

d. Wrap remainder of the samples with parafilm and store refrigerated.
e. Run the diluted samples in the assay.

6. Follow the general instructions of the EnviroGard™ Alachlor plate kit [4]. Adjust as needed to accommodate sample needs.
   a. Determine the number of microtiter plate wells needed to run in duplicate the kit negative control and 3 kit standards, the matrix negative control and 3 matrix standards, the samples, and an alachlor fortified control for each set of 3 strips. Remove the number of well strips needed (twelve wells per strip). Refrigerate the unused strips in the resealable plastic bag containing a desiccant provided in the kit.
   b. Bring the well strips and the remaining contents of the ELISA assay to ambient temperature before beginning the assay.
   c. Using a pipettor with aerosol resistant tips, in an orderly fashion, add 80 µL aliquots of the standards, samples, and controls to the microtiter plate wells in duplicate.
      NOTE: The ELISA assay is a time dependent matrix. Add reagents in a consistent, uninterrupted manner to avoid variability and a drift effect over the plate.
   d. In the same order the standards and samples were added to the plate, add 2 drops of enzyme conjugate from the enzyme conjugate bottle.
      NOTE: If more than 3 rows of wells are to be employed, use a multiwell pipettor. If the dropper is used, ensure that the drops are free falling and do not touch the sides of the well.
   e. Carefully mix the contents of the wells with circular motions.
   f. Cover the plate with parafilm. Incubate for 1 hour at ambient temperature with mechanical mixing on an orbital mixer or microtiter plate shaker. If necessary, sedentary incubation may be used.
   g. Wash the plate with tap or deionized water 6 times with a microtiter plate washer or manually. If done manually, vigorously flick the contents of the plate into a sink, flood the plate with water, and empty the water with a flick of the wrist. Repeat 6 times.
   h. Invert the plate over a laboratory towel to remove the excess water.
   i. As in the previous order of addition, add 80 µL (2 drops) of substrate, and add 40 µL (1 drop) of chromogen from kit.
      (1). If less than 3 or 4 well strips are used, substrate and chromogen may be added separately.
      (2). If more, freshly mix a 2:1 volume of the substrate and chromogen, respectively, and add 120 µL of the mixture to each well.
      NOTE: Use care to prepare sufficient reagent mixture to add to the contents of the wells plus a small reservoir so as not to interrupt the addition of the reagents. Any interruption in the addition of reagents may affect the color development relative to the standard curve. Discard the excess.
   j. Mix, cover with clean parafilm, and incubate the plate as before for 30 minutes.
   k. After incubation, add 40 µL (1 drop) of the stop solution (from the kit) to each well, and mix thoroughly until all of the blue has converted to yellow.
      NOTE: Plate must be read within 30 min after adding stop solution.

CALIBRATION AND QUALITY CONTROL:

7. Check the overall performance of the microplate reader according to the manufacture's instructions.
8. Prepare a calibration curve, using three standards: 100, 500, 2500 ng/L, each time the assay is run. To prepare the working standards in the appropriate matrix:
   a. Serially dilute an aliquot of the alachlor stock solution in a volume of matrix similar to the sample matrix yielding a 50,000 ng/L. (If the methanol concentration of the samples is less than 1%, water may be used. However, the higher the methanol concentration of the samples, the more desirable it is to use the same % of methanol standards as in the samples.
   b. Using the 50,000 ng/L solution, prepare the working standards 100 ng/L, 500 ng/L and 25000 ng/L, in the matrix solvent.
9. Run controls, 1 for every three rows of the assay to determine possible drift.
10. Zero the reader against air or deionized water before reading the assay.
11. Determine the concentration of alachlor using the data reduction capabilities of the microtiter plate reader, or appropriate software. Use a semi-log or 4 parameter logit-log curve fit to the standard curve.

Make the appropriate dilution corrections.

12. If data reduction capabilities are not available, perform the calculations as follows:
    a. Average the optical density (OD) for the negative control.
    b. Average the OD for each of the standards in the curve.
    c. Determine the percent binding ($\%B_o$) of the standards by:

$$\%B_o = standard_{average} / negative\ control_{average} \times 100$$

    d. Determine the $\%B_o$ of the samples by:

$$\%B_o = sample_{average} / negative\ control_{average} \times 100$$

    e. Prepare a calibration graph, $\%B_o$ vs. log concentration (ng/L) of alachlor.
13. Follow the EnviroGard alachlor assay guidelines to ensure accurate results [4].
    a. The coefficient of variation for optical density (OD) of each standard in the curve ≤ 15%.
    b. The percent binding ($\%B_o$) for each standard in the curve should also fall within the following ranges.

100 µg/mL	64-86%
500 µg/mL	33-55%
2500 µg/mL	11-21%

    NOTE: See the certification sheets of particular lots of kits provided with the assay.

MEASUREMENT:

14. Set wavelength on microtiter plate reader to 450 nm, and reference wavelength to 600 or 650 nm.
15. Zero the microtiter plate reader against air, or 200 µL of water in a blank well. Within 30 minutes of adding the stop solution, read the plates at 450 nm.

CALCULATIONS:

16. Record the actual solution volumes to which the samples, V_s (L), and blanks, V_b (L), were diluted.
17. From the calibration graph, determine the concentration of the sample solutions of the samples, C_s (ng/L), and media blanks, C_b (ng/L).
    NOTE: Blanks generally fall below the range of the calibration graph and are not included in the calculations. Variable readings for the blanks indicate a problem with the assay.
18. Using the solution volume of the samples, V_s (L), calculate the concentration, C (mg/m^3), of alachlor in the volume of air sampled, V_{air} (L):

$$C = \frac{C_s V_s \cdot 10^{-3}}{V_{air}}, \ mg/m^3$$

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

This method was evaluated with fortified SDB-xc extraction disks that had clean humidified air passed through them. The volume of air to be sampled was based on air levels found in a NIOSH field survey of herbicide applicators [5], and a 1:100 dilution factor in the assay. If sampling is done for longer periods of time, further dilution of the samples may be necessary. The method was evaluated over the range of 0.24 µg to 120 µg per sample. The sample precision was not statistically poolable over the entire range of the levels studied. However, they were poolable at the 12-, 24-, and 48-µg range. The overall precision ($\hat{S}_{rT}$) for these samples was 0.0783, with an accuracy estimate of ±17.4%. The precision, bias, and accuracy

at each level studied also were determined (See Table 1). The average recovery of all levels was 100%. Samples are stable for at least 7 days at ambient temperature and 30 days refrigerated. Breakthrough was not evident at a capacity of 144 µg.

REFERENCES:

[1] Sammons DL, Kennedy ER [1997]. Backup data for alachlor (unpublished report).
[2] Aga DS, Thurman EM, Pomes ML. Determination of alachlor and its sulfonic acid metabolite in water by solid-phase extraction and enzyme-linked immunosorbent assay. Analytical Chemistry. *66*:1495-1499 (1994).
[3] NIOSH [1998]. Chlorinated organonitrogen and acid herbicides in air: Method 5602. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed., 2nd supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.
[4] EnviroGard Alachlor Plate Kit. P 30128, Rev A 3/14/95. Millipore.
[5] Sanderson WT, Biagini R, Henningsen G, Ringenburg V, MacKenzie B [1995]. Exposure of commercial pesticide applicators to the herbicide alachlor. Am Ind Hyg Assoc J *56*:890-897.

METHOD WRITTEN BY: Deborah Sammons and Eugene Kennedy, Ph.D., NIOSH/DPSE

TABLE 1. METHOD SUMMARY

Method Evaluation Data

Arbitrary Exposure Limit (1 mg/m^3)[a]	Test Average (µg/sample)	Independent Average (µg/sample)	Precision[b] (sampling and analysis)	Bias [(test/indep) -1]	Calculated Accuracy (± %)
0.01x	0.259	0.24	0.109	0.080	27.7
0.1x	2.17	2.4	0.170	-0.094	35.3
0.5x	12.7	12.0	0.081	0.059	23.0
1x	23.9	24.0	0.063	-0.003	13.2
2x	48.9	48.0	0.090	0.019	18.4
5x	128.4	120	0.122	0.070	29.1

[a] Theoretical Exposure Concentrations were based on the NIOSH RELs of similarly classified pesticides.
[b] Precision is not statistically poolable.

ANILINE, *o*-TOLUIDINE, AND NITROBENZENE 2017

(1) Aniline C_6H_7N	MW: (1) 93.13	CAS: (1) 62-53-3	RTECS: (1) BW6650000
(2) *o*-Toluidine C_7H_9N	(2) 107.2	(2) 95-53-4	(2) XU2975000
(3) Nitrobenzene $C_6H_5NO_2$	(3) 123.1	(3) 98-95-3	(3) DA6475000

METHOD: 2017, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

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

PROPERTIES: Table 1

NAMES & SYNONYMS: **Aniline:** Aminobenzene, Benzenamine, phenylamine
***o*-Toluidine:** *o*-aminotoluene, 2-aminotoluene, 1-methyl-2-aminobenzene, *o*-methylaniline, 2-methylaniline
Nitrobenzene: nitrobenzol, oil of mirbane

SAMPLING

SAMPLER: FILTER + SOLID SORBENT
(Glass fiber filter, sulfuric acid treated + silica gel sorbent tube, 520/260 mg)
Alternate samplers: Gauze wipes, 4 x 4 in.,
Dermal badge sampler (1 g silica gel in cotton pouch)

FLOW RATE: 0.2 L/min [1]

VOL-MIN: 5 L
-MAX: 50 L

SHIPMENT: routine

SAMPLE STABILITY: aniline and *o*-toluidine 7 days @ 5 °C [2]; nitrobenzene 60 days [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 2

BIAS: not determined.

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

ACCURACY: not determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: aniline, o-toluidine, nitrobenzene

DESORPTION: 2 mL ethanol

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 to 150 °C (8 °C/min)

CARRIER GAS: Helium, 2.4 mL/min

COLUMN: capillary column, 30 m, 0.32-mm ID,1-µm film, (Rtx-5, or equivalent) [1]

CALIBRATION: solutions of analytes in ethanol

RANGE: Table 2 [1]

ESTIMATED LOD: Table 2 [1]

PRECISION ($\bar{S}_r$): Table 2 [1]

APPLICABILITY: Under the GC parameters stated in the method, aniline, o-toluidine, and nitrobenzene can be identified based upon retention time and quantified. Analyte recovery was optimized under conditions of moderate relative humidity (< 53%), low sampling rates (0.2 L/min), and sample volumes < 50 L [1]. Sulfuric acid-treated glass fiber filters were used to collect aniline and *o*-toluidine, while nitrobenzene was collected on the silica gel sorbent [1]. Nitrobenzene collection on silica gel tubes was significantly reduced under conditions of high relative humidity [1]. Dermal badge samplers (cotton pouch with 1 g silica gel) and gauze wipes were developed to estimate exposures via splashes, spills, and passive collection of aerosol vapors.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time may interfere.

OTHER METHODS: This method revises and combines methods 2002 (aniline and o-toluidine) [3], and 2005 (nitrobenzene) [4].

REAGENTS:

1. Aniline, reagent grade*
2. *o*-Toluidine, reagent grade*
3. Nitrobenzene, reagent grade*
4. Ethanol, chromatographic grade*
5. Sulfuric acid (H_2SO_4), reagent grade,* 0.26 *N*. Dilute 1.5 mL of 36 *N* H_2SO_4 to 200 mL with deionized water.
6. Aniline calibration stock solution, 102.2 mg/mL. Dilute 1 mL aniline to 10 mL with ethanol.
7. *o*-Toluidine calibration stock solution, 100.6 mg/mL. Dilute 1 mL *o*-toluidine to 10 mL with ethanol.
8. Nitrobenzene calibration stock solution, 120.3 mg/mL. Dilute 1 mL nitrobenzene to 10 mL with ethanol.
9. Helium, purified.
10. Hydrogen, prepurified.
11. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampling train:
   Filter, glass fiber, 37-mm (Gelman, or equivalent) treated with 0.26 *N* H_2SO_4 (see APPENDIX) in polystyrene cassette. Filters are commercially available (SKC, Inc. #225-9004, or equivalent).
   Sorbent tube: glass tube, 11 cm, 8-mm OD, containing two sections of silica gel (front = 520 mg /back = 260 mg) separated and retained by polyurethane foam plugs. A silylated glass wool plug precedes the front section. Tubes are commercially available (SKC, Inc. #226-15, Supelco ORBO-507).
2. Personal sampling pump, 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (page 2017-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Vials, 4-mL, with screw caps.
7. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.

SPECIAL PRECAUTIONS: Aniline is toxic, poisonous and a potential human carcinogen. o-Toluidine is toxic and a potential human carcinogen. Nitrobenzene is toxic and poisonous. Nitrobenzene has a synergistic effect on the toxicity of aniline and o-toluidine [5]. Ethanol is flammable and a dangerous fire risk. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Assemble sampling train. Attach filter cassette to sorbent tube and to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate (0.2 L/min) for a total sample size of 5 to 50 L.
   NOTE: High relative humidity reduces the sampling capacity of the silica gel sorbent.
4. Separate the cassettes and tubes, cap, and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front (include glass wool plug) and back sorbent sections of the sampler tube in separate 4-mL vials. Discard foam plugs. Remove glass fiber filters from cassettes and place in 4-mL vials.
6. Add 2 mL of ethanol to each vial and cap.
7. Place vials in an ultrasonic bath for 60 min to aid desorption.
8. Transfer 1-mL aliquot to autosampler vials and attach crimp caps.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range of interest.

a. Add known amounts of calibration stock solutions to ethanol 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 analyte).

10. Determine recovery (R) at least once for each lot of glass fiber filters and desorption efficiency (DE) for each lot of silica gel sorbent tubes used for sampling in the calibration range (step 9).
    a. Prepare three samplers at each of six levels plus three media blanks.
    b. Inject a known amount of calibration stock solutions directly onto the sulfuric acid-treated, 37-mm glass fiber filters and onto the front sorbent bed of each silica gel tube.
    c. Allow the filters and tubes to air equilibrate for several minutes, then cap the ends of the tubes and cassettes and allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with standards and blanks (steps 12 and 13).
    e. Prepare a graphs of R and DE vs. µg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration, R, and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2017-1. Inject a 1-µL 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 with ethanol, reanalyze, and apply the appropriate dilution factor in the calculations.
13. Measure peak areas.

CALCULATIONS:

14. Determine the mass, µg (corrected for R), for each analyte found on the glass fiber filter (W_{fil}) and glass fiber filter blank (B_{Fil}).
15. Calculate concentration, C_{fil}, for each analyte in the air volume sampled, V (L):
    NOTE: Use this equation to calculate wipe samples and dermal badges, if collected.

$$C_{Fil} = \frac{W_{Fil} - B_{Fil}}{V}, \text{ mg/m}^3$$

16. Determine the mass, µg (corrected for DE), for each analyte found in the sample front (W_f) and back (W_b) silica gel 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_{SG}, of each analyte in the air volume sampled, V (L):

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

The method was developed in response to a health hazard evaluation (HHE) request at a rubber tire manufacturing plant where there was a reported high incidence of bladder cancer [5,6]. The method was evaluated for the collection of aniline, o-toluidine, and nitrobenzene on gauze wipes, passive dermal samplers, and 37-mm glass fiber filter/silica gel sorbent tube sampling train.

Desorption efficiency (DE) for aniline (recovered from acid-treated filters) was determined to be 1.00 at 10 x LOD [1]. Aniline storage stability at 0.12 mg was 64% after 7 days [1]; however, at 0.2 to 0.7 mg recovery was 93.8% [2]. (Recoveries for storage stability samples must be ≥90% to be acceptable.) Aniline recovery from gauze wipes spiked and air equilibrated for 8 hours was 83% with a precision of 0.048, while recovery from passive dermal samplers, spiked and air equilibrated for 1 hour, was 88% [1].

Desorption efficiency (DE) for *o*-toluidine (recovered from acid treated filters) was determined to be 1.00 at 10 x LOD [1]. *o*-Toluidine storage stability at 0.6 to 2.5 mg was 96.3% after 7 days [2]; but at 0.1 mg was 76% [1]. *o*-Toluidine recovery from gauze wipes spiked and air equilibrated for 8 hours was 88% with a precision of 0.039, while recovery from passive dermal samplers, spiked and air equilibrated for 1 hour, was 95% [1].

Desorption efficiency (DE) for nitrobenzene (recovered from silica gel tubes) was determined to be 98% at 10 x LOD [1]. Nitrobenzene storage stability at 0.12 mg was acceptable after 60 days with a 95% recovery [1]. Nitrobenzene recovery from gauze wipes, spiked and air equilibrated for < 1 hour, was 89% with a precision of 0.092, while recovery from passive dermal samplers spiked and air equilibrated for 24 hours was >92% [1].

REFERENCES:

[1] Pendergrass SM [1994]. An approach for estimating workplace exposure to *o*-toluidine, aniline, and nitrobenzene. Am Ind Hyg Assoc J *55*:733-737.
[2] NIOSH [1977]. Documentation of NIOSH Validation Tests, S168, S217, S310. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-185.
[3] NIOSH [1994]. Aromatic Amines: Method 2002. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[4] NIOSH [1994]. Nitrobenzenes: Method 2005. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[5] Ward E, Carpenter A, Roberts D, *et al.* [1991]. Excess number of bladder cancers in workers exposed to ortho-toluidine and aniline. J Natl Cancer Inst *83(7)*:501-506.
[6] NIOSH [1990]. NIOSH Alert: preventing bladder cancer from exposure to *o*-toluidine and aniline. Cincinnati, OH: National Institute for Occupational Safety Health, DHHS (NIOSH) Publication No. 90-116; NTIS No. PB-91-188-953.

METHOD WRITTEN BY:

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TABLE 1. EXPOSURE LIMITS AND PHYSICAL PROPERTIES

Analyte	OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH TLV (ppm)	Physical Properties
Aniline	5	Ca; lowest feasible	2	Liquid; d 1.022 g/mL @ 20 °C; BP 184 °C; VP 0.089 kPa (0.3 mm Hg) @ 20 °C; MP -6 °C; explosive limits 1.3 to 11% in air.
o-Toluidine	Ca; 0.02	Ca; lowest feasible (skin)	Ca; 2	Liquid; d 1.006 g/mL @ 20 °C; BP 201 °C; MP -15 °C; VP 0.043 kPa (0.32 mm Hg) @ 20 °C
Nitrobenzene	1	1	1	Liquid, pungent odor; d 1.203 g/mL @ 20 °C; BP 211.0 °C; MP 5 °C; VP 37 kPa (0.28 mm Hg) @ 20 °C

Ca = potential human carcinogen

TABLE 2. ANALYTICAL MEASUREMENTS

Analyte	1 ppm = mg/m³ @ NTP	Range Studied (µg/sample)	LOD (µg/sample)	Precision ($\bar{S}_r$)
Aniline	3.87	31 to 255	4	0.016
o-Toluidine	4.46	30 to 252	3	0.015
Nitrobenzene	5.12	27 to 460	1	0.033

APPENDIX. PREPARATION OF SULFURIC ACID-TREATED FILTERS

Acid-treated Gelman Type A/E, 37-mm, glass fiber filters, or equivalent, are prepared by soaking each filter with 0.5 mL of 0.26 *N* sulfuric acid. (0.26 *N* sulfuric acid can be prepared by diluting 1.5 mL of 36 *N* sulfuric acid to 200 mL with deionized water.) The filters are dried in an oven at 100 °C for 1 h and then assembled into 37-mm polystyrene cassettes without support pads. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

Sulfuric acid-treated glass fiber filters also are available commercially - Two treated filters preloaded in a 3-piece cassette. These samplers may be used, although this method specifies only one treated filter.

BENZENE-SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME) 5042

MW: variable CAS: 8052-42-4 asphalt; none, asphalt fume RTECS: CI990000, asphalt; none, asphalt fume

METHOD: 5042, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA: No PEL
NIOSH: C 5 mg/m^3 (15-min) as total particulates
ACGIH: 5 mg/m^3

PROPERTIES: not defined

SYNONYMS: bitumen fumes

SAMPLING

SAMPLER:	FILTER (tared 37-mm, 2-µm, PTFE filter)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	28 L @ 5 mg/m^3
-MAX:	400 L @ 5 mg/m^3
SHIPMENT:	routine
SAMPLE STABILITY:	not determined
BLANKS:	5 field blanks per day

ACCURACY

RANGE STUDIED:	not determined
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	GRAVIMETRIC
ANALYTE:	Airborne total particulate (TP) material and the benzene-soluble fraction (BSF)
EXTRACTION:	3 mL benzene; ultrasonic bath, 20 minutes
BALANCE:	0.001 mg sensitivity; use same balance, if practical, before and after sample collection
CALIBRATION:	Check and maintain calibration of balance according to manufacturer's recommendations
RANGE:	TP: 0.13 to 2 mg per sample BSF: 0.14 to 2 mg per sample
ESTIMATED LOD:	TP: 0.04 mg per sample BSF: 0.04 mg per sample
PRECISION ($\hat{S}_r$):	TP: 0.048 at ≥ 0.10 mg per sample BSF: 0.061 at ≥ 0.21 mg per sample

APPLICABILITY: The working range is 0.14 to 2 mg/m^3 for a 1000-L sample. The method is applicable to 15-minute samples. The method was evaluated for asphalt fume; however, it is nonspecific and determines the concentrations of total particulate and the soluble fraction of the total particulate to which a worker is exposed. Therefore, for each sample matrix collected other than asphalt fume, a surrogate standard must be selected and spiked onto sampling media. These spiked samples will be used to determine recoveries, precision, and accuracy, also LOD and LOQ if necessary; moreover, other solvents besides benzene can be evaluated. The particle size of the particulate should be less than 40 µm, and preferably less than 30 µm. If particle sizes are larger than this, another sampler should be used.

INTERFERENCES: Changes in temperature or humidity during pre- and post-collection weighing may affect accuracy. A controlled laboratory environment is needed to exclude positive interferences due to dust contamination. Losses may occur from air stripping or volatilization of a collected sample during sampling, shipping, or analysis.

OTHER METHODS: The total particulate portion of this method is based on NMAM 0500 [1]. Other methods applicable to asphalt fume are NMAM 5800, Polycyclic Aromatic Compounds [2], and NMAM 2550, Benzothiazole in Asphalt Fume [3].

REAGENTS:

1. Benzene,* ≤ 5 ppm evaporation residue, e.g., Aldrich Chemical Co. Cat. No. 27,070-9 or equivalent.
2. Acetone,* HPLC grade.
3. Hexane,* HPLC grade.
4. Nitrogen,* purified and filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 2-µm pore size, PTFE membrane filter laminated to PTFE (Zefluor, Pall Gelman Sciences, Cat. No. P5PJ037; Supelco, Cat. No. 2-0043; SKC Cat. No. 225-17-07; or equivalent hydrophobic filter), with cellulose support pad in a 37-mm cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Balance, readable to 0.001 mg.
4. Static neutralizer, ^{210}Po; replace according to manufacturer's recommendations.
5. Environmental chamber or room for balance (e.g., 20 ± 1 °C, constant ± 5% relative humidity, and dust-free).
6. Weighing cups,* PTFE, 2-mL (Fisher Cat. No. 2006529, or equivalent), in a carrying rack.
7. Vacuum oven, equipped with in-line filter on vacuum release valve to remove dust.
   NOTE: Keep the interior of the vacuum oven dust-free for maximum sensitivity, reproducibility, and accuracy.
8. Forceps.
9. Test tubes,** glass, 13-mm x 100 mm, with PTFE-lined screw caps.
10. Pipet,** glass, volumetric, 3-mL, with bulb.
11. Pipet,** glass, Mohr, 2-mL, with bulb.
12. Clarification units, 6-mL PTFE-treated reservoir with 1-µm PTFE frit (Daigger and Company, Inc., Lincolnshire, IL, Cat. No. LID-2102-10US, or equivalent).
13. Pressure regulator, valve, tubing, in-line filter to remove dust and organics, with adapter for applying nitrogen pressure to the clarification unit.
14. Ultrasonic bath.

* Rinse the weighing cups as follows.
   a. Wash with acetone until all visible residue is removed.
   b. Rinse with hexane for several seconds.
   c. Air dry.
   d. Discard any weighing cups that are not visibly clean.

** Rinse all glassware with acetone then hexane; air dry.

SPECIAL PRECAUTIONS: Benzene is a suspect carcinogen [4]. Asphalt fumes are considered a potential occupational carcinogen [4]. Benzene, hexane, and acetone are highly flammable. Prepare samples and standards in a well-ventilated hood and avoid skin contact. Use care when working with compressed gases.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Number the backup pads with a ballpoint pen and place them, numbered side down, in the filter cassette bottom sections.
2. Preweigh the filters by the weighing procedure given in step 3. Record the mean tare weight of sample filters, W_1 and field blanks, B_1 (µg).
3. Weighing procedure:
   a. Equilibrate the filters or weighing cups in an environmentally controlled weighing area or chamber for at least two hours.
   b. Zero the balance before each weighing.
   c. Using forceps, pass each filter or weighing cup over a static neutralizer. Repeat this step if the filter or weighing cup does not release easily from the forceps or attracts the balance pan. Static electricity can cause erroneous weight readings.
   d. Weigh each filter or weighing cup until a constant weight is obtained (two successive weighings within 10 µg). Record the mean of the last two weighings to the nearest microgram.
4. Assemble the filter in the filter cassette and close firmly to prevent leakage. 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 an accurately known flow rate between 1 to 4 L/min for a total sample volume of 28 L to 400 L. Do not exceed a total filter loading of approximately 2 mg total particulate.
7. Collect five field blanks for each day of sampling for determining the limit of detection (LOD) and the limit of quantitation (LOQ).
8. Replace plugs in cassettes and pack securely for shipment to the laboratory. Recommend samples be refrigerated upon receipt at the laboratory.

CALIBRATION AND QUALITY CONTROL:

9. Use the same balance, if practical, for weighing filters and weighing cups before and after sample collection or benzene evaporation. Check and maintain calibration of balance according to manufacturer's recommendations. Zero the balance before each weighing.
10. Process three tared media blanks through the measurement procedures for total particulate and benzene-soluble fraction.

TOTAL PARTICULATE MEASUREMENT:

11. After sampling:
    a. Allow refrigerated sample cassettes to come to room temperature before proceeding.
    b. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
    c. Remove the top and bottom plugs from the filter cassette. Equilibrate sampler for at least two hours in the balance room or environmental chamber.
    d. Remove the shrink band, pry open the cassette, and gently remove the filter to avoid loss of sample.
    e. Reweigh (step 3) each filter, including field blanks. Record the mean post-sampling weight, W_2 or B_2 (µg). Also, record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)
    f. After weighing, transfer the filter carefully with forceps to a clean test tube and cap the tube.

CALCULATIONS FOR TOTAL PARTICULATE:

12. Calculate the concentration of total particulate, C_{TP} (mg/m^3), in the air volume sampled, V (L).

$$C_{TP} = \frac{(W_2 - W_1) - (B_2 - B_1)}{V}, \text{ mg/m}^3$$

where: W_1 = mean tare weight of filter before sampling (µg)
W_2 = mean post-sampling weight of sample-containing filter (µg)
B_1 = mean tare weight of field blank filters (µg)
B_2 = mean post-sampling weight of field blank filters (µg)

BENZENE-SOLUBLE FRACTION MEASUREMENT:

13. Condition clarification unit by rinsing the reservoir with 1.5 mL of benzene. Use nitrogen pressure to force the benzene through the frit. Appropriately dispose of the benzene rinse.
14. Extract benzene-soluble fraction.
    a. Add 3.0 mL benzene via a 3-mL volumetric pipet to the filter-containing test tube (step 11.e.) Recap the test tube.
    b. Place the test tube upright in beaker containing water to the same level as the liquid in the test tube. Place the beaker and test tube in ultrasonic bath and agitate for 20 minutes.
    c. Transfer benzene extract to conditioned clarification unit and force the extract through into a clean test tube, using nitrogen pressure as in step 13. Discard sampling filter and clarification unit.

    NOTE: Be sure the end of the clarification unit is well below the opening of the test tube to prevent sample loss by spattering.
15. Preweigh clean weighing cups by the weighing procedure in step 3. Record the mean tare weight, W_3 or B_3 (µg).

    NOTE: The weighing cup should already be prerinsed and dried as described in the Equipment section.

    a. Identify each tared weighing cup by labeling its place in the carrying rack.
    b. Transfer a 1.5-mL aliquot of the benzene extract via a 2-mL Mohr pipet to the tared weighing cup.

    NOTE: An aliquot may be taken from the remaining extract at this step if other analyses (e.g., polycyclic aromatic compounds) are to be performed on the sample. Apply the appropriate aliquot factor in calculations.
16. Place the weighing cup rack in a vacuum oven preheated to 40 °C. Apply vacuum until pressure in the oven is 7 to 27 kPa (50 to 200 mm Hg). Allow solvent to evaporate (about two hours). Release the vacuum by slowly opening a release valve that has an in-line filter to remove room dust.
17. Reweigh the weighing cup by the weighing procedure in step 3. Record the mean post-sampling weight, W_4 or B_4 (µg). Also, record anything remarkable about the sample (e.g., overload, leakage, wet, spattering, etc.).
18. After weighing, clean the weighing cup as described in the Equipment section.

CALCULATIONS FOR BENZENE-SOLUBLE FRACTION:

19. Calculate the concentration of benzene-soluble fraction, C_{BSF} (mg/m^3), in the volume of air sampled, V (L):

$$C_{BSF} = \frac{[(W_4 - W_3) - (B_4 - B_3)] \cdot 2}{V}, \text{ mg/m}^3$$

where: W_3 = mean tare weight of sample weighing cup (µg)
W_4 = mean post-sampling weight of sample weighing cup (µg)

B_3 = mean tare weight of field blank weighing cups (µg)
B_4 = mean post-sampling weight of field blank weighing cups (µg)
2 = aliquot factor

EVALUATION OF METHOD:

Asphalt fume collected during a previous NIOSH investigation [5] was spiked on tared PTFE filters, allowed to dry at least overnight, and extracted using benzene. The results are summarized in the table below.

Spiking level (mg)*	Total Particulates		Benzene-Soluble Fraction	
	Recovery (%)	S_r	Recovery (%)	S_r
1.85	102	5.97	97.9	0.738
1.17	103	3.98	98.8	2.02
0.62	94.0	5.85	94.8	1.85
0.23	91.6	3.50	96.9	6.10
0.12	82.1	3.91	80.9	9.54
0.058	110	16.4	92.1	13.5
0.025	105	11.4	73.1	17.4

*Six replicates per level

The pooled relative standard deviation ($\bar{S}_r$) for the total particulates was 4.8% at loadings greater than or equal to 0.10 mg per sample. For the benzene-soluble fraction, the pooled relative standard deviation was 6.1% at loadings greater than or equal to 0.21 mg per sample.

The accuracy criterion is based on determining the range of analyte loadings and the analyte loading on the sample media that will give at least 95% confidence of obtaining a measurement of the analyte that is within 25% of the true value 95% of the time. Since no independent method for determining the total particulate concentration is available, no estimate of the bias for the total particulate data was made; therefore, the maximum allowable bias was calculated at which the accuracy criterion could still be met. Based on the spiking data, if the total particulate loading was greater than or equal to 0.10 mg per filter, the measurement determination will be within 25% of the true value 95% of the time if the true bias is less than 10.0%. The bias for the benzene-soluble fraction was negative (see the data above), and since the bias for the benzene-soluble fraction varied little, the bias was pooled over the spiking range of 1.85 to 0.20 mg per filter. It was determined that the 25% accuracy criterion was met if the benzene-soluble fraction was greater than or equal to 0.20 mg per filter.

The limit of detection (LOD) and the limit of quantitation (LOQ) were determined using field blanks [6]. The LOD is equal to three times the standard deviation of the field blank weight differences (post-sampling weight - tare weight), and the LOQ is equal to ten times the standard deviation of the field blank weight differences. Field sample values should be compared to the LOD and LOQ values only after the field samples have been blank corrected.

The standard deviations of the field blank weights were 0.013 mg per sample for total particulates and 0.014 mg per sample for the benzene-soluble fraction. Therefore, the LOD and LOQ for total particulates were 0.04 and 0.13 mg per sample, respectively. The LOD and LOQ for the benzene-soluble fraction were 0.04 and 0.14 mg per sample, respectively. These LOD and LOQ values should only be compared to blank corrected field sample data.

A user check of the method was performed in which tared PTFE filters were spiked with 1.08, 0.392, or 0.216 mg of pyrene per filter and then analyzed by an independent chemist [6]. A mean total particulate recovery of 103% (S_r = 5.85%) was obtained, and the mean benzene-soluble fraction recovery was 109% (S_r = 9.91%). Correlation of benzene-soluble mass with total particulate was linear, with R^2 = 0.994, and the mean ratio of benzene-soluble mass to total particulate was 106% (S_r = 7.80%).

In other experiments, three of 60 field blanks (three sets of 20 field blanks each) had a significantly higher than expected benzene-soluble fraction when compared with the other field blanks [6]. This event had two undesirable consequences: (1) Because the average weight of the field blanks was increased, the field samples were over corrected, and (2) the standard deviation of the field blank weights was increased resulting in higher LOD and LOQ values. For example, if the set of twenty field blanks with one high result is randomly assigned to groups of three (repeatedly), the standard deviation of the groups with the high result could exceed the standard deviation of the other groups by more than 1.6 times. Since this event also may occur with field samples, these elevated results were not excluded when the data were evaluated. Although these events were observed with a syringe type clarification unit and not the recommended clarification unit, the cause of this event was not determined. Therefore, it is important to collect as many field blanks as is reasonable (five blanks per day); also, it may be advisable to establish a monitoring program to track the occurrence of elevated field blanks and, if possible, to identify and eliminate the cause(s).

In another experiment, the recommended clarification unit (PTFE-treated reservoir and a PTFE filter) was evaluated along with three syringe type clarification units [6]. The recommended clarification unit gave lower average extractable material than the syringe type clarification units; also, the recommended clarification unit did not release increasing amounts of extractable material upon prolonged contract with solvent. Prerinsing the recommended clarification unit appeared to lower the average amount of extractable material. Additionally, the recommended clarification unit eliminated the need for using a glass syringe and was more convenient to use than the syringe type clarification units.

In a preliminary asphalt fume spiking experiment, benzene and methylene chloride were evaluated as extraction solvents [6]. Asphalt fume [5] was spiked on tared PTFE filter media at the following concentrations: 3.38, 0.68, 0.14, and 0.034 mg per filter. Benzene gave recoveries greater than 100% for all concentrations of asphalt fume spiked on PTFE filters. While methylene chloride gave recoveries greater than 96% for the two highest levels spiked, at the two lower levels the recoveries were less than 67%.

REFERENCES:

[1] NIOSH [1994]. Particulate not otherwise regulated, total: Method 0500. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[2] NIOSH [1998]. Polycyclic aromatic compounds: Method 5800. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.

[3] NIOSH [1998]. Benzothiazole in asphalt fume: Method 2550. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed., 2nd Supplement Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No.98-119.

[4] NIOSH [1992]. NIOSH recommendations for occupational safety and health, compendium of policy documents and statements. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

[5] Sivak A, Niemeier R, Lynch D, Beltis K, Simon S, Salomon R, Latta R, Belinky B, Menzies K, Lunsford A, Cooper C, Ross A, Bruner R [1997]. Skin carcinogenicity of condensed asphalt roofing fumes and their fractions following dermal application to mice. Cancer Letters 117:113-123.

[6] NIOSH [1998]. NIOSH backup data report for total particulate and benzene-soluble fraction (asphalt fume), NIOSH Method 5042 (unpublished).

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BENZOTHIAZOLE IN ASPHALT FUME 2550

C_7H_5SN MW: 135.19 CAS: 95-16-9 RTECS: DL0875000

METHOD: 2550, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: liquid; d 1.246 g/mL @ 20 °C; MP 2 °C; BP 231 °C; vp 4.5 kPa (34.0 mm Hg) @ 131 °C; vapor density 4.7 (air = 1)

SYNONYMS: Benzosulfonazole; 1-Thia-3-azaindene

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (2-µm, 37-mm, PTFE + XAD-2, 100/50 mg)

FLOW RATE: 1.0 to 2.0 L/min

VOL-MIN: 480 L
-MAX: 960 L

SHIPMENT: Ship samples with refrigerant packs

SAMPLE STABILITY: ca. 28 days @ 4 °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, SULFUR CHEMILUMINESCENCE DETECTOR

ANALYTE: benzothiazole

DESORPTION: 4 mL hexane; stand 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 275 °C
-DETECTOR: 1000 °C
-COLUMN: 50 °C, 1.0 min; 15 °C/min to 225 °C, hold 15 min; 6 °C/min to 320 °C

CARRIER GAS: Helium @ 2.4 mL/min (splitless)

COLUMN: capillary, 30 m, 0.32-mm ID, 1.0-µm film, 100% dimethyl polysiloxane, Rtx-1® or equivalent

CALIBRATION: solutions of benzothiazole in hexane

RANGE: 1.0 to 250 µg per sample

ESTIMATED LOD: 0.30 µg per sample (instrumental) [1]

PRECISION ($\hat{S}_r$): 0.5 @ 1.0 to 20 µg per sample

APPLICABILITY: The working range is 0.002 to 0.5 mg/m^3 for a 480-L air sample. This method was developed to determine benzothiazole in the presence of other sulfur compounds in asphalt fume samples (see Figure 1). This method may be used in conjunction with method 5800, Polycyclic Aromatic Compounds, Total [2]. An aliquot of the desorbed sample from method 5800 can be analyzed for benzothiazole by this method, since the sampler and desorbing solvent are the same.

INTERFERENCES: None identified; however, compounds with a similar retention time may interfere. Positive identification may be confirmed by dual column chromatography using an appropriate alternative capillary column. Identification can also be confirmed by mass spectrometry.

OTHER METHODS: None identified.

REAGENTS:

1. Hexane,* chromatographic grade.
2. Benzothiazole,* reagent grade.
3. Benzothiazole primary stock solution, 10 mg/mL: Dissolve 1.0 g benzothiazole in 100 mL of hexane in a volumetric flask. (Correct for purity of standard.)
4. Benzothiazole secondary stock solution, 1 mg/mL: Dilute 1.0 mL of primary stock with hexane to 10 mL in a volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler
   a. Prefilter: PTFE-laminate membrane filter, 2-µm pore size, 37-mm, (Zefluor, Gelman Sciences, Ann Arbor, MI, 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: If sampling in bright sunlight, use opaque or foil-wrapped cassettes to prevent photodegradation.
   b. Solid sorbent: glass tube, 100 mm, 10-mm OD, sealed ends with plastic caps, containing two sections of washed XAD-2 resin (front = 100 mg; back = 50 mg), separated and retained with glass wool plugs (Supelco ORBO-42 Large or equivalent), connected to filter with minimum length PVC tubing.
2. Personal sampling pump capable of operating for 8 h at 2 L/min., with flexible connecting tubing.
3. Gas Chromatograph, autosampler, nitrogen chemiluminescence detector (Antek Model 704E, or equivalent), integrator, and column (Restek Rtx-1®, or equivalent)(page 2550-1)
4. Vials, glass, PTFE-lined screw caps, 5-mL.
5. Vials, Autoinjector, glass with PTFE-lined crimp caps, 1.8-mL.
6. Forceps.
7. Syringes, 5-, 10-µL, other sizes if needed.
8. Volumetric flasks, 10-mL, 100-mL.
9. Aluminum foil.
10. Refrigerant packs.
11. ORBO-43 sampling tubes (Supelco)

SPECIAL PRECAUTIONS: Hexane is highly flammable. Benzothiazole has an irritating odor and is highly toxic by ingestion. Handle in a well ventilated hood and wear protective clothing.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate of 1.0 to 2.0 L/min for a total volume of 480 to 960 L.
3. Pack securely for shipment in refrigerant packs.
4. Store samples at 4°C upon receipt at the laboratory.

SAMPLE PREPARATION:

5. Remove samples from refrigerator and allow to equilibrate to ambient temperature. Prefilters may be analyzed for benzothiazole adsorbed on dust, or discarded.

6. If prefilters are to be analyzed, extract as follows:
   a. Remove the filters from cassettes with forceps and transfer to 5-mL, or larger, vials.
   b. Add 4 mL of hexane.
   c. Allow the samples to stand a minimum of 30 minutes with occasional agitation.
7. Extract solid sorbent.
   a. Transfer front glass wool plug and front sorbent section to a 5-mL, or larger, sample vial.
   b. Transfer the back sorbent section and remaining glass wool plugs to a separate 5-mL, or larger, sample vial.
   c. Add 4 mL of hexane to each vial, cap, and agitate.
   d. Let stand for a minimum of 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six standards to cover the concentration range of the samples.
   a. Add known amounts of the standard stock solution to 10-mL volumetric flasks and bring to volume with hexane.
   b. Analyze with samples and blanks (steps 11 & 12).
   c. Prepare calibration graph (peak area vs. µg benzothiazole).
9. Determine desorption efficiency (DE) in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   NOTE: The sorbent bed of ORBO-42L tubes used for sampling is not always uniform in depth; therefore, ORBO-43 sampling tubes are recommended for determining DE (see EVALUATION OF METHOD).
   a. Inject a known amount (1 to 20 µL) of calibration stock solution, or a serial dilution thereof, directly onto the front sorbent section with a microliter syringe.
   b. Cap the tube and allow to stand overnight.
   c. Desorb (step 7) and analyze together with calibration standards (steps 11 & 12).
   d. Prepare a graph of DE vs. µg benzothiazole 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 2550-1. Inject sample manually using solvent flush technique or with autosampler.
    NOTE: If peak height is above the linear range of the calibration standards, dilute the sample with hexane, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area of benzothiazole peak and determine µg per sample from calibration graph.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of benzothiazole found in the sample tube 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 benzothiazole in the air volume sampled, V(L):
    NOTE: µg/L ≡ mg/m^3

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

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD

This method has been used to analyze field generated air samples from several NIOSH asphalt paving studies (Figure 1). It was not evaluated with laboratory generated air samples. All of the desorption efficiency, recovery and storage studies have been performed with laboratory spiked sorbent tubes.

Sampling was done with ORBO-42 Large sampling tubes, because the 10-mm OD allowed for a reduced pressure drop, which enabled 8-h samples to be collected at 2 L/min. Benzothiazole in the vapor state is adsorbed on the washed XAD-2 of the ORBO-42 Large sampling tube. However, samples taken during field studies where high particulate matter was present have shown some benzothiazole on the Teflon® prefilters. This is most likely caused by the entrapment or adsorption of the benzothiazole on the particulate matter. Spiking studies of fresh Teflon filters have shown that benzothiazole is not retained by the filter. It is, therefore, suggested that in those sampling circumstances where particulate matter will be encountered during the sampling process that a Teflon pre-filter be used and analyzed in the same manner as the sampling tube media beds. The quantity of benzothiazole determined on the filter can then be added to the quantity found on the sampling tube to give a total benzothiazole mass for the sample.

Because of the larger diameter of the ORBO-42 Large sampling tube, the front sorbent bed is not always uniform in depth, thus making laboratory spiking of the sampling tubes difficult and recoveries variable. For this reason, ORBO-43 tubes, which contain the same amount of XAD-2 resin, but have a smaller tube diameter (8-mm OD) and a more uniform resin bed, were utilized to determine extraction efficiency, recovery, and storage stability of benzothiazole. Extraction efficiency of the benzothiazole from the ORBO-43 sorbent tubes is typically 89 to 96% (Figure 2). A thirty day storage study at 4 °C for 20-µg samples showed a recovery of 89.1% based on day 1 data [1]. This falls slightly below the NIOSH stability criterion of ≥ 90% recovery.

REFERENCES:

[1] Jaycox LB [1997]. Backup Data Report for Method 2550, Benzothiazole in asphalt fume, (unpublished), NIOSH, DPSE.

[2] NIOSH [1998]. Polycyclic aromatic compounds: Method 5800. In: Eller PM, Cassinelli ME. Eds. NIOSH Manual of Analytical Methods, 4 th ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-

METHOD WRITTEN BY: Larry B. Jaycox, Ph.D. NIOSH/DPSE

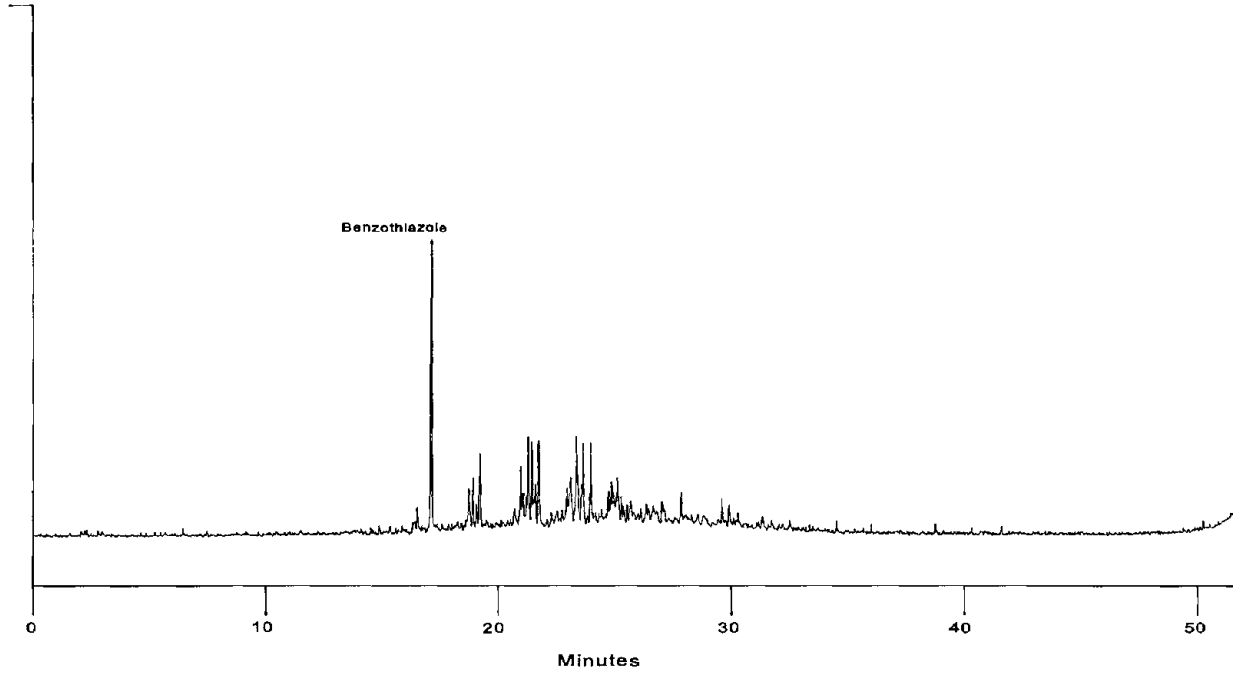


FIGURE 1: This is a chromatogram from the analysis of benzothiazole in an asphalt fume sample. The major peak at approximately 18 minutes is benzothiazole. In many cases, the sample matrix may not be this complex and the chromatographic conditions can be adjusted to suit the analysis needs.

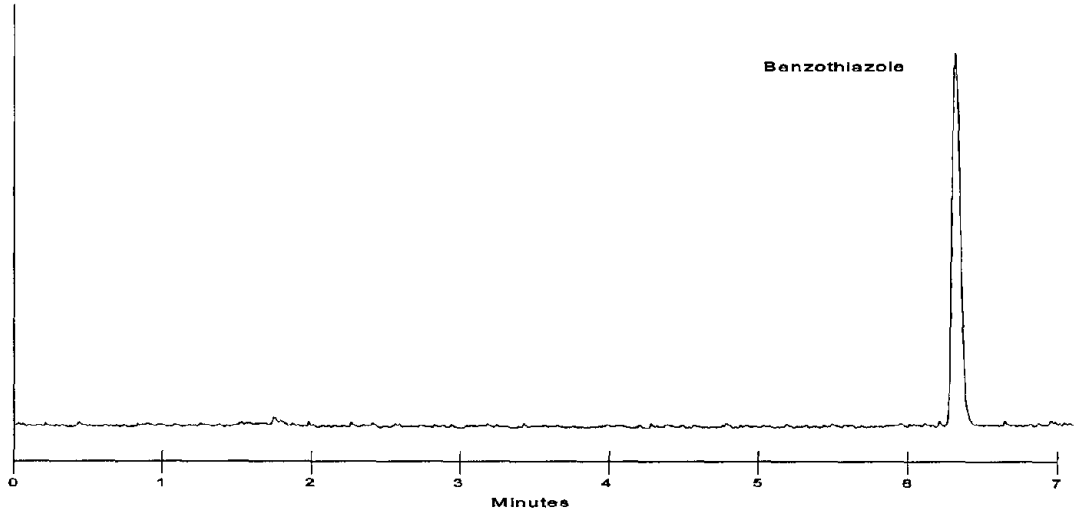


FIGURE 2: The chromatogram shown here is a typical chromatogram from the analysis of a desorbed laboratory spiked ORBO-43 sampling tube. The chromatographic conditions have been altered to give a shorter retention time for the benzothiazole because there are no other interfering compounds present.

BIOAEROSOL SAMPLING (Indoor Air) 0800

Culturable organisms: bacteria, fungi, thermophilic actinomycetes

METHOD: 0800, Issue 1	EVALUATION: N/A	Issue 1: 15 January 1998

PURPOSE: Identification of culturable microorganisms and assessment of possible proliferation and dissemination of bacteria or fungi from building reservoirs.

FIELD EQUIPMENT:

1. Samplers:
   a. Andersen 2-stage cascade impactor, or equivalent, for fungi and mesophilic bacteria.
   b. Andersen N-6 single-stage sampler, or equivalent, for thermophilic actinomycetes.
2. Sampling media, in plates prepared according to sampler manufacturer's recommendations:
   a. Malt extract agar (MEA) for fungi.
   b. Trypticase soy agar (TSA) for mesophilic bacteria and thermophilic actinomycetes.
   NOTE: Other media may be used, if appropriate, e.g., dichloran glycerol agar (DG18) for xerophilic molds, R2A agar for heterotrophic bacteria, and rose bengal agar for slow-growing fungi such as *Stachybotrys*.
3. Sampling pump capable of meeting sampler manufacturer's flow specification (e.g., 28.3 L/min), with flexible connecting tubing.
4. Cotton gauze pad, e.g., 4" x 4".
5. Rubbing alcohol, 70% isopropanol.
6. Refrigerant packs, if necessary for keeping samples cool during shipment.
   NOTE: Keep samples cool, but protect from freezing.

SAMPLING STRATEGY:

1. Select at least three sites, one each to represent complaint area, a noncomplaint area (otherwise as similar as possible to complaint area), and outdoors.
2. In turn at each site, sample simultaneously for fungi, mesophilic bacteria, and thermophilic actinomycetes. Typical sampling time is ten minutes. Before moving to the next site, repeat twice to obtain triplicate, consecutive samples.
3. Load and immediately unload one set of sampling media in each sampler to serve as field blanks.
4. Collect another complete set of samples and blanks on the next day.

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Before each run, carefully and thoroughly wipe each sampler stage with rubbing alcohol. Allow to dry. Make sure air passages are not blocked.
3. Load sampling media into sampler, remove covers from media, and attach sampler to pump with flexible tubing.
   NOTE: Take special care to prevent contamination of media during loading and unloading. Do not touch agar surface.
4. Sample at known preset flow for an accurately known time, e.g., 10 min. (In heavily contaminated areas, a shorter sampling time may be necessary.)
5. Replace covers on sampling media, unload, and pack securely for shipment (plates should be media side up).

SHIPPING: Keep collected samples and blanks cool (not necessarily ice-cold) and ship as quickly as possible to a laboratory for enumeration and identification.

ANALYSIS: Mesophilic bacteria and thermophilic actinomycetes are usually identified to species and fungi usually identified to genus. Interpretation is subjective and based on total numbers and rank order of taxa in complaint area compared with control areas (noncomplaint and outdoors).

METHOD WRITTEN BY: Miriam K. Lonon, Ph.D., NIOSH/DPSE

n-BUTYL MERCAPTAN 2525

$CH_3CH_2CH_2CH_2SH$ MW: 90.19 CAS: 109-79-5 RTECS: EK6300000

METHOD: 2525, Issue 2 **EVALUATION: FULL** **Issue 1: 5 May 1989**
Issue 2: 15 May 1996

OSHA: 0.5 ppm
NIOSH: C 0.5 ppm
ACGIH: 0.5 ppm
(1 ppm = 3.69 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.842 g/mL @ 25 °C; BP 98 °C; VP 4.7 kPa (35 mm Hg; 4.6% v/v) @ 20 °C

SYNONYMS: butanethiol; 1-butanethiol; 1-mercaptobutane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Chromosorb 104, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L
-MAX: 4 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 17 to 74 mg/m³ [1] (1.5-L samples)

BIAS: - 2% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 14.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE

ANALYTE: *n*-butyl mercaptan

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 150 °C
-DETECTOR: 200 °C
-COLUMN: 140 °C

COLUMN: glass, 1.2 m x 2-mm ID, packed with 60/80 mesh Chromosorb 104

CARRIER GAS: N_2, 50 mL/min

CALIBRATION: standard solutions of *n*-butylmercaptan in acetone

RANGE: 20 to 200 µg per sample [2]

ESTIMATED LOD: 3 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.015 @ 30 to 110 µg per sample [1]

APPLICABILITY: The working range is 5 to 50 mg/m³ (1.4 to 14 ppm) maximum sample size is based on the capacity of the Chromosorb 104 to collect vapors of *n*-butyl mercaptan in air at high relative humidity (94%) [1]. Smaller concentrations may be determined if desorption efficiency is adequate.

INTERFERENCES: None identified.

OTHER METHODS: This revises NIOSH Method S350 [2].

REAGENTS:

1. Acetone, chromatographic quality.
2. *n*-Hexane, reagent grade.
3. *n*-Butyl mercaptan.*
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.
8. Calibration stock solution, 13.47 mg/mL. Add 160 µL of pure *n*-butyl mercaptan to acetone and dilute to 10 mL. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps containing two sections of 60/80 mesh Chromosorb 104 (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. Pressure drop across the tube at 0.025 L/min airflow must be less than 3.4 kPa (25 mm Hg). The sampling tubes are commercially available (SKC, Inc. Cat. # 226-109).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector with sulfur filter, integrator, and column (page 2525-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL (readable to 0.1 µL) and 50-µL.
6. Flasks, volumetric, 10-mL.
7. Pipet, 1.0-mL.
8. File, triangular.

SPECIAL PRECAUTIONS: Store *n*-butyl mercaptan away from oxidizing and flammable materials [3,4]. The analyte is highly flammable and irritating to the eyes and mucous membranes. Work 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. 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. 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 covering the range 0.3 to 20 µg/mL.
   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 squared vs. µg *n*-butyl mercaptan).
9. Determine desorption efficiency (DE) at least once for the batch of Chromosorb 104 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 calibration stock solution (2 to 20 µL) containing a known amount of *n*-butyl mercaptan 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 *n*-butyl mercaptan 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 2525-1. Inject sample aliquot manually using solvent flush technique. Vent the acetone peak so that it will not extinguish the flame in the detector.
    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, µg (corrected for DE) of *n*-butyl mercaptan 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.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of *n*-butyl mercaptan 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 17 to 74 mg/m ^{3} at 22 °C and 759 mm Hg using a 1.5-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.062 with an average recovery of 0.98. The concentration of *n*-butyl mercaptan was independently determined from the syringe delivery rate and dilution flow rates. Desorption efficiency was 0.90 in the range 28 to 110 µg per sample. The breakthrough volume (effluent concentration = 5% of influent concentration) was 4.0 L; this was determined by sampling humid air (94% relative humidity), containing 74 mg/m ^{3} *n*-butyl mercaptan at 0.023 L/min.

REFERENCES:

[1] NIOSH [1977]. Backup data report for S350, prepared under NIOSH Contract 210-76-0123.
[2] NIOSH [1978]. *n*-Butyl mercaptan: Method S350. In: Taylor DG, Ed. NIOSH manual of analytical methods, 2nd. ed., V. 4. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No.78-175.
[3] General Electric [1982]. Material safety data sheet, #504 Butyl Mercaptan, General Electric Co., Schenectady, N.Y. 12305.
[4] NIOSH [1981]. NIOSH/OSHA Occupational health guidelines for occupational hazards. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE. Method S350 was originally validated under NIOSH Contract 210-76-0123.

CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING) 5602

ANALYTES: Figure 1 Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5602, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

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

PROPERTIES: Table 1

NAMES:	Alachlor	Atrazine	2,4-D acid	2,4-D, 2-ethylhexyl ester
	Cyanazine	Metolachlor	Simazine	2,4-D, 2-butoxyethyl ester

SAMPLING

SAMPLER: FILTER/SOLID SORBENT TUBE (OVS tube: 11-mm quartz filter; XAD-2)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 12 L
-MAX: 480 L

SHIPMENT: routine

SAMPLE STABILITY: at least 30 days @ 5 °C
at least 10 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 3

ACCURACY: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD)

ANALYTE: Table 1

EXTRACTION: 2 mL 10% methanol/90% methyl t-butyl ether (with diazomethane), shaker > 1 h

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 270 °C
-DETECTOR: 300 °C
-COLUMN: 90 °C, 1 min; 35 °C/min to 160 °C; 3 °C/min to 230 °C; hold 9 min.

CARRIER GAS: He at 1 mL/min

COLUMN: capillary, fused silica, 30 m X 0.25-mm ID, 0.25-µm film, 50% phenyl, 50% methyl silicone, DB-17 or equivalent. See Table 2.

CALIBRATION: standard solutions of herbicides in methanol/ methyl t-butyl ether (10:90)

RANGE: Table 3

ESTIMATED LOD: Table 3

PRECISION ($\hat{S}_r$): Table 3

APPLICABILITY: The working ranges, listed in Table 3, cover ranges from the LOQ to approximately 30 X LOQ. This method may be applicable to the determination of many other thermally stable organonitrogen, aryl and alkyl acidic, and phenolic pesticides after evaluation. Determination of cyanazine is semiquantitative using this method.

INTERFERENCES: Because of the great sensitivity of the ECD, there are many potential interferences. Those observed are plasticizers (e.g., dibutyl phthalate), methylated fatty acids (negative response), phenols, antioxidants, and other additives (e.g., BHT) , any volatile or semivolatile halogenated or nitrated organic, organophosphorous compounds, and other pesticides. Agricultural spray additives, such as solvents, emulsifiers, wetting agents, breakdown products, and fertilizers (e.g., fatty acids and urea), can present serious interferences. Second-column confirmation is very desirable (See Table 3). The background levels of different lots of OVS tubes vary widely and may interfere at the lower levels.

OTHER METHODS: This method replaces previously related pesticide methods. Alternate methods for the determination of 2,4-D in air are S279 [2] and 5001 [3]. The OVS tube is similar in concept to the device of Hill and Arnold [4], but offers greater convenience and lower flow resistance. Other methods allowing simultaneous determination of organonitrogen and acid compounds and their esters are unknown.

REAGENTS:

1. Analytes listed in Table 1.
2. Methanol, pesticide analytical grade.
3. Methyl t-butyl ether, pesticide analytical grade.
4. Extraction solvent. Add 10 mL of methanol to a 100-mL volumetric flask. Dilute to volume with methyl t-butyl ether.
5. Diazald® (N-methyl-N-nitroso-*p*-toluenesulfonamide.)*
6. Silicic Acid, 100-mesh.
7. Diazomethane* derivatizing reagent. (See APPENDIX)
8. Herbicide stock solutions. Prepare individual standard stock solutions of each herbicide of interest in extraction solvent.
   NOTE: All herbicides in Table 1 were found to be soluble to at least 1 mg/mL, except simazine, which is soluble to 0.5 mg/mL.
9. Calibration stock solution. Dilute the appropriate volume of herbicide stock solution to a known volume with extraction solvent.
   NOTE: Spiking solutions may contain more than one analyte.
10. Purified gases: helium, 5% methane in argon, or nitrogen.

*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 OD x 25 mm long tube (Figure 2). The enlarged part of the tube contains a 270-mg front section of 20/60 mesh XAD-2 sorbent held in place by a 11-mm quartz fiber filter and polytetrafluoroethylene (PTFE) retaining ring at inlet and a small plug of polyurethane foam at the back end. The back section consists of 140-mg XAD-2 sorbent held in place by a long plug of polyurethane foam. Tubes commercially available (SKC, Inc. Cat. No. 226-58).
2. Personal sampling pump, 0.2 to 1 L/min with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator, and column (Table 2).
4. Vials, glass, 4-, 2-, and 0.1-mL limited-volume vials with PTFE-lined caps.
5. Syringes, 1- and 5-mL; 10-, 50-, and 100-µL as needed.
6. Volumetric flasks, 2-, 5-, 10-, 25-, 50-, and 100-mL for working standard preparation and solutions.
7. Forceps.
8. PTFE syringe filters, 0.45-µm pore size (Gelman Sciences or equivalent).
9. Syringe, luer lock, 1-, 2.5-, or 5-mL, for sample filtering.
10. Platform shaker

SPECIAL PRECAUTIONS: Diazomethane has been cited as a carcinogen. It is extremely toxic and highly irritating. Diazomethane may explode under some conditions. Do not heat above 90 °C. Avoid rough surfaces: fire-polish glass tubing, or use Teflon®. Do not expose solutions to strong light. Keep dilute solutions at 0 °C. Prepare in a hood [5]. Avoid skin contact with *Diazald®* and herbicides. Avoid skin contact and open flame with solvents. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to the personal sampling pump with flexible tubing. The sampler should be placed vertically with the large end down.
3. Sample at a known flow rate between 0.2 and 1 L/min for a total sample size of 12 to 480 L.
4. Cap both ends of the sampler with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end of sampler and remove PTFE retainer ring; carefully transfer filter and front XAD-2 resin section to a 4-mL vial. Transfer the short polyurethane foam plug along with the back-up XAD-2 resin bed to a second 4-mL vial. Discard back-up plug.
6. Add 2 mL of diazomethane derivatizing reagent to each vial using a 5-mL syringe or 2-mL pipette; cap each vial. Mix by rotating at 5 to 10 RPM on a platform shaker for a minimum of one hour.

7. Add approximately 10 mg of silicic acid to the solution, mix, and allow to stand for one hour.
8. Filter an aliquot through a 0.45-µm PTFE filter into a 2-mL GC vial or limited volume GC vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to the diazomethane derivatizing reagent in a volumetric flask and let stand for 1 hour. Include a calibration blank of unspiked diazomethane derivatizing reagent solution.
   b. Add 10 mg silicic acid to each standard vial, and let stand for an additional hour.
   c. Filter through a 0.45-µm syringe filter into a GC vial.
   d. Analyze together with field samples and blanks (steps 12 and 13).
   e. Prepare calibration graph (peak area or height vs. µg analyte).
10. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling. Independently prepared quality control herbicide solutions in extraction solvent must be prepared at concentrations within the analytical range. Prepare three samplers at each of six levels plus three media blanks.
    a. Remove and discard back sorbent sections of samplers and media blanks.
    b. Remove cap from large end of sampler tube. Pull up PTFE retainer ring to prevent trapping of spiking solution under ring. Apply a known amount of calibration stock solution to face of quartz fiber filter. Pull air through for one hour at 0.2 to 1 L/min.
    c. Desorb the samples (steps 5 through 8) and analyze together with working standards and blanks (steps 12 and 13).
    d. Prepare a graph of DE vs. µg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 2.. Inject 2-µL aliquot manually using solvent flush technique or with autosampler. See Table 4 for retention times of selected analytes.
    NOTE: If peak height is greater than the range of the working standards, dilute with extraction solvent and reanalyze. Apply the appropriate dilution factor in calculations.
13. Measure peak height or area of analyte.

CALCULATIONS:

14. Determine the mass, 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 from the calibration graph.
    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):

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

NOTE: µg/mL ≡ mg/m^3

CONFIRMATION:

Whenever the identity of an analyte is uncertain, confirmation may be achieved by analysis on a column of different polarity. If primary analysis was performed using a nonpolar or weakly polar column *(e.g.*, DB-1 or DB-5) confirmation should be accomplished by reanalysis on a polar column (*e.g.*, DB-17 or DB-1701). See Table 4 for approximate retention times for each column type. For positive identification of high-level analytes (1 to 10 µg/mL or greater), GC/MS may be used. Figure 4 shows a typical chromatogram using a DB-17 column. Figure 5 shows a typical chromatogram using a DB-5 column. Table 5 gives notes on the analytical characteristics of the chlorinated organonitrogen and acid herbicides.

EVALUATION OF METHOD:

The method was evaluated over the ranges listed in Table 3. These ranges represent 3 x LOQ to 30 x LOQ for each of the compounds. Table 3 also lists the measurement precision ($\hat{S}_r$), overall sampling and measurement precision ($\hat{S}_{rT}$), bias, and accuracy for the compounds evaluated using this method. The analytical conditions used in the evaluation are in Table 4 with the DB-5ms column. The front filter of each sample tube was fortified with an aliquot of a solution containing the 8 herbicides. Air was then drawn through the tubes at 1 L/min for 8 h (480 L total volume)at 30 °C. One set of samplers was tested at 15% relative humidity (RH) and the other set was tested at 80% RH. All samples were stored at 4 °C. Humidity did not affect the analyte recoveries from the samplers. A long-term storage study also was done. Samples were loaded at the 10 x LOQ level and 480 L of 80% RH air was pulled through the samples. Average recovery for individual pesticides on Day 1 was 110 to 120% with cyanazine having a high recovery of 150% and 2,4-D acid having a recovery of 91%. Day 30 storage samples had a range of recoveries from 70 to 82% based on Day 1, with 2,4-D acid and simazine having recoveries of 104% and 88%, respectively. Day 50 samples had average recoveries of 80% of Day 1, with 2,4-D acid having 101 % recovery, and cyanazine having a 69% recovery.

REFERENCES:

[1] NIOSH [1995]. Back-up data report for chlorinated organonitrogen and carboxylic acid herbicides. Prepared under NIOSH Contract 200-88-2618 (unpublished).

[2] NIOSH [1977]. 2,4-D: Method S279. In: Taylor DG, ed. NIOSH Manual of Analytical Methods (NMAM), 2nd ed., v. 5. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 77-157C.

[3] NIOSH [1984]. 2,4-D and 2,4,5-T: Method 5001. In: Eller PM, ed. NIOSH Manual of Analytical Methods (NMAM), 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100

[4] Hill RH Jr, Arnold JE [1979]. A personal air sampler for pesticides. Arch Environ Contam Toxicol 8:621-628.

[5] Black TH [1983]. The preparation and reactions of diazomethane. Aldrichimica Acta 16(1).

METHOD WRITTEN BY:

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APPENDIX - DIAZOMETHANE DERIVATIZING REAGENT

The diazomethane generator (see Figure 3) consists of two 40-mL test tubes, each fitted with a two-hole rubber stopper. In one hole of the first test tube, a glass tube is placed which extends to within one centimeter of the bottom. The other end of the glass tube is connected to a supply of nitrogen. A short piece of Teflon® tubing is placed in the second hole and is directed to the bottom of the second tube through the second stopper. A third piece of Teflon® tubing leads from the second tube into the receiving flask. The first test tube contains a small quantity of diethyl ether. Nitrogen bubbled through the ether is led to the second tube containing 3 mL of a 37% KOH-in-water solution and 4 mL *Diazald*® Reagent," which is prepared by dissolving 10 g of *Diazald*® in 100 mL of 1:1 Ethyl ether: Carbitol. Diethyl ether vapor in the first tube prevents loss of diethyl ether from the second tube by evaporation. Diethyl ether stabilizes diazomethane through adduct formation. The resulting diazomethane gas is swept by a flow of nitrogen gas into a flask of chilled (0 °C) methyl t-butyl ether/methanol extraction solvent (maximum volume, 500 mL).

NOTE: KOH solution (37% w/v) will become weaker over time owing to adsorption of atmospheric carbon dioxide. Under such circumstances, diazomethane generation will be considerably slower.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name / Synonym	Empirical Formula	Molecular Weight	Physical Properties	Solubility in Water (mg/L)	LD50 mg/kg	TWA (mg/m3)
Alachlor 2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide CAS #15972-60-8 RTECS AE1225000	$C_{14}H_{20}ClNO_2$	269.77	Colorless crystals; d 1.133 g/mL@ 25°C; MP 39.5-41.5°C; VP 0.0029 Pa (2.2 x 10^{-5} mm Hg) @ 25°C	140 @23°C	1200	
Atrazine 6-Chloro-N^2-ethyl-N-isopropyl-1,3,5-triazine-2,4-diamine CAS # 1912-24-9 RTECS XY5600000	$C_8H_{14}ClN_5$	215.68	Colorless crystals; MP 173-175°C; VP 4 x 10^{-5} Pa (3.0 x 10^{-7} mm Hg) @ 20°C	70 @ 25°C	1780	NIOSH 5 ACGIH 5
Cyanazine 2[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile CAS #21725-46-2 RTECS UG1490000	$C_9H_{13}ClN_6$	240.69	White crystalline solid; MP 167.5-169°C; VP 2.1 x 10^{-7} Pa (1.6 x 10^{-9} mm Hg) @ 20°C	171 @ 25°C	182	
2,4-D acid 2,4-Dichlorophenoxyacetic acid CAS #94-75-7 RTECS AG6825000	$C_8H_6Cl_2O_3$	221.04	White powder; MP 140.5°C; <10^{-5} Pa (<7.5 x 10^{-8} mm Hg) @ 25°C	almost insoluble	375	NIOSH 10 ACGIH 10 OSHA 10
2,4-D, ME 2,4-Dichorophenoxyacetic acid, methyl ester CAS #1928-38-7	$C_9H_8Cl_2O_3$	235.07				
2,4-D, BE 2,4-Dichlorophenoxyacetic, 2-butoxyethyl ester CAS #1929-73-3 RTECS AG7700000	$C_{14}H_{18}Cl_2O_4$	321.20			150	
2,4-D, EH 2,4-2,4-Dichlorophenoxyacetic acid, 2-ethylhexylester CAS #1928-43-4	$C_{16}H_{22}Cl_2O_3$	333.25			300 - 1000	
Metolachlor 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide CAS #51218-45-2 RTECS AN3430000	$C_{15}H_{22}Cl_2NO_2$	283.80	Odorless tan liquid; 0.0017 Pa (1.3 x 10^{-5} mm Hg) @ 20°C	530 @ 20°C	2780	
Simazine 6-Chloro-N,N'-diethyl-1,3,5-trazine-2,4-diamine CAS #122-34-9 RTECS XY5250000	$C_7H_{12}ClN_5$	201.66	Crystals; MP 225 -227°C; 8.1 x 10^{-7} Pa (6.1 x 10^{-7} mm Hg) @ 20°C	3.5 @ 20°C	5000	

TABLE 2. USEFUL GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS [1]

Parameter	Conditions							
Column Parameters:								
Stationary phase[2]	DB-1	DB-5	DB-5ms	DB-17[3]	DB-1701[4]	DB-210[4]	DB-225[4]	DB-WAX
Length (meters)	30	30	30	30	30	30	30	30
I.D. (millimeters)	0.25	0.32	0.32	0.25	0.53	0.32	0.32	0.32
Film thickness (µm)	0.25	0.50	1.00	0.25	1.00	0.25	0.25	0.50
Oven Temperatures:								
Initial temperature (°C)	120	50	90	90	90	140	140	160
Initial temperature hold time (min.)	0	1	1	1	0.5	0	0	0
First temperature ramp (°C/min.)	5	10	35	35	15	3	5	5
First intermediate temperature (°C)			160	160	180			
Second temperature ramp (°C/min.)			5	5	2			
Second intermediate temperature (°C)			200	200	210			
Third temperature ramp (°C/min.)			3	3	10			
Final temperature (°C)	250	290	230	230	235	215	220	250
Final temperature hold time (min.)	4	5	9	9	10	5	15	20
Mobile Phase and Injection conditions:								
Carrier Gas	Helium	Helium	Helium	Helium	Helium	Helium	Helium	Helium
Head pressure (p.s.i.)	10	10	12	12	3.5	10	10	10
Injection volume (µL)	2-4	2-4	2-4	2-4	2	2-4	2-4	2-4
Injection mode	splitless	splitless	splitless	splitless	splitless	splitless	splitless	splitless

(1) Actual column and conditions may vary depending on analyte, interferences, and analytical objectives. The conditions given above correspond to Table 4.

(2) Other types of fused silica capillary columns may also work well.

(3) Column and conditions used for method evaluation. Good column for separation of atrazine and simazine.

(4) Useful columns for separating cyanazine from other listed analytes.

TABLE 3. METHOD EVALUATION

Compound	Range Studied (µg/sample)	Accuracy	Bias	Precision-Measurement $\bar{S}_r$	Precision-Method $\hat{S}_{rT}$	Limit of Detection (µg/sample)
Alachlor	0.5 - 5	±0.139	0.025	0.041	0.0644	0.05
Atrazine	2.5 - 25	±0.154	0.032	0.0487	0.0698	0.2
Cyanazine	0.75 - 7.5	±0.320	0.16	0.0662	0.0830	0.08
2,4-D acid	0.3 - 3	±0.151	0.029	0.0484	0.0696	0.03
2,4-D, BE	0.4 - 4	±0.215	0.057	0.0739	0.0892	0.04
2,4,-D, EH	0.3 - 3	±0.173	0.056	0.0447	0.0671	0.03
Metolachlor	0.5 - 5	±0.135	0.030	0.033	0.0601	0.05
Simazine	2.0 - 20	±0.130	0.0007	0.0438	0.0665	0.2

TABLE 4. APPROXIMATE RETENTION TIMES OF SELECTED CHLORINATED ORGANONITROGEN AND CARBOXYLIC ACID COMPOUNDS[1]

	Compound (by retention time on DB5)	Retention Times in Minutes (Capillary Column by Approximate Increase in Polarity)							
	Capillary Column:	DB-1	DB-5	DB-5ms	DB-17	DB-1701	DB-210	DB-225	DB-WAX
1	**CDAA**		14.37						
2	**2,4-D, ME[2]**			10.13	10.25	12.25			
3	**Dicamba, ME[2]**		16.72						
	2,4-D, iPE[3]		19.20						
5	**Simazine**	12.90	19.42	12.02	12.91	16.52	7.59	16.90	18.62
6	**Atrazine**	12.96	19.50	12.18	12.59	16.34	7.79	15.93	17.17
7	**Propazine**		19.61						
8	**2,4-DB, ME[2]**				14.03				
9	**Metribuzin**	13.89	21.10		17.51		9.72	22.01	23.08
10	**Dimethenamid**		21.13						
11	**Acetochlor**		21.18		14.66				
12	**Alachlor**	14.37	21.44	15.24	15.19	19.78	12.95	17.45	14.95
13	**Cyanazine**	14.97	22.23	17.17	19.99	27.07	19.67	30.00	36.00
14	**Metolachlor**	15.11	22.26	16.96	16.67	22.17	14.85	19.43	15.96
15	**Pendimethalin**		22.98		18.67				
16	**2,4-D, BE[4]**	17.01	23.73	21.46	20.60	26.25	16.79	25.86	20.50
17	**2,4-D, EH[5]**	17.70	24.38	22.73	20.12	26.71	17.17	23.49	18.55

(1) Actual retention times will vary with individual columns and chromatographic conditions. Column conditions are give in Table 2. Data is from Backup Data Report [1].

(2) ME = Methyl ester. Methyl ester formed by reaction of the free acid form with diazomethane.

(3) iPE = Isopropyl ester.

(4) BE = 2-Butoxyethyl ester.

(5) EH = 2-Ethylhexyl ester.

TABLE 5. NOTES ON ANALYTICAL CHARACTERISTICS OF CHLORINATED ORGANONITROGEN AND ACID HERBICIDES

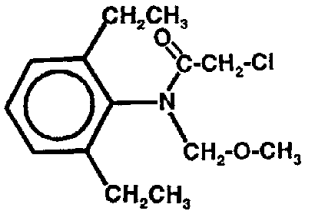
	Compound (alphabetically)	A. CHEMICAL AND PHYSICAL	B. SAMPLE PREPARATION	C. GAS CHROMATOGRAPHIC
1	Alachlor		3	1
2	Atrazine		3	2,3
3	Cyanazine	2	1,3,4	2,4
4	2,4-D, acid		2(methyl ester)	
5	2.4-D, BE	1	1,2,4	5
6	2,4-D, EH	1	2	
7	Metoloachlor		3	1
8	Simazine		3	2,3

A. CHEMICAL AND PHYSICAL
   1. Esters may hydrolyze to the free acid. Free acid may also be present in formulations.
   2. Cyanazine contains a cyano group that appears to adversely affect analytical behavior.

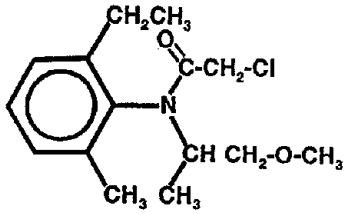
B. SAMPLE PREPARATION
   1. Lower recoveries from glass fiber filters compared to quartz fiber filters.
   2. The esters are not affected by the diazomethane reagent provided the solutions are quenched within one hour with silicic acid. Recoveries for all esters diminish otherwise. This makes possible the speciation of 2,4-D esters and of the free acid in one analysis.
   3. Analytes were not affected by the diazomethane reagent.
   4. Generally high recoveries (120 to 150% or more) from XAD-2 resin compared to liquid standards for reasons unknown. Recoveries appear to be more realistic (80 to 90%) if the filter and the XAD-2 are desorbed and analyzed separately and the analytical results combined.

C. GAS CHROMATOGRAPHIC
   1. Very good peak shape.
   2. Analyte has tendency to tailing on most column phases. Columns and injection ports must be clean and in good condition.
   3. The s-triazines, simazine, atrazine, and propazine, elute very close in that order on the non-polar columns DB1and DB-5. The order is reversed on most polar columns.
   4. Cyanazine is very polar and tends to tail and to elute very late on very polar columns. It has very unpredictable behavior and peak areas either diminish or increase noticeably in subsequent injections. This behavior appears to be associated with the cyano group.
   5. 2,4-D BE behaves similarly to cyanazine, chromatographically (see C.4.), though to a much lesser extent.

ACETANILIDES:

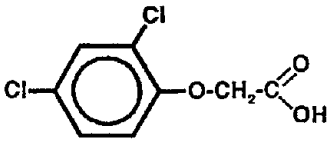


1. ALACHLOR

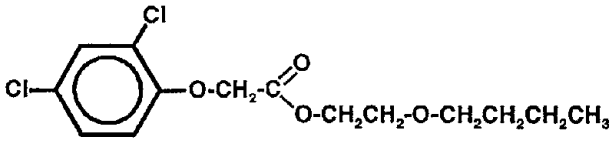


2. METOLACHLOR

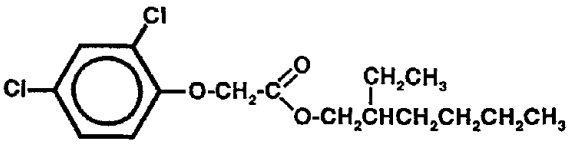
PHENOXYALKANOIC ACID AND ESTERS:



3. 2,4-D, ACID

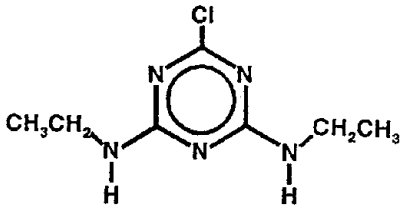


4. 2,4-D, 2-BUTOXYETHYL ESTER

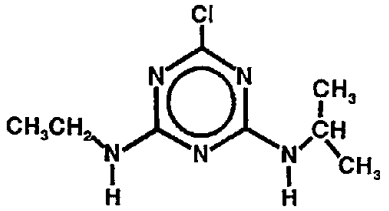


5. 2,4-D, 2-ETHYLHEXYL ESTER

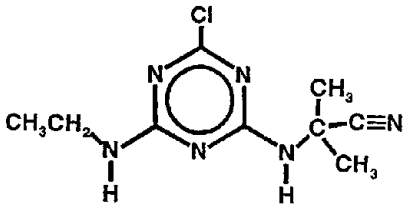
s-TRIAZINES:



6. SIMAZINE



7. ATRAZINE



8. CYANAZINE

STRUCTURES OF CHLORINATED ORGANONITROGEN and ACID HERBICIDES

Figure 1.

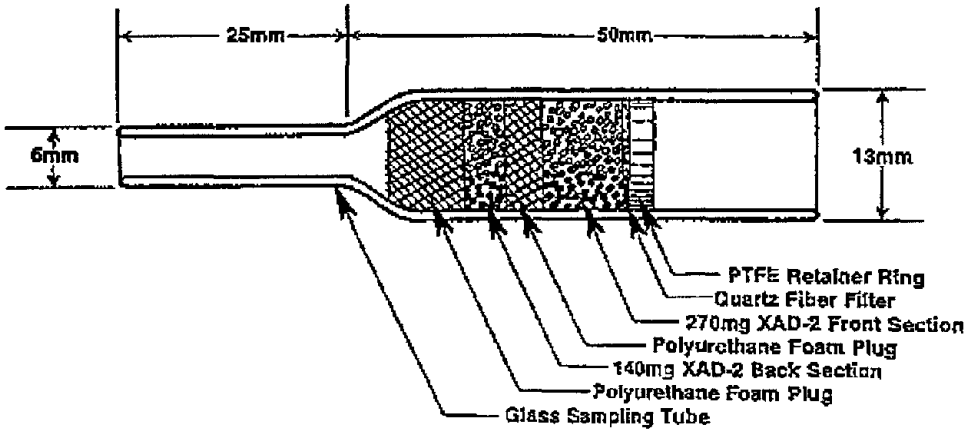


Figure 2. Diagram of OVS Sampler

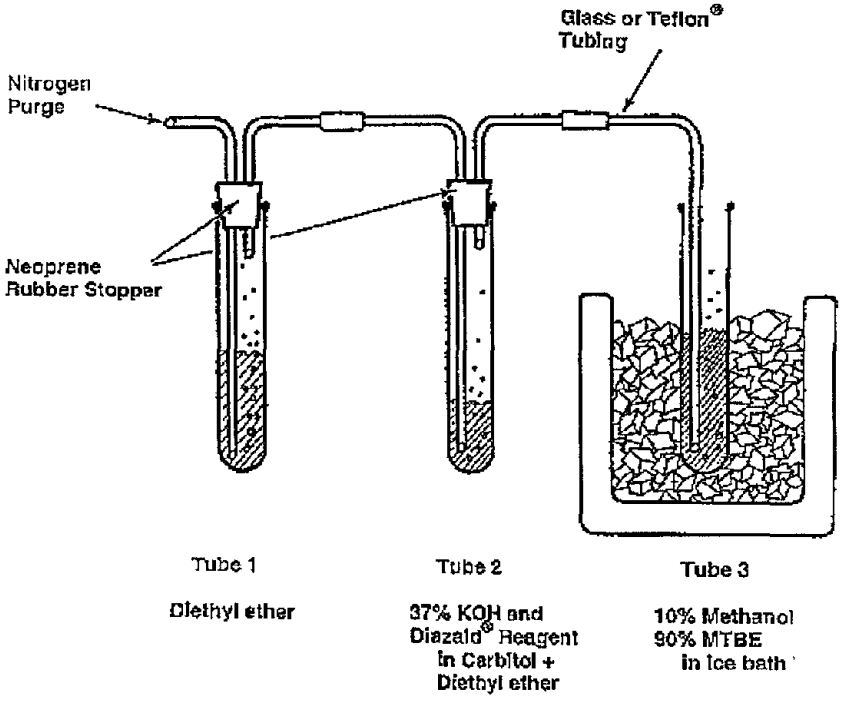


Figure 3. Diazomethane Generator

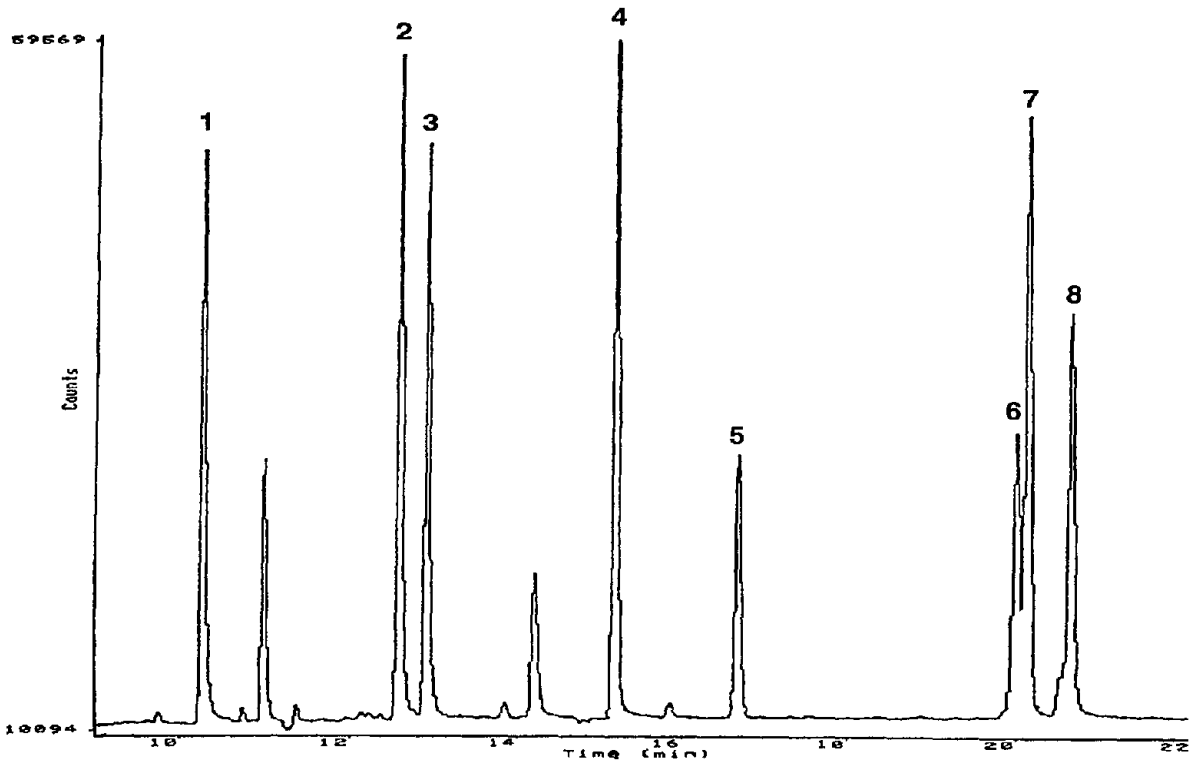


FIGURE 4. TYPICAL CHROMATOGRAM OF CHLORINATED HERBICIDE STANDARDS ON DB-17 COLUMN

COLUMN: DB-17 Fused Silica Capillary Column, 30 meters X 0.25 mm I.D. X 0.25 µm thick film.
TEMPERATURE PROGRAM: 90 °C (1 min. Hold), to 160 °C at 35 °C/min, then to 200 °C at 5 °C/min, then to 230 °C at 3 °C/min, hold for 9 minutes.
INJECTION VOLUME AND MODE: 2- µL, splitless.

ANALYTES:

1. 2,4-D, Methyl ester	0.15 µg/mL
2. Atrazine	4.50 µg/mL
3. Simazine	4.50 µg/mL
4. Alachlor	0.22 µg/mL
5. Metolachlor	0.25 µg/mL
6. Cyanazine	0.25 µg/mL
7. 2,4-D, 2-Ethylhexyl ester	0.22 µg/mL
8. 2,4-D, Butoxyethyl ester	0.22 µg/mL

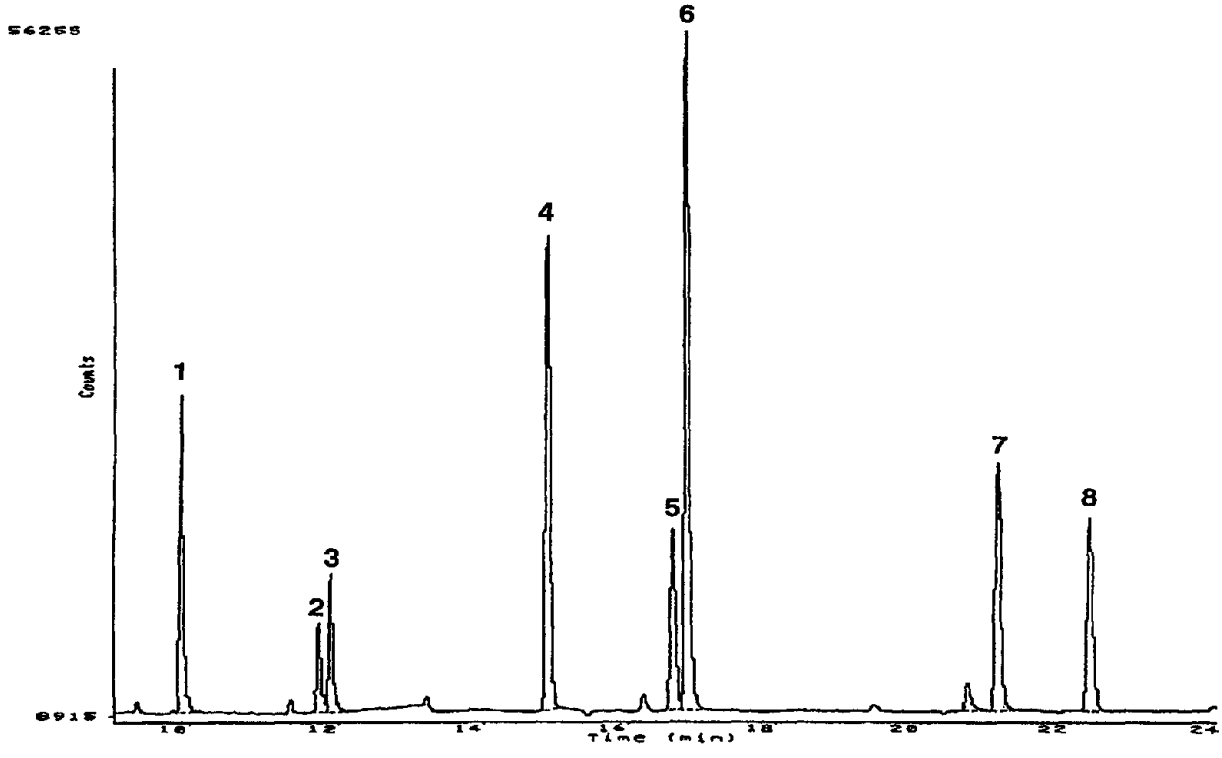


FIGURE 5. TYPICAL CHROMATOGRAM OF CHLORINATED HERBICIDE STANDARDS ON DB-5 COLUMN

COLUMN: DB-5ms Fused Silica Capillary Column, 30 meters X 0.32 mm I.D. X 1.0 µm thick film.
TEMPERATURE PROGRAM: 90 °C (1 min. Hold), to 160 °C at 35 °C/min, then to 200 °C at 5 °C/min, then to 230 °C at 3 °C/min, hold for 9 minutes.
INJECTION VOLUME AND MODE: 2-µL, splitless.

ANALYTES:

1. 2,4-D, Methyl Ester	0.3 µg/mL
2. Simazine	2.0 µg/mL
3. Atrazine	2.5 µg/mL
4. Alachlor	0.5 µg/mL
5. Metolachlor	0.5 µg/mL
6. Cyanazine	0.8 µg/mL
7. 2,4-D, Butoxyethyl ester	0.4 µg/mL
8. 2,4-D, 2-Ethylhexyl ester	0.3 µg/mL

CHLORINATED AND ORGANONITROGEN HERBICIDES (HAND WASH) 9200

ANALYTES: Figure 1 Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 9200, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

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

PROPERTIES: Table 1

NAMES: Alachlor, Atrazine, Simazine, 2,4-D, 2-ethylhexyl ester, Cyanazine, Metolachlor, 2,4-D acid, 2,4-D, 2-butoxyethyl ester

SAMPLING

SAMPLER: POLYETHYLENE BAG
12" x 18", polyethylene bag containing 150 mL isopropanol

SHIPMENT: transfer wash to 250-mL wide-mouthed glass jars with PTFE-lined caps.

SAMPLE STABILITY: at least 30 days at 5 °C [1]

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: GAS CHROMATOGRAPHY/ ELECTRON CAPTURE (GC/ECD)

ANALYTE: listed above or Table 1

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 270 °C
-DETECTOR: 300 °C
-COLUMN: 90 °C for 1 min; ramp to 160°C at 35 °C/min; then ramp to 230 °C at 3 °C/min; hold for 9 min.

CARRIER GAS: He at 1 mL/min

COLUMN: capillary, fused silica, 30 m X 0.25-mm ID, 0.25-µm film, 50% phenyl, 50% methyl silicone, DB-17 or equivalent. See Table 2

CALIBRATION: standard solutions of herbicides in isopropanol

RANGE: Table 3

ESTIMATED LOD: Table 3

PRECISION ($\hat{S}_r$): Table 3

APPLICABILITY: The working ranges are listed in Table 3. These cover from the LOQ to approximately 30 x LOQ. This method may be applicable to the determination of many other thermally stable organonitrogen, aryl and alkyl acidic, and phenolic pesticides after evaluation for sample stability and precision.

INTERFERENCES: Because of the great sensitivity of the ECD, there are many potential interferences. Among those observed are plasticizers (*e.g.*, dibutyl phthalate), methylated fatty acids (give negative responses), phenols, and antioxidants and other additives (*e.g.*, BHT), any volatile or semivolatile halogenated or nitrated organics, organophosphorous compounds, and other pesticides. Agricultural spray additives can contribute serious interferences. Such additives include solvents, emulsifiers, wetting agents, breakdown products, and fertilizers (*e.g.*, fatty acids and urea). Second-column confirmation is very desirable.

OTHER METHODS: Other hand wash methods allowing simultaneous determination of organonitrogen and acid compounds and their esters are unknown.

REAGENTS:

1. Analytes listed in Table 1.
2. Isopropanol*, pesticide analytical grade.
3. Silicic Acid, 100-mesh.
4. Diazomethane* derivatizing reagent. (See APPENDIX)
5. Diazald® (N-methyl-N-nitroso-p-toluene-sulfonamide.
6. Herbicide stock solutions*. Prepare individual standard stock solutions of each herbicide of interest in isopropanol.
   NOTE: All herbicides in Table 1 were found to be soluble to at least 1 mg/mL, except simazine, which is soluble to 0.5 mg/mL.
7. Calibration stock solution. Dilute the appropriate volume of herbicide stock solution to a known volume with isopropanol.
   NOTE: Spiking solutions may contain more than one analyte.
8. Purified gases: helium, 5% methane in argon, or nitrogen.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Bags, polyethylene, 12 in x 8", 4-mil wall thickness. (Scienceware®, or equivalent.
   NOTE: Test bags from each lot and supplier for interfering contaminants before use.
2. Gas chromatograph, electron-capture detector, integrator, and column (page 9200-1 and Table 2).
3. Syringes, 2-, 5-mL, and 10-, 50-, and 100-µL for making standard solutions and GC injections.
4 Syringes, luer lock, 1-, 2.5-, or 5-mL for sample filtering.
5. PTFE syringe filters, 0.45-µm pore size. (Gelman Acrodisc® CR, or equivalent).
6. Volumetric flasks, 2-, 5-, 10-, 25-, 50-, and 100-mL for working standard preparation and solutions.
7. Jars, glass, 250-mL, PTFE-lined caps.
8. Vials, 2-mL, GC autosampler vials with PTFE-lined crimp caps.
9. Test tubes, glass, screw-top, with PTFE seals, 16 x 125 mm, 16-mL volume.

SPECIAL PRECAUTIONS: Diazomethane has been cited as a carcinogen. It is extremely toxic and highly irritating. Diazomethane may explode under some conditions. Do not heat above 90 °C. Avoid rough surfaces: fire-polish glass tubing, or use Teflon®. Do not expose solutions to strong light. Keep dilute solutions at 0 °C. Prepare in a hood [2]. Diazald® is far more convenient to use on a large scale than the alkylnitrosonitroguanidines. Avoid skin contact with Diazald® and herbicides. Avoid skin contact and open flame with solvents. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Pour 150 mL of isopropanol into the polyethylene bag.
2. Insert hand into bag. Wrap the top of the bag securely around the forearm, several inches above the wrist.
   NOTE: Allergies to alcohols are extremely rare. Before conducting the handwash, check to see if the person has ever had a reaction to alcohols, or is taking medications that could react with the alcohol. Some skin conditions, such as cuts, abrasions, and eczema can be irritated by contact with alcohols. If the person's hand seems "dried-out" after the handwash, hand lotion can be applied.
3. Shake hand in alcohol with constant back and forth motion for 30 seconds. Remove hand from bag and dry with paper towel.
4. Transfer solution to glass jar, cap securely.
5. Label and pack for shipment.
6. For field blank, add 150 mL isopropanol to a clean bag, shake for 30 seconds, then transfer the solvent to a glass jar for shipment.

SAMPLE PREPARATION:

7. Pipette 10 mL of sample into a screw-top test tube with a PTFE-lined cap.

8. Add 0.5 mL of diazomethane derivatizing reagent. Mix and allow to stand for one hour.
9. Add approximately 10 mg of silicic acid to the solution. Mix and allow to stand an additional hour.
10. Filter an aliquot through a 0.45-µm PTFE filter into a 2-mL GC vial; label.
    NOTE: It is important to filter the samples because the silicic acid fines can build-up in the chromatographic system and cause deterioration of analytical column performance.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes. Three standards (in duplicate) should cover the range from LOD to LOQ.
    a. Add known amounts of calibration stock solution to isopropanol in a 10-mL volumetric flask. Add 0.5 mL of the diazomethane derivatizing reagent. Let stand for 1 hour.
    b. Add 10 mg silicic acid to each standard vial and let stand for another hour.
    c. Filter through a 0.45-filter into a GC vial.
    d. Include a calibration blank of unspiked diazomethane derivatizing reagent solution.
    e. Analyze together with field samples and blanks (steps 13 and 14).
    f. Prepare calibration graph (peak height or area vs. µg analyte).
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 3. Inject 2-µL aliquot manually using solvent flush technique or with autosampler. See Table 4 for retention times of selected analytes.
    NOTE: If peak height is greater than the range of the working standards, dilute with isopropanol and reanalyze. Apply the appropriate dilution factor in calculations.
14. Measure peak height of analyte.

CALCULATIONS:

15. Determine the concentration, C (µg/mL), of the herbicide found in the sample from the calibration graph.
16. Calculate the mass of herbicide, M (µg), found in the volume, V (mL), of hand wash solution.

$$M = C \cdot V \text{ , } \mu g$$

CONFIRMATION:

Whenever the identity of an analyte is uncertain, confirmation may be achieved by analysis on a column of different polarity. If primary analysis was performed using a nonpolar or weakly polar column *(e.g.*, DB-1 or DB-5) confirmation should be accomplished by reanalysis on a polar column (*e.g.*, DB-17 or DB-1701). See Table 4 for approximate retention times for each column type. For positive identification of high-level analytes (1 to 10 µg/mL or greater), GC/MS may be used. Table 5 provides notes on the analytical characteristics of the chlorinated and organonitrogen herbicides.

EVALUATION OF METHOD:

This method was evaluated over the ranges specified in Table 3. These ranges represent 3 x LOQ to 30 x LOQ for each of the compounds. The analytical conditions used in the evaluation are listed in Table 2 for the DB-5ms column. Humidity did not seem to have an effect on the analyte recoveries from the samplers. Measurement precision ($\bar{S}_r$), LOD, LOQ, and storage stability data are also presented in Table 3. The LOD and LOQ were determined by taking a series of liquid standards, prepared in triplicate, analyzed, and the data fitted to a quadratic curve. The Limit of Detection (LOD) and Limit of Quantitation (LOQ) were estimated with Burkart's Method [3]. A long-term storage study was done at the 10 x LOQ level. Handwash solutions were

stored at 4 ± 2 °C for 30, 60, or 120 days in glass containers sealed with caps having PTFE-faced liners. The stored samples were analyzed on the DB-17 column using the conditions listed in Table 2. The results are summarized in Table 3. The 30-Day storage samples had acceptable recoveries of nearly 100%, with the extremes being simazine and alachlor having recoveries of 127.7% and 87.1%, respectively. Day 60 and Day 120 storage samples had significantly lower recoveries.

REFERENCES:

[1] NIOSH [1995]. Back-up data report for chlorinated organonitrogen and carboxylic acid herbicides. Prepared under NIOSH Contract 200-88-2618 (unpublished).
[2] Black TH [1983]. The preparation and reactions of diazomethane. Aldrichimica Acta 16(1).
[3] Burkart JA [1986]. General procedures for limit of detection calculations in the industrial hygiene chemistry laboratory. Appl Ind Hyg *1*(3):153–155.

METHOD WRITTEN BY:

Don C. Wickman, John M. Reynolds, and James B. Perkins, DataChem Laboratories, Salt Lake City, Utah

APPENDIX. DIAZOMETHANE DERIVATIZING REAGENT [2]

The diazomethane generator (see Figure 2) consists of two 40-mL test tubes, each fitted with a two-hole rubber stopper. A glass tube which extends to within one centimeter of the bottom of the first test tube is inserted in one hole of the stopper. The other end of the glass tube is connected to a supply of nitrogen. A short piece of PTFE tubing is placed in the second hole and is directed to the bottom of the second tube through the second stopper. A third piece of PTFE tubing leads from the second tube into the receiving flask. The first test tube contains a small quantity of diethyl ether. Nitrogen bubbled through the ether is led to the second tube containing 3 mL of a 37% (w/v) KOH/water solution and 4 mL "Diazald® Reagent," which is prepared by dissolving 10 g Diazald in 100 mL of 1/1 Ethyl ether/Carbitol. (Nitrogen becomes saturated with diethyl ether vapor in the first tube in order that nitrogen does not deplete the second tube of diethyl ether; diethyl ether stabilizes diazomethane through adduct formation.) The resulting diazomethane gas is swept by a flow of nitrogen gas into a flask of chilled (0 °C) isopropanol (maximum volume, 500 mL).

NOTE: The KOH solution (37% w/v) will become weaker over time from the absorption of atmospheric carbon dioxide. Under such circumstances, diazomethane generation will be considerably slower.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name / Synonym	Empirical Formula	Molecular Weight	Physical Properties	Solubility in Water (mg/L)	LD50 mg/kg	TWA (mg/m3)
Alachlor 2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide CAS #15972-60-8 RTECS AE1225000	$C_{14}H_{20}ClNO_2$	269.77	Colorless crystals; d 1.133 g/mL@ 25°C; MP 39.5-41.5°C; VP 0.0029 Pa (2.2 x 10^{-5} mm Hg) @ 25°C	140 @23°C	1200	
Atrazine 6-Chloro-N-ethyl-N'-isopropyl-1,3,5-triazine-2,4-diamine CAS # 1912-24-9 RTECS XY5600000	$C_8H_{14}ClN_5$	215.68	Colorless crystals; MP 173-175°C; VP 4 x 10^{-5} Pa (3.0 x 10^{-7} mm Hg) @ 20°C	70 @ 25°C	1780	NIOSH 5 ACGIH 5
Cyanazine 2[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile CAS #21725-46-2 RTECS UG1490000	$C_9H_{13}ClN_6$	240.69	White crystalline solid; MP 167.5-169°C; VP 2.1 x 10^{-7} Pa (1.6 x 10^{-9} mm Hg) @ 20°C	171 @ 25°C	182	
2,4-D acid 2,4-Dichlorophenoxyacetic acid CAS #94-75-7 RTECS AG6825000	$C_8H_6Cl_2O_3$	221.04	White powder; MP 140.5°C; <10^{-5} Pa (<7.5 x 10^{-8} mm Hg) @ 25°C	almost insoluble	375	NIOSH 10 ACGIH 10 OSHA 10
2,4-D, ME 2,4-Dichorophenoxyacetic acid, methyl ester CAS #1928-38-7	$C_9H_8Cl_2O_3$	235.07				
2,4-D, BE 2,4-Dichlorophenoxyacetic, 2-butoxyethyl ester CAS #1929-73-3 RTECS AG7700000	$C_{14}H_{18}Cl_2O_4$	321.20			150	
2,4-D, EH 2,4-2,4-Dichlorophenoxyacetic acid, 2-ethylhexylester CAS #1928-43-4	$C_{16}H_{22}Cl_2O_3$	333.25			300 - 1000	
Metolachlor 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide CAS #51218-45-2 RTECS AN3430000	$C_{15}H_{22}ClNO_2$	283.80	Odorless tan liquid; 0.0017 Pa (1.3 x 10^{-5} mm Hg) @ 20°C	530 @ 20°C	2780	
Simazine 6-Chloro-N,N'-diethyl-1,3,5-trazine-2,4-diamine CAS #122-34-9 RTECS XY5250000	$C_7H_{12}ClN_5$	201.66	Crystals; MP 225 -227°C; 8.1 x 10^{-7} Pa (6.1 x 10^{-7} mm Hg) @ 20°C	3.5 @ 20°C	5000	

TABLE 2. USEFUL GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS [1]

Parameter	Conditions							
Column Parameters:								
Stationary phase[2]	DB-1	DB-5	DB-5ms	DB-17[3]	DB-1701[4]	DB-210[4]	DB-225[4]	DB-WAX
Length (meters)	30	30	30	30	30	30	30	30
I.D. (millimeters)	0.25	0.32	0.32	0.25	0.53	0.32	0.32	0.32
Film thickness (µm)	0.25	0.50	1.00	0.25	1.00	0.25	0.25	0.50
Oven Temperatures:								
Initial temperature (°C)	120	50	90	90	90	140	140	160
Initial temperature hold time (min.)	0	1	1	1	0.5	0	0	0
First temperature ramp (°C/min.)	5	10	35	35	15	3	5	5
First intermediate temperature (°C)			160	160	180			
Second temperature ramp (°C/min.)			5	5	2			
Second intermediate temperature (°C)			200	200	210			
Third temperature ramp (°C/min.)			3	3	10			
Final temperature (°C)	250	290	230	230	235	215	220	250
Final temperature hold time (min.)	4	5	9	9	10	5	15	20
Mobile Phase and Injection conditions:								
Carrier Gas	Helium	Helium	Helium	Helium	Helium	Helium	Helium	Helium
Head pressure (p.s.i.)	10	10	12	12	3.5	10	10	10
Injection volume (µL)	2-4	2-4	2-4	2-4	2	2-4	2-4	2-4
Injection mode	splitless	splitless	splitless	splitless	splitless	splitless	splitless	splitless

(1) Actual column and conditions may vary depending on analyte, interferences, and analytical objectives. The conditions given above correspond to Table 4.

(2) Other types of fused silica capillary columns may also work well.

(3) Column and conditions used for method evaluation. Good column for separation of atrazine and simazine.

(4) Useful columns for separating cyanazine from other listed analytes.

TABLE 3. METHOD EVALUATION

	Applicable working range					Storage Stability					
				LOD[1]	LOQ[2]	30 Days		60 days		120 days	
Compound	(µg/mL)	(µg/sample)	$\bar{S}_r$	(µg/mL)	(µg/mL)	%Recovery	S_r	%Recovery	S_r	%Recovery	S_r
Alachlor	0.0015 - 0.2	0.22 - 30	0.028	0.001	0.004	103.0	0.027	87.1	0.149	95.4	0.137
Atrazine	0.088 - 1.1	13 - 160	0.024	0.010	0.037	100.9	0.041	86.0	0.123	89.4	0.075
Cyanazine	0.0099 - 0.2	1.5 - 30	0.094	0.002	0.006	105.3	0.120	88.1	0.197	87.7	0.167
2,4-D acid	0.0017 - 0.11	0.26 -16	0.035	0.001	0.004	101.9	0.019	108.4	0.169	105.5	0.111
2,4-D, BE	0.0019 - 0.12	0.28 - 18	0.084	0.001	0.004	103.5	0.071	79.3	0.175	76.5	0.159
2,4-D, EH	0.0075 - 0.05	1.1 - 7.5	0.040	0.0005	0.002	104.4	0.069	85.6	0.135	81.7	0.108
Metolachlor	0.0039 - 0.22	0.58 - 33	0.030	0.002	0.007	102.8	0.025	87.1	0.145	89.8	0.103
Simazine	0.082 - 1.1	12 - 160	0.031	0.010	0.037	127.7	0.045	83.4	0.140	91.4	0.2

(1) Limit of Detection

(2) Limit of Quantitation

TABLE 4. APPROXIMATE RETENTION TIMES OF SELECTED CHLORINATED AND ORGANONITROGEN COMPOUNDS[1]

	Compound (by retention time on Capillary Column:	Retention Times in Minutes (Capillary Column by Approximate Increase in Polarity) DB-1	DB-5	DB-5ms	DB-17	DB-1701	DB-210	DB-225	DB-WAX
1	**CDAA**		14.37						
2	**2,4-D, ME[2]**			10.13	10.25	12.25			
3	**Dicamba, ME[2]**		16.72						
4	**2,4-D, IPE[3]**		19.20						
5	**Simazine**	12.90	19.42	12.02	12.91	16.52	7.59	16.90	18.62
6	**Atrazine**	12.96	19.50	12.18	12.59	16.34	7.79	15.93	17.17
7	**Propazine**		19.61						
8	**2,4-DB, ME[2]**				14.03				
9	**Metribuzin**	13.89	21.10		17.51		9.72	22.01	23.08
10	**Dimethenamid**		21.13						
11	**Acetochlor**		21.18		14.66				
12	**Alachlor**	14.37	21.44	15.24	15.19	19.78	12.95	17.45	14.95
13	**Cyanazine**	14.97	22.23	17.17	19.99	27.07	19.67	30.00	36.00
14	**Metolachlor**	15.11	22.26	16.96	16.67	22.17	14.85	19.43	15.96
15	**Pendimethalin**		22.98		18.67				
16	**2,4-D, BE[4]**	17.01	23.73	21.46	20.60	26.25	16.79	25.86	20.50
17	**2,4-D, EH[5]**	17.70	24.38	22.73	20.12	26.71	17.17	23.49	18.55

(1) Actual retention times will vary with individual columns and chromatographic conditions. Column conditions are give in Table 2. Data is from Backup Data Report [1].

(2) ME = Methyl ester. Methyl ester formed by reaction of the free acid form with diazomethane.

(3) IPE = Isopropyl ester.

(4) BE = 2-Butoxyethyl ester.

(5) EH = 2-Ethylhexyl ester.

TABLE 5. NOTES ON ANALYTICAL CHARACTERISTICS OF CHLORINATED AND ORGANONITROGEN HERBICIDES

	Compound (alphabetically)	A. CHEMICAL AND PHYSICAL	B. SAMPLE PREPARATION	C. GAS CHROMATOGRAPHIC
1	Alachlor		3	1
2	Atrazine		3	2,3
3	Cyanazine		3	2,4
4	2,4-D, acid		1	
5	2.4-D, BE	1	2	5
6	2,4-D, EH	1	2	
7	Metolachlor		3	1
8	Simazine		3	2,3

A. CHEMICAL AND PHYSICAL

1. Esters may hydrolyze to the free acid. Free acid may also be present in formulations.

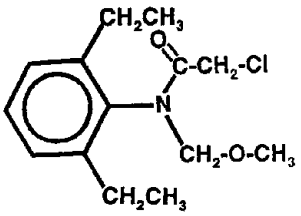
B. SAMPLE PREPARATION

1. Methylation via diazomethane is possible in isopropanol having up to 1% water present. The isopropanol must be anhydrous, and at least 99% pure.
2. The esters are not affected by the diazomethane reagent provided the solutions are quenched within one hour with silicic acid. Recoveries for all esters diminish otherwise. This makes possible the speciation of 2,4-D esters and of the free acid in one analysis.
3. Analytes were not affected by the diazomethane reagent.

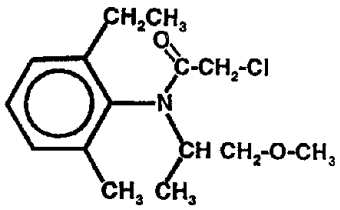
C. GAS CHROMATOGRAPHIC

1. Very good peak shape.
2. Analyte has tendency to tail on most column phases. Columns and injection ports must be clean and in good condition.
3. The s-triazines, simazine, Atrazine, and propazine, elute very close in that order on the non-polar columns DB-1 and DB-5. The order is reversed on most polar columns.
4. Cyanazine is very polar and tends to tail and to elute very late on very polar columns. It has very unpredictable behavior and peak areas either diminish or increase noticeably in subsequent injections. This behavior appears to be associated with the cyano group.
5. 2,4-D BE behaves similarly to cyanazine, chromatographically (see C.4.), though to a much lesser extent.

ACETANILIDES:

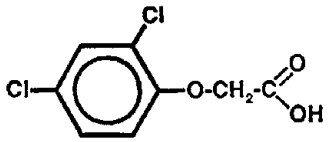


1. ALACHLOR

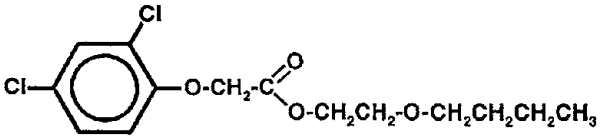


2. METOLACHLOR

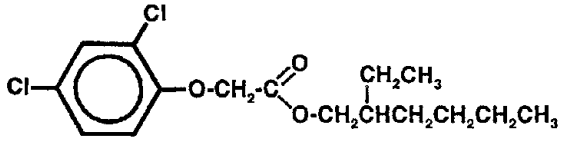
PHENOXYALKANOIC ACID AND ESTERS:



3. 2,4-D, ACID

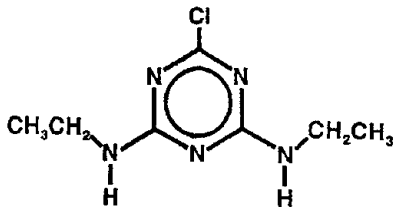


4. 2,4-D, 2-BUTOXYETHYL ESTER

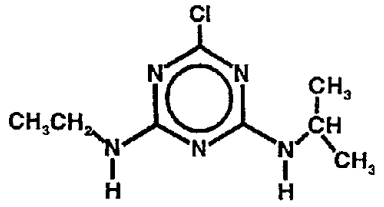


5. 2,4-D, 2-ETHYLHEXYL ESTER

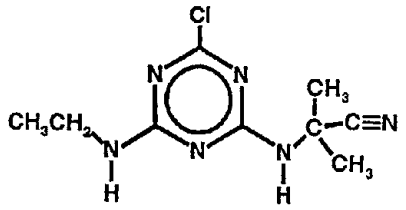
s-TRIAZINES:



6. SIMAZINE



7. ATRAZINE



8. CYANAZINE

STRUCTURES OF CHLORINATED ORGANONITROGEN and ACID HERBICIDES

Figure 1.

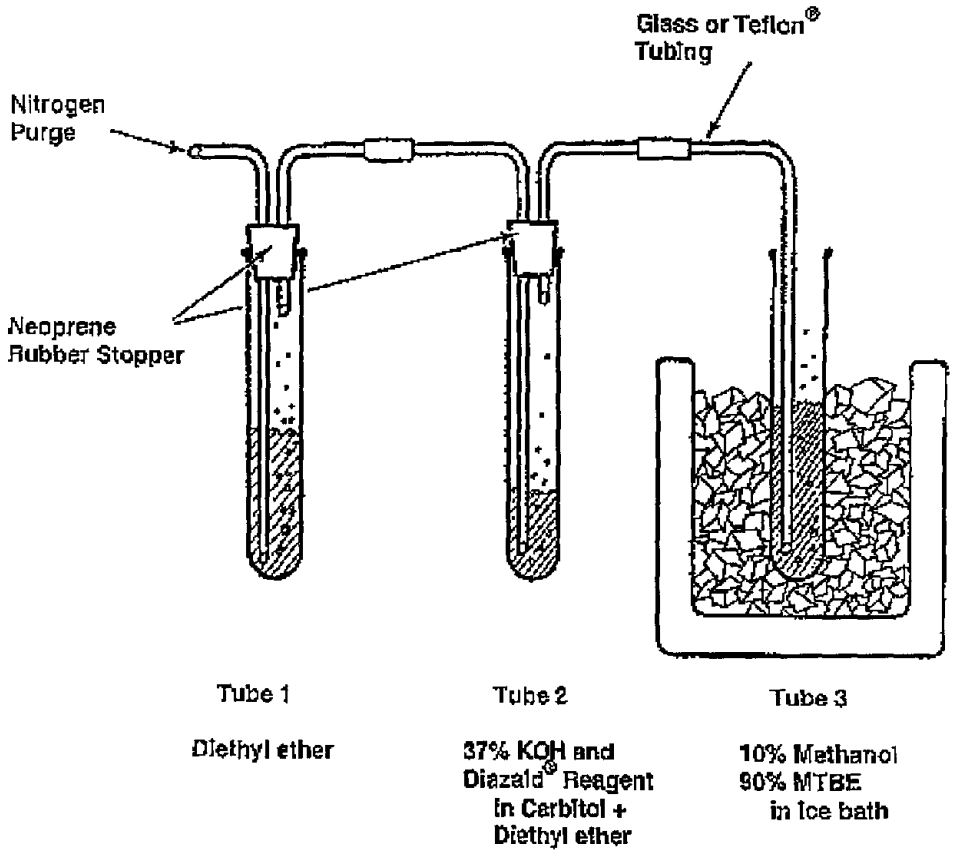


Figure 2. Diazomethane generator

ANALYTES: Figure 1 FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 9201, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

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

PROPERTIES: Table 1

NAMES: Alachlor, Atrazine, 2,4-D acid, 2,4-D, 2-ethylhexyl ester, Cyanazine, Metolachlor, Simazine, 2,4-D, 2-butoxyethyl ester

SAMPLING

SAMPLER: DERMAL PATCH (Polyurethane Foam [PUF] pads, 10 x 10-cm, 3 to 4 mm thick)

PASSIVE EXPOSURE: place pad in an aluminized card holder with 7.6-cm diameter circle cut in one side. Affix to worker's clothing or skin.

SHIPMENT: transfer pads to 120-mL wide-mouthed glass jars with PTFE-lined caps.

SAMPLE STABILITY: at least 30 days at 4 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTRON CAPTURE DETECTOR, (GC/ECD)

ANALYTE: Table 1

DESORPTION: 40 mL isopropanol (containing diazomethane)

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 270 °C
-DETECTOR: 300 °C
-COLUMN: 90 °C for 1 min; ramp to 160 °C at 35 °C/min; ramp to 200 °C at 5°C/min; ramp to 230 °C at 3 °C/min; hold 9 min. Total run time = 30 min.

CARRIER GAS: He, mL/min

COLUMN: capillary, fused silica, 30 m X 0.25-mm ID, 0.25-µm film, 50% phenyl, 50% methyl silicone, DB-17 or equivalent. See Table 2

CALIBRATION: standard solutions of herbicides in isopropanol

RANGE: Table 3

ESTIMATED LOD: Table 3

PRECISION ($\hat{S}_r$): Table 3

APPLICABILITY: The working ranges are listed in Table 3. These cover from the LOQ to approximately 30X the LOQ [1]. This method may be applicable to the determination of many other thermally stable organonitrogen; aryl and alkyl acidic; and phenolic pesticides after evaluation for desorption efficiency, sample stability, and precision and accuracy.

INTERFERENCES: Because of the great sensitivity of the ECD, there are many potential interferences. Among those observed are plasticizers (*e.g.*, dibutyl phthalate), methylated fatty acids (give negative responses), phenols, and antioxidants and other additives (*e.g.*, BHT), any volatile or semivolatile halogenated or nitrated organic, organophosphorous compounds, and other pesticides. Agricultural spray additives can presentserious interferences. Such additives include solvents, emulsifiers, wetting agents, breakdown products, and fertilizers (*e.g.*, fatty acids and urea). Second-column confirmation is very desirable. Poorly precleaned pads and poor technique present significant interferences at low levels. These include phthalate plasticizers and PUF manufacturing additives and monomers.

OTHER METHODS: Other patch methods allowing simultaneous analysis of organonitrogen and acid compounds and their esters are unknown.

REAGENTS:

1. Analytes* listed in Table 1.
2. Isopropanol, pesticide analytical grade.
3. Silicic Acid, 100-mesh. Aldrich Chemical Co. or equivalent.
4. Diazomethane* derivatizing reagent. (See APPENDIX)
5. Diazald® (N-methyl-N-nitroso-*p*-toluenesulfonamide*), Aldrich Chemical Co. or equivalent.
6. Herbicide stock solutions. Prepare individual standard stock solutions of each herbicide of interest in isopropanol.
   NOTE: All herbicides in Table 1 were found to be soluble to at least 1 mg/mL, except simazine, which is soluble to 0.5 mg/mL.
7. Calibration stock solution. Dilute the appropriate volume of herbicide stock solution to a known volume with isopropanol.
   NOTE: Spiking solutions may contain more than one analyte.
8. Purified gases: Helium, 5% methane in Argon, or nitrogen.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Polyurethane foam (PUF) patch. 10 x 10 x 0.6-cm, contained in a aluminized card holder, 10 x 10 cm, which has a 7.6-cm-diameter circle in one side. (SKC Inc., Eighty Four, PA 15330 or equivalent.)
   NOTE: Before use, clean the PUF patch by soxhlet extraction for 20 hours in acetone/methanol, 88/12, v/v, followed by three hexane rinses.
2. Gas chromatograph, electron capture detector, integrator, and column (see Page 9201-1 and Table 2).
3. Syringes, 2-, 5-mL, and 10-, 50-, and 100-µL for making standard solutions and GC injections
4. Syringes, luer lock, 1-, 2.5-, or 5-mL for sample filtering.
5. PTFE syringe filters, 0.45-µm pore size. (Gelman Acrodisc® CR or equivalent).
6. Volumetric flasks, 2-, 5-, 10-, 25-, 50-, and 100-mL for working standard preparation and solutions..
7. Jars, glass, 120-mL, PTFE-lined cap.
8. Vials, glass, 2-mL, GC autosampler, with PTFE-lined caps.
9. Test tubes, glass screw-top, with PTFE seals, 16 x 125 mm, 16-mL volume.
10. Forceps.
11. Platform shaker.

SPECIAL PRECAUTIONS: Diazomethane has been cited as a carcinogen. It is extremely toxic and highly irritating. Diazomethane may explode under some conditions. Do not heat above 90 °C. Avoid rough surfaces: fire-polish glass tubing, or use Teflon®. Do not expose solutions to strong light. Keep dilute solutions at 0 °C. Prepare in a hood [2]. *Diazald®* is far more convenient to use on a large scale than the alkyl-nitrosonitroguanidines. Avoid skin contact with *Diazald®* and herbicides. Avoid skin contact and open flame with solvents. Use in a hood.

SAMPLING:

1. Dermal Patch
   a. Insert a cleaned PUF patch into patch holder. Secure to desired location on clothing or skin.
   b. At the conclusion of the sampling period, remove PUF patch from holder with solvent-washed (acetone or isopropanol) forceps and place in a 120-mL jar; cap securely.
   c. Label and pack for shipment.

SAMPLE PREPARATION:

2. Add 20 mL of isopropanol to PUF in jar. Add an additional 20 mL diazomethane derivatizing reagent to jar. Cap securely, and using platform shaker rotate 5 to 10 RPM for a minimum of 1.5 hours.
3. Transfer a 10-mL sample aliquot into a screw-top test tube with a PTFE-lined cap. Add approximately 10 mg of silicic acid to the solution. Allow to stand an additional hour.
4. Filter an aliquot through a 0.45-µm PTFE filter into a 2-mL GC vial. Label.
   NOTE: It is important to filter the samples because the silicic acid fines can build-up in the chromatographic system and cause deterioration of analytical column performance.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes.
   a. Add known amounts of calibration solution to the diazomethane derivatizing reagent in a volumetric flask. Let stand for 1 hour. Include a calibration blank of unspiked diazomethane derivatizing reagent solution.
   b. Add 10 mg silicic acid to each flask and let stand for another hour.
   c. Filter through a 0.45 PTFE syringe filter into a GC vial.
   d. Analyze together with field samples, field blanks, and laboratory control samples (steps 8 and 9).
   e. Prepare calibration graph (peak height or area vs. µg/mL analyte).
6. Determine desorption efficiency (DE) at least once for each lot of PUF samplers used for sampling in the calibration range (step 5).
   a. Prepare three samples at each of six levels plus three media blanks.
   b. Place PUF patch in a 120-mL glass jar. Apply a known amount of calibration stock to patch. Replace lid on jar and allow to stand over night.
   c. Desorb the samples (steps 2 through 4) and analyze together with standards and blanks (steps 8 and 9).
   d. Prepare a graph of DE vs. µg analyte recovered.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and DE graphs are in control.

MEASUREMENT:

8. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 2. Inject sample aliquot manually using solvent flush technique or with autosampler. See Table 4 for retention times of selected analytes.
   NOTE: If peak height is greater than the range of the working standards, dilute the sample with isopropanol and reanalyze. Apply the appropriate dilution factor in calculations.
9. Measure peak height of analyte.

CALCULATIONS:

10. Determine the concentration, µg/mL, (corrected for DE) of the respective herbicide found on the patch sample (C_p) and in the media blank (B_b) from the calibration graph.
11. Calculate the mass of herbicide, M (µg), on patch in the desorption volume, V (mL):

$$M = (C_p V_p - B_b V_b), \mu g$$

CONFIRMATION:

Whenever the identity of an analyte is uncertain, confirmation may be achieved by analysis on a column of different polarity. If primary analysis was performed using a nonpolar or weakly polar column (*e.g.*, DB-1 or DB-5), confirmation should be accomplished by reanalyzing on a polar column (*e.g.*, DB-17 or DB-1701). See Table 4 for approximate retention times for each column type. For positive identification of high-level analytes (1 to 10 µg/mL or greater), GC/MS may be used. Table 5 gives notes on the analytical characteristics of the chlorinated and organonitrogen herbicides.

EVALUATION OF METHOD:

This method was evaluated over the ranges specified in Table 3. For the method evaluation, the GC

analyses were done using the DB-17 column. See Table 2 and Table 4 for chromatographic conditions. The upper limits of the analytical range were set at approximately the upper ranges studied. Also presented in Table 3 are the LOD, $\bar{S}_{r1}$ (pooled relative standard deviation), and sample storage stability for these eight compounds. To determine the LOD and LOQ values, a series of media-spiked standards was prepared in triplicate, analyzed, and fitted with a quadratic curve. The Limit of Detection (LOD) and Limit of Quantitation (LOQ) were estimated with Burkart's Method [3]. Actual LOD and LOQ results were inconsistent owing to periodic low level interferences in the media. Therefore, higher arbitrary LODs and LOQs were selected in order to circumvent the problem. The higher LODs were assumed to be more realistic and were used for evaluation of the method. A set of samples for long-term storage study was prepared and analyzed after 1, 30, and 120 days. The results are summarized in Table 3. The day 1 results show that the compounds, except for 2,4-D acid and the 2,4-D-butoxy ester, give 90% or better recovery based on the amount spiked onto the samplers. When compared to day 1, the day 30 sample results were all ≥92%. The PUF patch samples were shown to be stable for at least 30 days when refrigerated at 4 °C.

REFERENCES:

[1] NIOSH [1995]. Back-up data report for chlorinated organonitrogen and carboxylic acid herbicides. Prepared under NIOSH Contract 200-88-2618 (unpublished).
[2] Black TH [1983]. The preparation and reactions of diazomethane. Aldrichimica Acta 16(1).
[3] Burkart JA [1986]. General procedures for limit of detection calculations in the industrial hygiene chemistry laboratory, Appl Ind Hyg *1*(3):153-155.

METHOD WRITTEN BY:

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APPENDIX. DIAZOMETHANE GENERATOR

The diazomethane generator (see Figure 2) consists of two 40-mL test tubes, each fitted with a two-hole rubber stopper. A glass tube which extends to within one centimeter of the bottom of the first test tube is inserted in one hole of the stopper. The other end of the glass tube is connected to a supply of nitrogen. A short piece of PTFE tubing is placed in the second hole and is directed to the bottom of the second tube through the second stopper. A third piece of PTFE tubing leads from the second tube into the receiving flask. The first test tube contains a small quantity of diethyl ether. Nitrogen bubbled through the ether is led to the second tube containing 3 mL of a 37% (w/v) KOH/water solution and 4 mL "Diazald® Reagent," which is prepared by dissolving 10 g Diazald in 100 mL of 1/1 Ethyl ether/Carbitol. (Nitrogen becomes saturated with diethyl ether vapor in the first tube in order that nitrogen does not deplete the second tube of diethyl ether; diethyl ether stabilizes diazomethane through adduct formation.) The resulting diazomethane gas is swept into a flask of chilled (0 °C) isopropanol (maximum volume, 500 mL) by a flow of nitrogen gas.

NOTE: The KOH solution (37% w/v) will become weaker over time from the absorption of atmospheric carbon dioxide. Under such circumstances, diazomethane generation will be considerably slower.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name / Synonym	Empirical Formula	Molecular Weight	Physical Properties	Solubility in Water (mg/L)	LD50 mg/kg	TWA (mg/m3)
Alachlor 2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide CAS #15972-60-8 RTECS AE1225000	$C_{14}H_{20}ClNO_2$	269.77	Colorless crystals; d 1.133 g/mL@ 25°C; MP 39.5-41.5°C; VP 0.0029 Pa (2.2 x 10^{-5} mm Hg) @ 25°C	140 @23°C	1200	
Atrazine 6-Chloro-N-ethyl-N'-isopropyl-1,3,5-triazine-2,4-diamine CAS # 1912-24-9 RTECS XY5600000	$C_8H_{14}ClN_5$	215.68	Colorless crystals; MP 173-175°C; VP 4 x 10^{-5} Pa (3.0 x 10^{-7} mm Hg) @ 20°C	70 @ 25°C	1780	NIOSH 5 ACGIH 5
Cyanazine 2[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile CAS #21725-46-2 RTECS UG1490000	$C_9H_{13}ClN_6$	240.69	White crystalline solid; MP 167.5-169°C; VP 2.1 x 10^{-7} Pa (1.6 x 10^{-9} mm Hg) @ 20°C	171 @ 25°C	182	
2,4-D acid 2,4-Dichlorophenoxyacetic acid CAS #94-75-7 RTECS AG6825000	$C_8H_6Cl_2O_3$	221.04	White powder; MP 140.5°C; <10^{-5} Pa (<7.5 x 10^{-8} mm Hg) @ 25°C	almost insoluble	375	NIOSH 10 ACGIH 10 OSHA 10
2,4-D, ME 2,4-Dichorophenoxyacetic acid, methyl ester CAS #1928-38-7	$C_9H_8Cl_2O_3$	235.07				
2,4-D, BE 2,4-Dichlorophenoxyacetic, 2-butoxyethyl ester CAS #1929-73-3 RTECS AG7700000	$C_{14}H_{18}Cl_2O_4$	321.20			150	
2,4-D, EH 2,4-2,4-Dichlorophenoxyacetic acid, 2-ethylhexylester CAS #1928-43-4	$C_{16}H_{22}Cl_2O_3$	333.25			300 - 1000	
Metolachlor 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide CAS #51218-45-2 RTECS AN3430000	$C_{15}H_{22}Cl_2O_3$	283.80	Odorless tan liquid; 0.0017 Pa (1.3 x 10^{-5} mm Hg) @ 20°C	530 @ 20°C	2780	
Simazine 6-Chloro-N,N'-diethyl-1,3,5-trazine-2,4-diamine CAS #122-34-9 RTECS XY5250000	$C_7H_{12}ClN_5$	201.66	Crystals; MP 225 -227°C; 8.1 x 10^{-7} Pa (6.1 x 10^{-7} mm Hg) @ 20°C	3.5 @ 20°C	5000	

TABLE 2. USEFUL GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS [1]

Parameter	Conditions							
Column Parameters:								
Stationary phase[2]	DB-1	DB-5	DB-5ms	DB-17[3]	DB-1701[4]	DB-210[4]	DB-225[4]	DB-WAX
Length (meters)	30	30	30	30	30	30	30	30
I.D. (millimeters)	0.25	0.32	0.32	0.25	0.53	0.32	0.32	0.32
Film thickness (µm)	0.25	0.50	1.00	0.25	1.00	0.25	0.25	0.50
Oven Temperatures:								
Initial temperature (°C)	120	50	90	90	90	140	140	160
Initial temperature hold time (min.)	0	1	1	1	0.5	0	0	0
First temperature ramp (°C/min.)	5	10	35	35	15	3	5	5
First intermediate temperature (°C)			160	160	180			
Second temperature ramp (°C/min.)			5	5	2			
Second intermediate temperature (°C)			200	200	210			
Third temperature ramp (°C/min.)			3	3	10			
Final temperature (°C)	250	290	230	230	235	215	220	250
Final temperature hold time (min.)	4	5	9	9	10	5	15	20
Mobile Phase and Injection conditions:								
Carrier Gas	Helium	Helium	Helium	Helium	Helium	Helium	Helium	Helium
Head pressure (p.s.i.)	10	10	12	12	3.5	10	10	10
Injection volume (µL)	2-4	2-4	2-4	2-4	2	2-4	2-4	2-4
Injection mode	splitless	splitless	splitless	splitless	splitless	splitless	splitless	splitless

(1) Actual column and conditions may vary depending on analyte, interferences, and analytical objectives. The conditions given correspond to Table 4.

(2) Other types of fused silica capillary columns also may work well.

(3) Column and conditions used for method evaluation. Good column for separation of atrazine and simazine.

(4) Useful columns for separating cyanazine from other listed analytes.

TABLE 3. APPLICABLE WORKING RANGE AND ESTIMATED LOD

		Applicable working range		LOD[1]		$\bar{S}_{r1}$	Storage Stability		
							Day 1 [2]	Day 30 [3]	Day 120 [3]
	Compound	(µg/mL)	(µg/sample)	(µg/mL)	(µg/sample)		% Recovery	% Recovery	% Recovery
1	Alachlor	0.0075 - 0.25	0.30 - 10	0.0025	0.1	0.0247	90.8	103.9	97.5
2	Atrazine	0.0525 - 50	2.10 - 200	0.0175	0.7	0.0267	101.8	92.5	95.6
3	Cyanazine	0.0098 - 0.25	0.39 - 10	0.0025	0.1	0.0789	112.0	97.1	101
4	2,4-D acid	0.0075 - 0.25	0.30 - 10	0.0025	0.1	0.0453	75.1	97.3	79.5
5	2,4-D, BE	0.035 - 0.25	1.40 - 10	0.0025	0.1	0.0424	88.0	113.8	97.6
6	2,4-D, EH	0.0085 - 0.25	0.34 - 10	0.0025	0.1	0.0354	92.8	104.2	95.4
7	Metolachlor	0.0075 - 0.25	0.30 - 10	0.0025	0.1	0.0254	107.8	95.6	86.1
8	Simazine	0.0525 - 50	0.33 - 200	0.0175	0.7	0.0189	100.3	93.9	95.7

(1) Limit of Detection

(2) Based on mass of analyte spiked

(3) Based on Day 1 results

TABLE 4. APPROXIMATE RETENTION TIMES OF SELECTED CHLORINATE COMPOUNDS[1]

	Compound (by retention time on Capillary Column:)	Retention Times in Minutes (Capillary Column by Approximate Increase in Polarity)							
		DB-1	DB-5	DB-5ms	DB-17	DB-1701	DB-210	DB-225	DB-WAX
1	**CDAA**		14.37						
2	**2,4-D, ME[2]**			10.13	10.25	12.25			
3	**Dicamba, ME[2]**		16.72						
4	**2,4-D, IPE[3]**		19.20						
5	**Simazine**	12.90	19.42	12.02	12.91	16.52	7.59	16.90	18.62
6	**Atrazine**	12.96	19.50	12.18	12.59	16.34	7.79	15.93	17.17
7	**Propazine**		19.61						
8	**2,4-DB, ME[2]**				14.03				
9	**Metribuzin**	13.89	21.10		17.51		9.72	22.01	23.08
10	**Dimethenamid**		21.13						
11	**Acetochlor**		21.18		14.66				
12	**Alachlor**	14.37	21.44	15.24	15.19	19.78	12.95	17.45	14.95
13	**Cyanazine**	14.97	22.23	17.17	19.99	27.07	19.67	30.00	36.00
14	**Metolachlor**	15.11	22.26	16.96	16.67	22.17	14.85	19.43	15.96
15	**Pendimethalin**		22.98		18.67				
16	**2,4-D, BE[4]**	17.01	23.73	21.46	20.60	26.25	16.79	25.86	20.50
17	**2,4-D, EH[5]**	17.70	24.38	22.73	20.12	26.71	17.17	23.49	18.55

(1) Actual retention times will vary with individual columns and chromatographic conditions. Column conditions are give in Table 2. Data is from Backup Data Report [1].

(2) ME = Methyl ester. Methyl ester formed by reaction of the free acid form with diazomethane.

(3) IPE = Isopropyl ester.

(4) BE = 2-Butoxyethyl ester.

(5) EH = 2-Ethylhexyl ester.

TABLE 5. NOTES ON ANALYTICAL CHARACTERISTICS OF CHLORINATED AND ORGANONITROGEN HERBICIDES

	Compound (alphabetically)	A. CHEMICAL AND PHYSICAL	B. SAMPLE PREPARATION	C. GAS CHROMATOGRAPHIC
1	Alachlor		3	1
2	Atrazine		3	2,3
3	Cyanazine		1,3	2,4
4	2,4-D, acid		2 (methyl ester)	
5	2.4-D, BE	1	1,2	5
6	2,4-D, EH	1	2	
7	Metolachlor		3	1
8	Simazine		3	2,3

A. CHEMICAL AND PHYSICAL

1. Esters may hydrolyze to the free acid. Free acid may also be present in formulations.

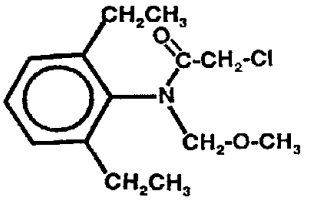
B. SAMPLE PREPARATION

1. Generally high recoveries from PUF patches compared to liquid standards for reasons unknown.
2. The esters are not affected by the diazomethane reagent provided the solutions are quenched within one hour with silicic acid. Otherwise, recoveries for all esters will diminish. This makes possible the speciation of 2,4-D esters and of the free acid in one analysis.
3. Analytes were not affected by the diazomethane reagent.

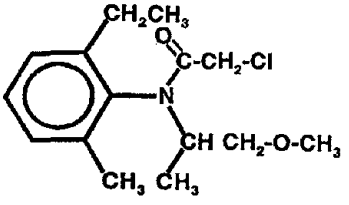
C. GAS CHROMATOGRAPHIC

1. Very good peak shape.
2. Analyte has tendency to tail on most column phases. Columns and injection ports must be clean and in good condition.
3. The s-triazines, simazine, atrazine, and propazine, elute very closely in that order on the non-polar columns DB1and DB-5. The order is reversed on most polar columns.
4. Cyanazine is very polar and tends to tail and to elute very late on highly polar columns. It has extremely unpredictable behavior. Peak areas either diminish or increase noticeably in subsequent injections. This behavior appears to be associated with the cyano group.
5. 2,4-D BE behaves similarly to cyanazine chromatographically (see C.4.), although to a much lesser extent.

ACETANILIDES:

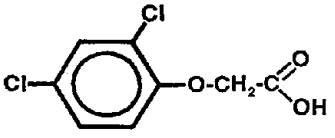


1. ALACHLOR

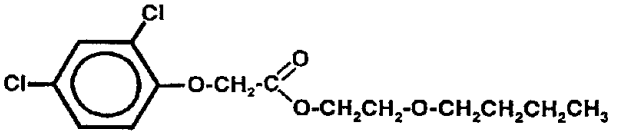


2. METOLACHLOR

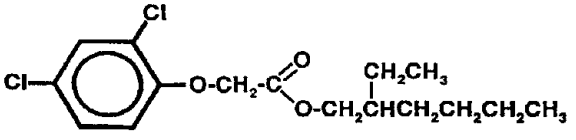
PHENOXYALKANOIC ACID AND ESTERS:



3. 2,4-D, ACID

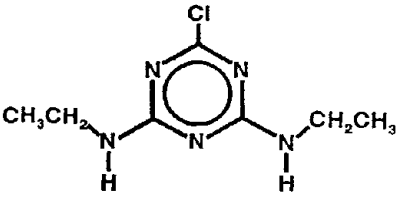


4. 2,4-D, 2-BUTOXYETHYL ESTER

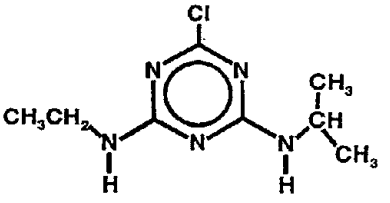


5. 2,4-D, 2-ETHYLHEXYL ESTER

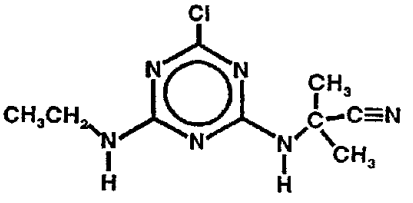
s-TRIAZINES:



6. SIMAZINE



7. ATRAZINE



8. CYANAZINE

STRUCTURES OF CHLORINATED ORGANONITROGEN and ACID HERBICIDES

Figure 1.

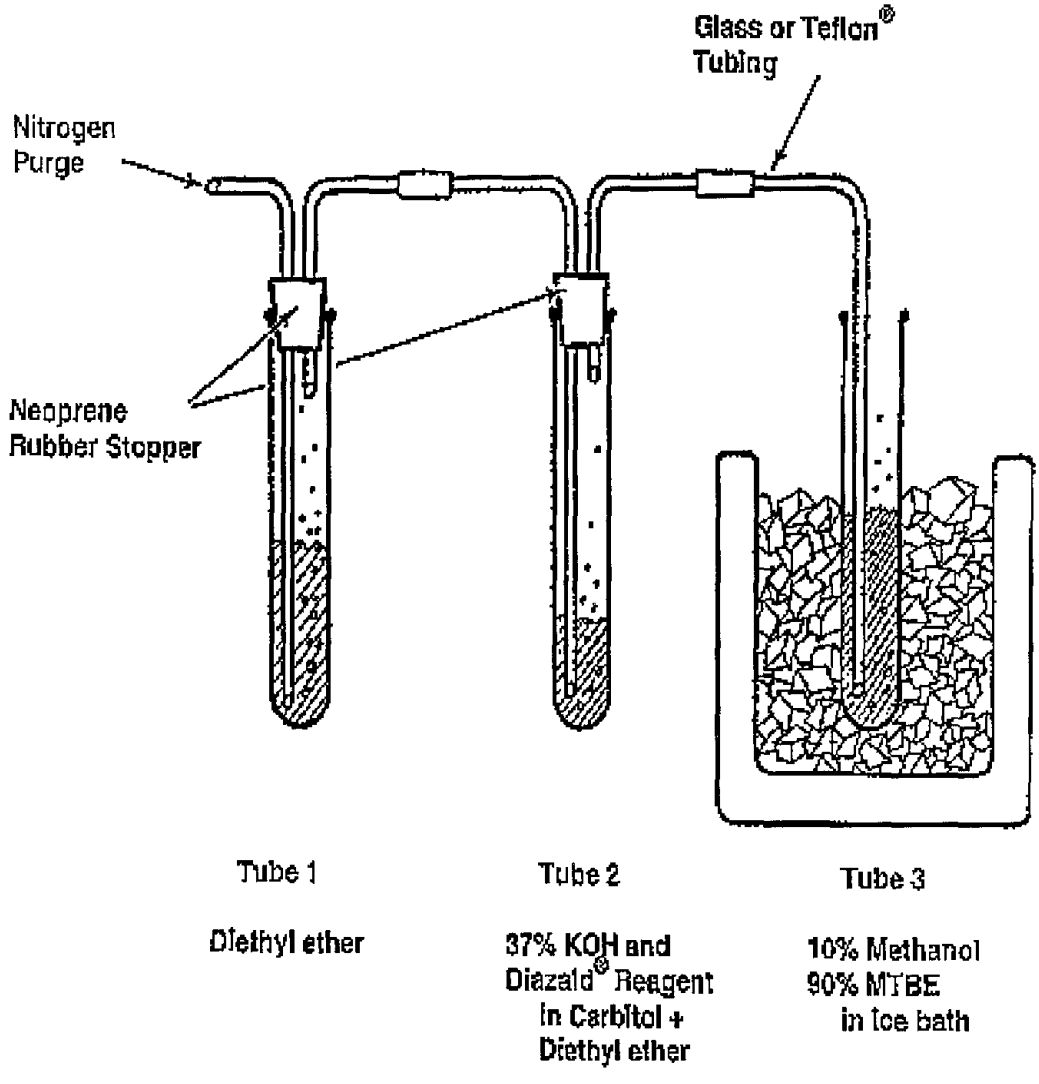


Figure 2. Diazomethane Generator

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 : 0.1 mg/m³
NIOSH: 0.05 mg/m³
ACGIH: 0.05 mg/m³ (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/m³
-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/m³ [1] (270-L samples)

BIAS: 5.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.070 [1]

ACCURACY: ± 18.0%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: cobalt

ASHING: aqua regia, 3 mL, 140 °C;conc. HNO3, 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: D2 or H2 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 ($\hat{S}_r$): 0.03 [1]; 0.02 [3]

APPLICABILITY: The working range is 0.01 to 0.3 mg/m3 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 D2 or H2 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 (HNO_3, conc.
2. Hydrochloric acid (HCl), 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 (µg/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):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

NOTE: µg/mL ≡ 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/DSHEFS; S203 originally validated under NIOSH Contract CDC-99-74-45.

ELEMENTAL CARBON (DIESEL PARTICULATE) 5040

C MW: 12.01 CAS: none RTECS: none

METHOD: 5040, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1996**
Issue 2: 15 January 1998

OSHA : no REL
NIOSH: no PEL
ACGIH: see APPENDIX A

PROPERTIES: nonvolatile solid; MP >350 °C

SYNONYMS (related terms): soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter

SAMPLING

SAMPLER: FILTER (quartz fiber, 37-mm; size-selective sampler may be required, see APPENDIX B)

FLOW RATE: 2 to 4 L/min (see APPENDIX B)

VOL-MIN: 142 L @ 40 µg/m³
-MAX: 19 m³ (for filter load of ~ 90 µg/cm²)

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 23 to 240 µg/m³ (see EVALUATION OF METHOD)

BIAS: none (see EVALUATION OF METHOD)

OVERALL PRECISION ($\hat{S}_{rT}$): 0.085 at 23 µg/m³ (see EVALUATION OF METHOD)

ACCURACY: ± 16.7% at 23 µg/m³ (see EVALUATION OF METHOD)

MEASUREMENT

TECHNIQUE: EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer

ANALYTE: elemental carbon (EC)

FILTER PUNCH SIZE: 1.5 cm² (see APPENDIX C)

CALIBRATION: methane injection [1]

RANGE: 1 to 105 µg per filter portion (see EVALUATION OF METHOD)

ESTIMATED LOD: 0.3 µg per filter portion

PRECISION ($\hat{S}_r$): 0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C

APPLICABILITY: The working range is approximately 6 to 630 µg/m³, with an LOD of ~ 2 µg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.5 cm² punch from the sample filter. If a lower LOD is desired, a larger sample volume and/or 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.4 µg/m³). The split between organic-based carbon (OC) and EC may be affected at higher EC loadings (e.g., > 20 µg/cm² of filter), depending on type and amount of OC present. Because pyrolysis correction normally is not required with high EC loadings, the split is assigned manually [1] in such cases and an upper limit of 800 µg/m³ (90 µg/cm²) can be determined.

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolytic correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Cigarette smoke and carbonates do not interfere, but if heavy loadings of carbonate are anticipated, a cyclone should be used (see APPENDIX B). For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC have been described in the literature [4], but alternative instrumentation is currently not commercially available.

REAGENTS:

1. Aqueous organic-based carbon (OC) solutions (e.g., sucrose), 0.1 to 3 mg C per mL solution (ensure range brackets that for samples).
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

EQUIPMENT:

1. Sampler: Quartz-fiber filter, precleaned (Clean in low temperature asher 2 to 3 h, or muffle furnace for 1 to 2 h at ~ 800 °C), 37-mm, in a 3-piece, 37-mm, cassette with support (stainless steel screen or cellulose pad). See also alternative samplers (APPENDIX B).
   NOTE: Cellulose supports give higher OC blanks than stainless.
2. Personal sampling pump, 2 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer (see APPENDIX C) or other analyzer capable of EC speciation.
4. Punch for removal of 1.5 cm^2 rectangular portion of filter.
   NOTE: Smaller portion may be taken (e.g., with cork borer), but portion $\geq$0.5 cm^2 with diameter or width $\leq$ 1 cm is recommended.
5. Syringe, 10-µL.
6. Aluminum foil.
7. Needle (for lifting filter punch portion).

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Open-faced cassettes give even deposits over the entire flow-rate range specified, but are not practical in some workplaces (e.g., mining). Alternative samplers also can be used (see APPENDIX B) provided that an even deposit of diesel particulate results. An even deposit is necessary because the sample portion analyzed must be representative of the entire deposit. If the deposit is not homogeneous, the entire sample must be analyzed.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette, unless sampling environment dictates otherwise (i.e., closed-face or other type sampler is required).
3. Sample at an accurately known flow rate (see APPENDIX B).
4. After sampling, replace top piece of cassette and pack securely for shipment to laboratory.

SAMPLE PREPARATION:

5. Place sample filter on a freshly cleaned aluminum foil surface. Punch out a representative portion of the filter. Take care not to disturb deposited material and avoid hand contact with sample. A needle inserted at an angle is useful for removal of the filter portion from the punch body.

CALIBRATION AND QUALITY CONTROL:

6. Analyze at least one replicate sample. For sets of up to 50 samples, replicate 10% of the samples. For sets over 50 samples, replicate 5% of the samples. If a particular filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition.
   NOTE: Precision of replicate analyses of a filter is usually better than 5% (1 to 3% is typical).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration

is in control. Prepare spike as follows:

a. With 10-µL (or other) syringe, apply an aliquot of OC standard solution directly to filter portion taken (step 5) from a precleaned filter. For best results, the precleaned filter punch should be cleaned again in the sample oven prior to application.

NOTE: With small aliquots (e.g., ≤ 10 µL), disperse standard solution over one end of filter portion to ensure standard is in laser beam. To prevent possible solution loss to surface, hold the portion off the surface. Larger volumes can easily penetrate to the underside of the filter portion.

b. Allow water to evaporate and analyze spikes with samples and blanks (steps 9 and 10).

NOTE: A decrease in filter transmittance during the first temperature step of the analysis indicates water loss. Allow portions to dry longer if this occurs.

8. Determine instrument blank (results of analysis with freshly cleaned filter portion) for each sample set.

MEASUREMENT:

9. Set analyzer according to manufacturer's recommendations (see APPENDIX C). Place sample portion into sample oven.

NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite, some diesel particulate matter [DPM] collected in mines) may require a longer period and higher temperature during the 2nd part of the analysis to ensure that all EC is removed (the EC peak should never merge with the calibration peak). Adjust time and temperature accordingly. A maximum temperature above 940 °C should not be required.

10. Determine EC (and OC) mass, µg. Analyzer results are reported in units µg/cm^2 of C. The reported values are based on a sample portion of 1.5 cm^2, which is the area of the punch provided by the manufacturer. If the portion area differs from this value, multiply the reported result by 1.5 and divide the product by the actual area of the portion analyzed to obtain an area-corrected result (i.e., reported result x 1.5/actual punch area = corrected result in µg/cm^2).

CALCULATIONS:

11. Multiply the reported (or area-corrected) EC result (µg/cm^2) by filter *deposit area*, cm^2, (typically 8.55 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each filter sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b). (OC masses may be calculated similarly.)

12. Calculate EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} = \frac{W_{EC} - W_b}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Diesel exhaust is a chemically complex mixture containing thousands of compounds; therefore, some measure of exposure must be selected (See APPENDIX A). Rationale for selection of EC has been discussed elsewhere [1].

Because a suitable reference material is not available for determining the organic and elemental carbon content of a complex carbonaceous aerosol, only the accuracy of the method in the determination of total carbon (TC) could be examined. No discernable differences in the responses of five different organic compounds were noted. Linear regression of the data (43 analyses total) for all five compounds gave a slope and correlation coefficient (r) near unity [slope = 0.99 (± 0.01), r^2 = 0.999, n = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition to the OC standards, eight different carbonaceous materials were analyzed by the

thermal-optical method and the results were in good agreement with those reported by two other independent laboratories. These findings [1] indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon in a sample is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate determination of carbon in samples of unknown composition.

To calculate the estimated limit of detection (LOD) of the method (i.e.,≈ 0.24 µg C, or 0.15 µg/cm^2), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., µg C reported vs. actual) were then used to calculate the LOD as 3 σ_y/**m** (where σ_y is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = $3\sigma_{blank}$, which gives a value of ≈ 0.3 µg C. The mean (n = 40) instrumental blank was 0.03 (± 0.1) µg C.

Like all OC-EC methods, the thermal-optical method is an *operational* method in the sense that the analytical procedure itself defines the analyte. Of the possible approaches for OC-EC analysis, this particular technique was investigated because it offers greater selectivity (pyrolysis correction) and flexibility (automated analysis, programmable parameter files) than previously used methods. The method is considered unbiased (i.e., it is the reference method), and the overall precision reflects method accuracy. The S_r of the mean EC concentration found with fourteen samplers (two each of seven types) for collection of diesel exhaust in a loading dock area where a diesel truck was operating was 5.6% [1]. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n =14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [5] is fulfilled. The amount of EC collected (240 µg per sample) would be equivalent to sampling an EC level of 250 µg/m^3 for 8 h at 2 L/min.

In addition to this initial field test, laboratory-generated diesel particulate samples were analyzed. A dilution tunnel equipped with a dynamometer was used for generation of the samples. Four EC concentrations ranging from 23 to 240 µg/m^3 (EC loadings from 2.7 µg/cm^2 to 27 µg/cm^2) were generated. Again, analytical results indicate that the method meets the NIOSH accuracy criterion. The variance is roughly inversely proportional to mean concentration levels; therefore, the S_r decreases with increasing concentration. The accuracy was calculated accordingly. The pointwise accuracy is ± 16.7% at loadings as small as 2.7 µg/cm^2, where $\hat{S}_{rT}$ is 0.085.

When the thermal-optical method was evaluated [1] only one instrument existed. More recently, a private laboratory constructed additional instruments [6] (10 total: 7 in the U.S., 1 in Canada, 1 in Australia, 1 in Hong Kong). An interlaboratory comparison [7] was undertaken. Nine laboratories participated in the study, including four in Europe that employ an alternative thermal technique based on coulometric detection of CO_2. For the comparison, carbonaceous aerosols were collected on quartz-fiber filters (8" x 10") and portions of the filters were distributed to the participating laboratories for analysis in triplicate. Prior to distribution of the filter portions, multiple analyses were performed across all filters to ensure matched sample sets. Two aqueous solutions containing OC standards also were included in the sample sets. These standards provided a check on the accuracy of the TC data as well as a check on the pyrolysis correction feature of the thermal-optical method (both standards char during analysis).

As seen in a previous study [4], good agreement (within 15%) between TC values reported by all laboratories was obtained. In the analysis of samples containing diesel particulate, reasonable agreement was seen between the EC results obtained by each method (variability of the thermal-optical method was about 8% and variability for the coulometric method ranged from 9 to 23%). However, the EC content found by the two methods differed significantly. Given the operational nature of such methods, significant between-method variability was expected. Significant differences in the OC-EC results obtained by different methods also were reported previously [4].

With all filter samples, coulometric results were positively biased *relative* to thermal-optical results. In addition,

the coulometric method gave a true positive bias in the analysis of the OC standard solutions. About 52% and 70% of the carbon found in two aqueous solutions (sucrose and EDTA, respectively) were quantified as elemental, while EC contents of about 1% and 0.1% (respectively) were found by the thermal-optical method. The positive bias in the results for OC standards is attributed largely to inadequate removal of all OC during the first part of the analysis (maximum temperature ~ 550 °C); lack of correction for pyrolysis (char) also is a factor. Because no increase in transmittance was seen during the first stage (helium only) of thermal-optical analysis, use of a higher maximum temperature during this stage did not appear to cause loss of light-absorbing carbon. This implies that the EC results (filter samples) obtained with the coulometric method are positively biased. Elevating the maximum temperature of the thermal program gave better agreement with the thermal-optical method. Results of the intercomparison were presented at an international conference on element speciation [7]. Conference proceedings will be published in the journal *Analyst* during 1998.

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Different sampling requirements usually are required in the mining industry (see APPENDIX B).

REFERENCES:

[1] Birch ME, Cary RA [1996]. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aeros. Sci. And Techno. *25*:221-241.

[2] McCartney TC, Cantrell BK [1992]. A cost-effective personal diesel exhaust aerosol sampler. In: Diesels in underground mines: Measurement and control of particulate emissions (Information circular 9324), Proceedings of the Bureau of Mines information and technology transfer seminar, Minneapolis, MN, September 29-30, pp 24-30.

[3] Haney RA [1990]. Society for Mining, Metallurgy, and Exploration, AIME preprint 90-40, 7 pages.

[4] Countess, RJ [1990]. Interlaboratory analyses of carbonaceous aerosol samples, Aeros. Sci. and Technol. *12(1)*:114-121.

[5] Kennedy ER, Fischbach TJ, Song, R, Eller PM, Shulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

[6] Sunset Laboratory, 2017 19th Avenue, Forest Grove, Oregon 97116.

[7] Birch ME [1997]. Analysis of Carbonaceous aerosols: Methods comparison and health implications of exposure. Third International Symposium on Speciation of Elements in Biological, Environmental, and Toxicological Sciences, Port Douglas, Queensland, Australia, September 15-19, 1997.

[8] Birch ME, Cary RA [1996]. Elemental carbon-based method for occupational monitoring of particulate diesel exhaust: methodology and exposure issues. Analyst *121*:1183-1190.

[9] IARC [1989]. IARC monographs on the evaluation of carcinogenic risks to humans: diesel and gasoline exhausts and some nitroarenes. Vol. 46, Lyon, France: World Health Organization, International Agency for Research on Cancer, 458 pp.

[10] NIOSH [1988]. Current Intelligence Bulletin No. 50: carcinogenic effects of exposure to diesel exhaust. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 88-116.

[11] NIOSH [1992]. Recommendations for Occupational Safety and Health, Compendium of Policy Documents and Statements. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

[12] ACGIH [1997]. 1997 Threshold Limit Values (TLVs®) and Biological Exposure Limits (BEIs®). Cincinnati, OH: American Conference of Governmental Industrial Hygienists.

[13] Johnson RI, Jitendra JS, Cary RA, Huntzicker JJ [1981]. An automated thermal-optical method for

analysis of carbonaceous aerosol. In: Macias ES, Hopke PK, Eds., ACS Symposium Series No. 167, Atmospheric Aerosol: Source/Air Quality Relationships, American Chemical Society, Washington, D.C.
[14] DataChem Laboratories, 960 West Levoy Dr., Salt Lake City, Utah, 84123-2547.
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APPENDIX A. GENERAL

Diesel exhaust has been classified by IARC as a probable human carcinogen [9]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced [10,11]. Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Rationale for selection of EC has been provided elsewhere [1].

The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m^3 for diesel particulate [12]. The TLV is expressed in terms of submicrometer particulate matter, which includes the solid carbon core of diesel particulate and particle-adsorbed components. Other submicrometer aerosols will be collected as well (see APPENDIX B).

In general, three methods have been used for monitoring exposures to DPM: submicrometer particulate mass (gravimetric), respirable combustible dust (RCD; also gravimetric), and EC. These methods are mentioned in the draft TLV documentation, but the latter two (RCD and EC) do not give a direct measure of the stated analyte (submicrometer particulate). The RCD method targets the *respirable* fraction, not just submicrometer, and it is not a specific measure of DPM. The EC method is highly selective for diesel particulate, but the EC fraction of diesel particulate is variable, so a single constant cannot be used for extrapolation to submicrometer mass. Use of TC as a measure of diesel particulate has been considered because there is less variability in the carbon content of DPM. Although the TC fraction of DPM is relatively constant (typically 85% or more), other OC sources can interfere with the determination of the diesel-source carbon. A discussion of analytical methods is provided in the next appendix (APPENDIX B).

APPENDIX B. GUIDELINES ON METHODS

Gravimetric methods for DPM target submicrometer aerosol because diesel particulate is largely submicrometer and interference of larger dusts is minimized; however, if other submicrometer aerosols are present (e.g., cigarette smoke, fumes, oil mists) they will interfere in the gravimetric determination of diesel particulate. With personal monitoring, this approach is limited to relatively high concentrations because of poor sensitivity. This applies to the traditional gravimetric approach, as well as a "respirable combustible dust" (RCD) method used in the Canadian mining industry. RCD involves gravimetric determination of the combustible material on a silver membrane (or quartz-fiber) filter. The filter is weighed pre- and post-combustion, and the difference is considered RCD. This method is subject to interferences from other (nondiesel) respirable combustible matter and other potential problems (e.g., hygroscopic materials, negative bias with metal oxide formation).

A suitable impactor for personal monitoring of submicrometer particulate mass concentrations is not commercially available. A specialized impactor with a 0.8-µm cutpoint has been applied for the gravimetric determination of diesel particulate in underground coal mines. The cutpoint was based on bimodal particle size distributions found in dieselized underground coal mines, which is the only environment where the impactor must be used. Although it excludes most of the coal dust while collecting most of the diesel particulate, some sub-0.8-µm coal dust is collected. To determine the potential contribution of sub-0.8-µm, coal-source EC, laboratory studies and surveys of underground coal mines were conducted. When sampling a laboratory-generated, respirable coal dust concentration of 1.5 mg/m^3, a submicrometer TC concentration

of about 54 µg/m^3 was found, but the corresponding EC concentration was only about 8 µg/m^3. Even when the concentration of respirable coal dust was as high as 5 mg/m^3, which is more than 2.5 times the US compliance level, only a relatively low EC concentration was seen (EC = 30 µg/m^3; TC concentration = 156 µg/m^3). These results are in good agreement with those found in preliminary field studies. Only low levels ($\leq$15 µg/m^3) of EC were found in non-dieselized underground coal mines when a submicrometer cutpoint was used [8], indicating that the thermal-optical method could be applied in coal mines with only a minor contribution of coal-source EC if an impactor with appropriate design specifications is used. It is important to emphasize that the cutpoint of the prototype impactor was based on particle size distributions found in *coal mines*. Size distributions (of both diesel and non-diesel particles) found in coal mines may differ from those found in metal/nonmetal mines. With respect to diesel particles in particular, distributions might differ because water scrubbers are used in coal mines and these may affect particle size (e.g., by trapping larger respirable particles). If larger (e.g., 1 to 2 µm) diameter particles are present, these will be excluded if an impactor with a submicrometer cutpoint is used.

Unlike submicrometer particulate, RCD, and TC, EC is a specific marker of occupational exposure to diesel particulate, so use of an impactor is unnecessary (except in coal mines). In some workplaces, a preclassifier (e.g., cyclone) should be used with a 37-mm cassette (or alternative cassette giving an even deposit) as a "sample cleanup" step (e.g., to reduce loadings of inorganic dusts), but a submicrometer cut is not necessary. Although uneven deposition of larger particles (i.e., non-diesel) can occur, an even deposit of DPM is ordinarily found. If an uneven deposit should form, the entire filter must be analyzed (in portions) to quantify the total OC and EC.

Different samplers can be expected to give equivalent results for EC because diesel exhaust is a combustion aerosol (particle diameters generally $\leq$ 1 µm). As such, particles will be evenly deposited on the filter and collected with the same efficiency (near 100%). To confirm this assumption, seven different sampler types (open-faced, 25-mm and 37-mm cassettes; 298 personal cascade impactor (7 stages, 0.9 µm cutpoint); 4 prototype impactors) were used to collect diesel aerosol at the loading dock of an express mail facility. The S_r of the mean EC concentration found was only 5.6% [1]. Higher variability (about 12%) was seen in the OC result, which is expected when using filters to collect aerosol containing volatile and semivolatile components. Similar results were obtained when collecting samples in an underground molybdenum mine, where non-diesel particulate also was present. Five different sampler types were used (closed-face, 25-mm and 37-mm cassettes; 298 (7 stages, 0.9 µm cutpoint); cyclone with filter; in-house impactor). The S_r of the mean EC concentration found (297 µg/m^3) was only 7%. An even deposition of EC was obtained with all five sampler types, even when the deposit of other mine particulate was visually heavier in the center of the filter (e.g., with the closed-face 37-mm cassette). These results indicate that any of a variety of samplers can be used in some cases. In trona and limestone mines, a cyclone should be used to minimize the amount of carbonate collected (non-respirable-sized particles in particular). Specificity of the OC (and TC) determination can be even further improved by removal of carbonate through acidification of the sample portion (see APPENDIX C). Although an impactor can improve the selectivity of an OC measurement (and TC) in some cases, it will not necessarily do so because OC interferences are often submicrometer as well (e.g., oil mists, fumes, cigarette smoke).

APPENDIX C. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION

In the thermal-optical analysis of carbonaceous aerosols, speciation of organic and elemental carbon is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below (Figure 1). The instrument is a modified version of a design previously described in the literature [13]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). Laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850 °C are employed during the analysis, quartz-fiber filters are required. A punch from the sample filter is taken for analysis, and organic and elemental carbon are reported in terms of µg per cm^2 of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. Just prior to the end of the

analysis (i.e., after EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate (if present) carbon are evolved in a helium atmosphere as the temperature is stepped to about 850 °C (750 °C if EC loss is evident). The evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2, then reduced to CH_4 in a Ni/firebrick methanator. CH_4 is quantified by an FID. In the second stage, the sample oven temperature is reduced, an oxygen-helium mix is introduced, and the temperature is stepped (to about 940 °C). As oxygen enters the oven, pyrolytically generated carbon (PC) is oxidized and a concurrent increase in filter transmittance occurs (see Figure 2). The point at which the filter transmittance reaches its initial value is defined as the "split" between OC and EC. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered elemental (EC).

The presence of carbonate can be verified by exposing a second portion of the filter to HCl vapor prior to analysis. Place the portion in a petri dish containing concentrated HCl (Place the portion on a microscope slide inside the dish to prevent direct contact with acid), cover, and expose to HCl vapor for about 1 h (less for fine particles, more for large particles). After acidification, remove the portion from the dish, transfer to a clean surface (e.g., Pyrex dish, aluminum foil) in a hood and allow acid vapor to volatilize for at least 30 minutes before analyzing. When the acidified sample is analyzed, absence of the suspect peak is indicative of carbonate in the original sample. The difference between the OC results obtained for the two portions (i.e., before and after acidification) gives an estimate of carbonate-source carbon (presuming it is evenly deposited on the filter). Acid treatment may change the appearance of the carbon profile, but the EC result itself should not be affected. More recent versions of the calculation software allow estimation of carbonate carbon through integration of the carbonate peak.

Currently, only three laboratories [6,14,15] perform thermal-optical analysis on a commercial basis, and the commercial availability of the instrument has been limited to a single supplier [6]. To continue support of the new method, a collaborative effort between NIOSH and external partners is planned.

Currently, only three laboratories [6,14,15] perform thermal-optical analysis on a commercial basis, and the commercial availability of the instrument has been limited to a single supplier [6]. To continue support of the new method, a collaborative effort between NIOSH and contract laboratories is planned.

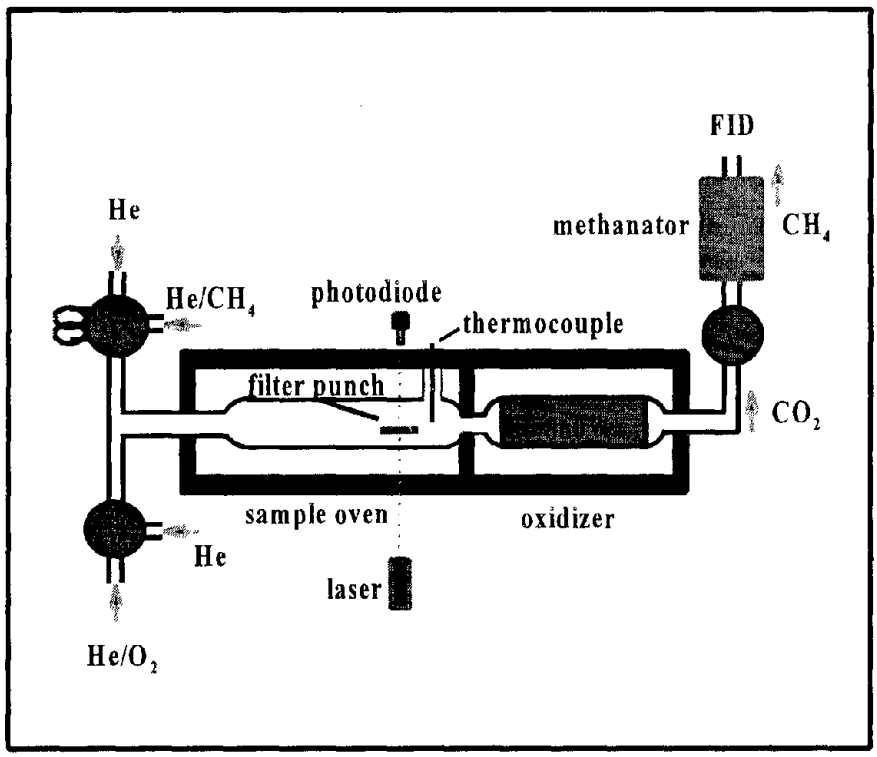


Figure 1. Schematic of Thermal-Optical Instrument (V=valve)

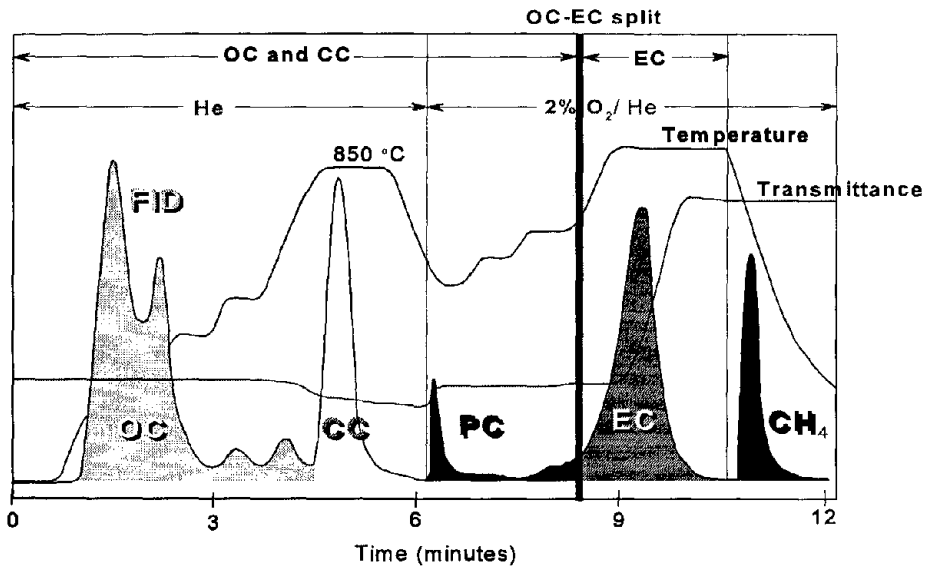


Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources are pulverized sugar beet pulp, rock dust (carbonate), and diesel particulate.

ELEMENTS by ICP 7300

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

METHOD: 7300, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

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

PROPERTIES: Table 1

ELEMENTS:

aluminum*	chromium*	lithium*	phosphorus	tellurium	zinc
aresenic	cobalt*	magnesium	platinum*	thallium	zirconium*
beryllium*	copper	manganese*	selenium	titanium	
Cadmium	iron	molybdenum*	silver	vanadium	
calcium	lead*	nickel	sodium	yittrium	

*Some compounds of these elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane)

FLOWRATE: 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 ($\hat{S}$): 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 ($\hat{S}$): 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.

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.

* See SPECIAL PRECAUTIONS.

** 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% HNO3/1% HClO4:

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, Cs (μg/mL), and the average media blank, Cb (µg/mL), from the instrument.
18. Using the solution volumes of sample, Vs (mL), and media blank, Vb (mL), calculate the concentration, C (mg/m3), 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.

REFERENCES:

[1] Hull, R.D. "Multielement Analysis of Industrial Hygiene Samples," NIOSH Internal Report, presented at the American Industrial Hygiene Conference, Portland, Oregon (May 1981).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 351, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
[3] Ibid, S341 (Lead).
[4] Ibid, V. 2, S5 (Manganese), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Ibid, V. 4, P&CAM 271 (Tungsten), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] Ibid, V. 5, P&CAM 173 (Metals by Atomic Absorption), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

[7] Ibid, V. 3, S183 (Tin), S185 (Zirconium), and S376 (Molybdenum), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[8] DataChem Laboratories, NIOSH Sequence 7998-J (NIOSH/DPSE, unpublished, April 12, 1994).
[9] DataChem Laboratories, NIOSH Sequence 7396-K (NIOSH/DPSE, unpublished, February 4, 1992).
[10] DataChem Laboratories in-house procedure for microwave sample digestion.
[11] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, SW-846 (1986).
[12] Kingston, H.M. and L.B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory." Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, (1988).
[13] 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water; ASTM, Philadelphia, PA, D1193 - 77 (1985).
[14] Introduction to Microwave Sample Preparation: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington DC (1988).
[15] Kingston, H.M. EPA IAG #DW1-393254-01-0 January 1 - March 31, 1988, Quarterly Report.
[16] Binstock, D.A., Yeager, W.M., Grohse, P.M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460 (November, 1989).

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: Atomic Weight	Properties: MP, °C	Air Volume, L @ OSHA PEL: MIN	Air Volume, L @ OSHA PEL: 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	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Platinum (Pt)	195.09	1769	1250	2000
Selenium (Se)	78.96	217	13	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/m³ (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	0.05
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 (S_r) (N = 3) @ 2.5 µg/ filter	Precision (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 µg/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 the following table.

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.

EPICHLOROHYDRIN 1010

CH_2OCHCH_2Cl MW: 92.53 CAS: 106-89-8 RTECS: TX4900000

METHOD: 1010, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1990**
Issue 2: 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: lowest feasible (carcinogen)
ACGIH: 2 ppm (skin) (carcinogen)
(1 ppm = 3.78 mg/m3 @ NTP

PROPERTIES: liquid; d 1.1812 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

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/m3 [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 CS2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 215 °C
-COLUMN: 135 °C

CARRIER GAS: N2 or He, 20 mL/min

COLUMN: 1.8 m x 2-mm ID glass; 80/100 Chromosorb 101 [1]

CALIBRATION: epichlorohydrin in CS2

RANGE: 0.04 to 1.2 mg per sample [2]

ESTIMATED LOD: 1.0 µg per sample

PRECISION ($\hat{S}r$): 0.031 [2]

APPLICABILITY: The working range is 0.5 to 16 ppm (2 to 60 mg/m3) 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 CS2.

* 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 CS2 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 CS2 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 CS2, 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 (Wf) and back (Wb) sorbent sections, and in the average media blank front (Bf) and back (Bb) sorbent sections.
    NOTE: If Wb > Wf/10, report breakthrough and possible sample loss.
14. Calculate concentration, C, of epichlorohydrin in the air volume sampled, V (L):

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

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/m3 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 WRITTEN (REVISED) BY:

James E. Arnold, NIOSH/DPSE; S118 validated under NIOSH Contract CDC-99-74-45.

$CH_2(O)CH_2$ 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

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/m³) 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. Pipets, volumetric, 2- to 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":

$$\frac{1.763\ \text{g}\ \ 2\text{-BrEt}}{10\ \text{mL}} \cdot 0.95 \cdot \frac{44.05}{124.97} \cdot 10^6\ \mu\text{g} = 59{,}036\ \mu\text{g EtO/mL}.$$

       Standard Solution "B":

       3 mL • 59,030/25 mL = 7084 µg EtO/mL.

       Standard Solution "C":

       1 mL • 7084/10 mL - 708.4 µg 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:

[1] Cummins, K.J. OSHA Method No. 50, "Ethylene Oxide," OSHA Analytical Laboratory, Salt Lake City, UT (unpublished, January, 1985).
[2] User check, DataChem, Inc., NIOSH Seq. #5860-J (unpublished, May 15, 1987).
[3] NOSH Manual of Analytical Methods, 2nd. ed., V. 3, S286, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157C (1977); also cited in NIOSH Special Occupational Hazard Review with Control Recommendations - Use of Ethylene Oxide as a Sterilant in Medical Facilities, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-200 (1977).
[4] Threshold Limit Values and Biological Exposure Indices for 1993-94, ACGIH, Cincinnati, OH (1993).
[5] NIOSH Testimony to USDOL at OSHA rulemaking hearing for ethylene oxide (July 20, 1983); also see Current Intelligence Bulletin 35, "Ethylene Oxide," U.S. Department of Health and Human Services, Publ. (NIOSH) 81-130 (May 22, 1981).
[6] 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.
[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:

George Williamson, NIOSH/DPSE.

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:

$$\frac{mg\ EtO}{mL\ EtO\ stock\ solution} = (N_o - N_s) \cdot \frac{20\ mL}{10^3\ mL} \cdot \frac{44.05\ g}{1\ equivalent} \cdot \frac{1}{2\ mL} \cdot \frac{10^3\ mg}{1\ g} = (N_o - N_s) \cdot 440.5$$

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/m³ (fluorides); 3 ppm (HF)
NIOSH: 2.5 mg/m³ (fluorides); 3 ppm (HF); STEL 6 ppm (HF)
ACGIH: 2.5 mg/m³ (fluorides); C 3 ppm (HF)
(1 ppm HF = 0.818 mg/m³ @ 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/m³ (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: 1.25 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/m³) and 1.2 to 8 mg/m³ 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, 1.25 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):

$$C_p = \frac{W_p V_p - B_p V_{pb}}{V}, \ mg/m^3 \qquad C_g = \frac{W_g V_g - B_g V_{gb}}{V}, \ mg/m^3.$$

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 ($\hat{S}_r$) 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).
[5] 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).
[6] Einfeld, W. and S.W. Hoestmann. Investigation of a Dual Filter Sampling Method for the Gaseous and Particulate Fluorides. Am. Ind. Hyg. Assoc. J. 40(7), 626 (1979).
[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 #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD WRITTEN BY:

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FORMALDEHYDE 2016

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2016, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA : 0.75 ppm; 2 ppm STEL
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 % (v/v) in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v formaldehyde), methylene oxide

SAMPLING

SAMPLER:	CARTRIDGE (Silica gel containing cartridge coated with 2,4-dinitrophenylhydrazine)
FLOW RATE:	0.1 to 1.5 L/min
VOL-MIN:	1 L @ 0.6 mg/m^3
-MAX:	15 L @ 2.5 mg/m^3
SHIPMENT:	Place caps on cartridge. Ship cold.
SAMPLE STABILITY:	14 days @ 4 °C
BLANKS:	2 to 10 field blanks per set 6 to 10 media blanks per set

ACCURACY

RANGE STUDIED:	0.025 to 2.45 mg/m^3 [1] (22-L sample)
BIAS:	+ 4.4%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.057 [1]
ACCURACY:	± 19.0%

MEASUREMENT

TECHNIQUE:	HPLC, UV DETECTION
ANALYTE:	2,4-dinitrophenylhydrazone derivative of formaldehyde
EXTRACTION:	10 mL carbonyl-free acetonitrile eluted through the cartridge @ 3 mL /min
INJECTION VOLUME:	20 µL
MOBILE PHASE:	45% acetonitrile/55% water (v/v), 1.3 mL/min, isocratic
COLUMN:	C_{18}, 150 x 3.9-mm, 5-µm particles (with a C_{18} guard column), Symmetry™ or equivalent
DETECTOR:	UV @ 360±2 nm
CALIBRATION:	standard solutions of formaldehyde spiked onto samplers
RANGE:	0.60 to 38 µg per sample [1,2]
ESTIMATED LOD:	0.04 µg per sample [1]
PRECISION ($\bar{S}_r$):	0.023 @ 2.2 to 46.4 µg per sample [1]

APPLICABILITY: The working range is 0.025 to 2.5 mg/m^3 for a 15-L air sample. This method can be used for the determination of formaldehyde for both STEL and TWA exposures.[1]

INTERFERENCES: Ozone has been observed to consume the 2,4-DNPH reagent and degrades the hydrazone derivative. Other aldehydes may react with the 2,4-DNPH but can be chromatographically resolved under appropriate conditions.

OTHER METHODS: NIOSH Method 5700 [2] uses a similar analysis procedure. The analysis procedure used in this method has also been used for the determination of formaldehyde in automobile exhaust [3]. Other methods available for formaldehyde analysis include OSHA Method 52 [4], NIOSH methods 3500 [5], and 2541 [6].

REAGENTS:

1. 2,4-Dinitrophenylhydrazine (DNPH), recrystallized from ethanol.
2. Formaldehyde stock solution,* 1 mg/mL (see APPENDIX).
3. DNPH derivative of formaldehyde (MW=210.15) [7]. Derivative is commercially available from Supelco, Inc.
4. Acetonitrile, distilled in glass, low carbonyl content.**
5. Ethanol, absolute, low carbonyl content.**
6. Calibration stock solution. Dissolve 40 mg formaldehyde DNPH derivative and 50 mg DNPH in 100 mL of acetonitrile.
7. Water, deionized and distilled.

* See SPECIAL PRECAUTIONS

** Carbonyl content of the solvents can be determined by mixing the solvent with DNPH-coated sorbent and analyzing by HPLC. Formaldehyde content should be similar to sorbent tube manufacturer's specification.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 500-1000 µm silica gel coated with 0.9 mg 2,4-dinitrophenylhydrazine. Pressure drop across the sampler should be less than 20 inches of water (5 kPa) at 1.5 L/min. Samplers are commercially available. (Waters Sep-Pak XPoSure Aldehyde Sampling Cartridge; similar types of samplers are manufactured by Supelco [Supelclean LPD DNPH Cartridge, part no. WAT047205] and SKC [catalog no. 226-119, DNPH coated silica gel tube].)
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible polyethylene or PTFE tubing.
3. Vials, 4-mL glass.
   NOTE: DO NOT use vials with 'polycone' liners (source of high formaldehyde blank).
4. Liquid chromatograph with UV detector, recorder, integrator, and column (page 2016-1).
5. Syringes, 10-, 25-, 50-, 100- and 1000-µL.
6. Volumetric flasks, 10-, 100-mL and 1-L.
7. Pipets, 0.1-, 0.5-, 1.0-, and 3-mL glass, delivery, with pipet bulb.
8. Graduated cylinders, glass, 25-mL.
9. Equipment for standardizing formaldehyde stock solution, Burets, 50-mL.
10. pH meter.
11. Magnetic stirrer.
12. Beaker, 50-mL.
13. Disposable syringes, 10-mL.
14. Disposable syringe filters

SPECIAL PRECAUTIONS: Formaldehyde is a suspect carcinogen [9] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. Sampler is bi-directional (Waters and Supelco) and can be connected at either end.
   NOTE 1: The sampler has no backup section to detect breakthrough. If high concentrations are anticipated, connect two samplers in series. The back pressure of the sampling train will be increased and flow rate limited.
   NOTE 2: The glass tube can be sampled in one direction with the larger bed in the front. These samplers have a backup section, and should not be used in tandem.
4. Sample 1 to 15 L of air at 0.1 to 1.5 L/min flow rate.
5. Replace end caps on the sampler and return sampler to packet with appropriate sampling information included. Keep samples away from heat (e.g., storage in automobile, etc.)
6. Ship samples on ice, if possible. Samples are stable at room temperature for 4 days before significant analyte losses are observed.

SAMPLE PREPARATION:

NOTE: Check acetonitrile for formaldehyde content by eluting a blank cartridge. The formaldehyde levels should be below the limit of detection. Since background formaldehyde levels on the samplers may change during storage and/or the acetonitrile may become contaminated, always compare samples to a sampler blank from the same lot, stored under the same conditions.

7. a. Elute the formaldehyde derivative from cartridge samplers with 10 mL of acetonitrile into a 10-mL volumetric flask. Control rate of elution to <3 mL/min. Higher flow rates may result in reduced recovery of formaldehyde. Add acetonitrile to the flask to make the total volume 10 mL.
   b. For the glass sorbent tube, place front and back sorbent sections into separate 4-mL vials, add 3 mL of acetonitrile to each vial, and allow to stand for 30 to 60 min with frequent agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Pipet aliquots of calibration stock solution (e.g., 10, 50, 100, 300, and 1000 µL) into 10-mL volumetric flasks.
   b. Bring the volume of each working standard to 10 mL acetonitrile.
   b. Transfer a 3-mL aliquot to a 4-mL vial, cap the vial, and analyze (steps 11 through 14).
   c. Prepare a calibration graph, peak area vs. µg formaldehyde.
9. Determine recovery of formaldehyde from sampler.
   a. Add aliquots (≥50 µL) of a calibrated formaldehyde solution to unused samplers to prepare recovery standards. Recovery is expected to be between 95-100%.
      NOTE: If the volume of calibrated formaldehyde solution to be added is less than 50 µL, prepare a 1:10 or 1:100 dilution of the calibrated formaldehyde solution, so the volume added is 50 µL or more. Then draw a small volume (10 mL) of air through the sampler with a disposable 10-mL syringe to pull the solution into the sorbent bed. In cases where the glass sampling tubes are used, the solution volume added should be 10 to 30 µL to prevent flooding the tube.
   b. Desorb the recovery standards in the same manner as the samplers (step 7).
   c. Analyze working standards together with samples and blanks (steps 11 through 14).
   d. Prepare calibration graph of recovery vs. amount (µg) of formaldehyde added.
10. Analyze three quality control spikes and three analyst spikes to ensure that calibration and recovery graphs are in control.

MEASUREMENT:

11. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2016-1.
12. Transfer a 3-mL aliquot of the solution from step 7. to a 4-mL vial. Cap the vial.
13. Inject a 20-µL sample aliquot.
14. 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 acetonitrile , reanalyze, and apply appropriate dilution factor in the calculations.
    NOTE 2: To ensure validity of the samples, all samples containing over 6 to 7 µg/mL should be reported as a lower limit and the samples recollected at a lower total sample volume, since the maximum amount of formaldehyde that can react with 2,4-dinitrophenylhydrazine is 70 µg. In these instances, the capacity of the sampler may have been exceeded
    NOTE 3: The peak area for the DNPH peak should be at least 20 % of the formaldehyde-DNPH peak. If the DNPH peak area is less than this amount, then the capacity of the sampler may have been exceeded and the analytical results will be biased low. If this situation is observed the sample results may be reported as a lower limit and the workplace resampled using a smaller total sample volume.

CALCULATIONS:

19. Determine mass, µg, of formaldehyde, W, found in the sample and the average media blank, B, from the calibration graph.
    NOTE: Include dilution factor for any sample which exceeded the highest calibration standard.
20. Calculate concentration, C, of formaldehyde in the air volume sampled, V (L).

$$C = \frac{W - B}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

The evaluation of this method was based in part on data generated at NIOSH and Waters Corporation. Generated sample results were provided by Waters [1] and spiked sample results were obtained at NIOSH. This method was evaluated over the range of 0.5 to 55 µg/sample. Overall measurement precision, $\hat{S}_{rT}$, was 0.057 based on NIOSH guidelines [8] including a 5% pump error factor and estimated bias was +4.4%. Sample stability during storage was evaluated over the range of 0.5 to 55 µg formaldehyde/sample. Samples showed from 1 to 20% loss (dependent on loading) after storage for 7 days at ambient temperature and 4 to 7% loss when stored up to 14 days at 4 °C, compared to one-day old samples. An additional study found that losses were 5% or less after 4 days' storage at ambient temperature.

Capacity of the sampler was found to vary with relative humidity (RH). When sampling a concentration of 2.5 mg/m^3 of formaldehyde, capacity of the sampler to collect formaldehyde at 85% RH was 95 µg and at 10% RH, 59 µg. Based on this information, a maximum capacity of 38 µg was calculated. The limit of quantitation of the method for formaldehyde was 0.6 µg per sampler. This corresponds to a concentration of 0.02 ppm in a 22.5 liter sample.

The method can be used for the measurement of both STEL and time weighted average exposure measurements. The estimated accuracy of the method is 19% with a 95% confidence interval of 16 to 22%. The upper 95% confidence limit on accuracy for the method is 22%, which meets the NIOSH accuracy criterion of ±25% [8].

REFERENCES:

[1] Iraneta PC, Collamati RA, Costello DN, Crowley RJ, Fernandes RL, Hopkins MR, Knowles CE, Martin DM. A validation study of a new active sampler for the analysis of formaldehyde in workplace and indoor air. Am Ind Hyg Assoc J: In press.

[2] NIOSH [1994]. Formaldehyde: Method 5700. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] Lipari F, Swarin S [1982]. Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4-dinitrophenylhydrazine method. J Chromatography *247*:297-306.

[4] OSHA [1985]. Method 52. OSHA Analytical Methods Manual. Salt Lake City, UT: U. S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory.

[5] NIOSH [1994]. Formaldehyde: Method 3500. In:Eller PM, Cassinelli ME, Ed. NIOSH Manual of Analytical Methods (NMAM),4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[6] NIOSH [1994]. Formaldehyde: Method 2541. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM),4th ed. Cincinnati, OH: National Institute for Occupational Safety snd Health, DHHS (NIOSH) Publication No. 94-113.

[7] Waters Corporation [1994]. Waters Sep-Pak XPoSure Aldehyde Sampler Care and Use Manual. Milford, MA: Waters Corporation:p. 31.

[8] Kennedy ER, Fischbach TJ, Song R, Eller PE, Shulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

[9] NIOSH/OSHA [1981]. Occupational health guidelines for occupational hazards. U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health ,DHHS (NIOSH) Publication No. 81-123. Available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, D. C. 20402.

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:

$$C_s = \frac{30.0\ (N_a\ V_a - N_b\ V_b)}{V_s}$$

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)

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 ($\hat{S}_r$): 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).
   NOTE: The hydrochloride salt provides an acid catalyst for the reaction of glutaraldehyde with the dinitrophenylhydrazine. Other acids may be used as catalyst.
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. The hydro
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:

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APPENDIX: PREPARATION AND STANDARDIZATION OF GLUTARALDEHYDE STOCK SOLUTION

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).

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

METHOD: 5523, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA : No PEL
NIOSH: No REL
ACGIH: C 50 ppm (ethylene glycol)
(1 ppm = 2.54 mg/m³ @ NTP)

PROPERTIES: See Table 1

NAMES & SYNONYMS: (1) ethylene glycol: 1,2-ethanediol; (2) propylene glycol: 1,2-propanediol
(3) 1,3-butylene glycol: 1,3-butanediol (4) diethylene glycol: 2-hydroxyethyl ether, 2,2'-oxydiethanol

SAMPLING

SAMPLER: XAD-7 OVS tube (glass fiber filter, 13-mm; XAD-7, 200mg/100mg)

FLOW RATE: 0.5 to 2 L/min

VOL-MIN: 5 L
-MAX: 60 L

SHIPMENT: pack cold for shipment

SAMPLE STABILITY: 28 days @ 5 °C [1]
ethylene glycol 14 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: compounds above

DESORPTION: 2 mL methanol; ultrasonicate 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 40 °C, 8 °C/min to 230 °C

CARRIER GAS: He_2 @ 2.4 to 2.6 mL/min

COLUMN: Rtx-35 fused silica capillary, 30 m, 0.53-mm ID, 3-µm film

CALIBRATION: solutions of glycols in methanol

RANGE: 15 to 800 µg/sample

ESTIMATED LOD: see Table 2

PRECISION ($\bar{S}_r$): 0.04 to 0.09 [1]

APPLICABILITY: Under the GC parameters given in the method, the glycols listed above are baseline separated and can be identified based on retention time and quantified. Hexylene glycol can be determined by this method; however, no sampling or analytical evaluation has been conducted.

INTERFERENCES: No specific interferences were identified. The method yields baseline separation for all analytes.

OTHER METHODS: This method replaces NMAM 5500 [2], which was found deficient in the collection of ethylene glycol in aerosol form. Also ethylene glycol was not separated from propylene glycol by the chromatography.

REAGENTS:

1. Ethylene glycol, reagent grade.*
2. Propylene glycol, reagent grade.*
3. 1,3-Butylene glycol, reagent grade.*
4. Diethylene glycol, reagent grade.*
5. Triethylene glycol, reagent grade.*
6. Tetraethylene glycol, reagent grade.*
7. Methanol, chromatographic grade.*
8. Calibration stock solution, 10 mg/mL: Weigh aliquots of each glycol and dissolve in methanol.
9. Helium, purified.
10. Hydrogen, prepurified.
11. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: XAD-7 OVS tube, 13-mm OD, containing two sections of XAD-7 (200 mg front/100 mg back section) separated by polyurethane foam plug. A glass fiber filter plug precedes the front section and a polyurethane foam plug follows the back section. Tubes are commercially available (SKC, Inc., #226-57).
2. Personal sampling pump, 0.5 to 2 mL/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (page 5523-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Vials, 4 mL, with screw caps.
7. Syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.

SPECIAL PRECAUTIONS: Inhalation of glycol mists causes respiratory irritation, shortness of breath, and coughing. Methanol is flammable and a dangerous fire risk. Work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove front and rear caps from the tube immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 5 to 60 L.
4. Cap the samplers and pack securely in dry ice for shipment.

SAMPLE PREPARATION:

5. Place front sorbent section and glass fiber filter in a 4-mL screw cap vial. Place backup sorbent section in a separate vial. Discard foam plugs.
6. Add 2 mL of methanol to each vial and cap.
7. Place vials in an ultrasonic bath for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.
   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 (peak area or height vs. µg glycol).
9. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 8).
   a. Prepare three samplers at each of six levels plus three media blanks.

b. Inject a known amount of calibration stock solution directly onto the filter of OVS tubes. Draw air through the sampler at 1 L/min for 60 min.
c. Cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with standards and blanks (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 ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5523-1. 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 the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of each glycol 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 each 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:

The method was evaluated for six glycols (ethylene, propylene, 1,3-butylene, diethylene, triethylene, and tetraethylene). Desorption efficiency (DE) was determined by spiking known amounts of each glycol in methanol solution onto the glass fiber filter plug of the XAD-7 OVS tubes, drawing air through the spiked tubes at 1 L/min for 60 min, and analyzing. Recovery data along with LODs and LOQs for each analyte are listed in Table 2. When stored at 5 °C, ethylene glycol samples on XAD-7 OVS tubes were stable for 14 days, and the other glycols were stable up to 28 days. Glycol aerosols were generated at three concentration levels (6 samples per concentration) from a ROSCO™ Model 1500 Fog Machine. Precision [as calculated from the pooled relative standard deviation ($\bar{S}_r$)] and mean bias for the glycols are as follows:

Analyte	Range Studied (µg/sample)	Precision ($\bar{S}_r$)	Bias
Ethylene glycol	33 to 218	0.043	-15%
Propylene glycol	26 to 187	0.062	-3.2%
1,3-butylene glycol	34 to 178	0.054	-0.5%
Diethylene glycol	68 to 219	0.047	-0.2%
Triethylene glycol	33 to 201	0.075	-4.0%
Tetraethylene glycol (2 levels)	32 to 197	0.035	+20%

The low recovery for ethylene glycol possibly may be attributed to increased volitility when sampled at 1 L/min [1]. Although hexylene glycol is separated by the chromatographic conditions given in the method, no evaluation of sampling or analytical parameters was done for this compound.

REFERENCES:

[1] Pendergrass, S.M. [1994]. Development of a sampling and analytical methodology for the determination of glycols in air: Application to theatrical smokes. Unpublished paper presented at Pittsburgh Conference, Chicago, IL, March 1994.

[2] NIOSH [1984]. Ethylene glycol: Method 5500. In: Eller PM, Ed. NIOSH manual of analytical methods, 3rd ed. Cincinnati, OH: U.S. Department of Health and Human Services, HHS (NIOSH) Publication No. 84-100.

METHOD WRITTEN BY:

Stephanie M. Pendergrass, MRSB, DPSE

TABLE 1. GLYCOLS GENERAL INFORMATION

Analyte	Formula	MW	CAS #	RTECS #	Properties
Ethylene glycol	$C_2H_6O_2$	62.07	107-21-1	KW2975000	liquid; BP 197.2 °C; FP -13 °C; d 1.113 g/mL @ 20 °C; n_D 1.4310; vp 0.007 kPa (0.05 mm Hg) @ 20 °C; explosive limits 3.2 to 15.3% v/v in air
Propylene glycol	$C_3H_8O_2$	76.10	57-55-6	TY2000000	liquid; BP 188 °C; FP -60 °C ; d 1.038 g/mL @ 20 °C; n_D 1.4320; vp 0.009 kPa (0.07 mm Hg) @ 20 °C; explosive limits 2.6 to 12.5% v/v in air
1,3-Butylene glycol	$C_4H_{10}O_2$	90.12	107-88-0	EK0440000	liquid; BP 207.5 °C; d 1.0059 g/mL @ 20 °C; n_D 1.4400; vp 0.06 mm Hg @ 20 °C
Diethylene glycol	$C_4H_{10}O_3$	106.12	111-46-6	ID5950000	liquid; BP 245 °C; FP -6.5 °C; d 1.118 g/mL @ 20 °C; n_D 1.4460 @ 25 °C; vp <0.01 mm Hg @ 20 °C; explosive limits 3 to 7% v/v in air
Triethylene glycol	$C_6H_{14}O_4$	150.17	112-27-6	YE4550000	liquid; BP 285 °C; FP -5 °C; d 1.125 g/mL @ 20 °C; n_D 1.4550; vp <0.001 mm Hg @ 20 °C; explosive limits 0.9 to 9.2% v/v in air
Tetraethylene glycol	$C_8H_{18}O_5$	194.23	112-60-7	XC2100000	liquid; BP 327.3 °C; FP -4 °C; d 1.125 g/mL @ 20 °C; n_D 1.4577; vp >0.001 mm Hg @ 20 °C

TABLE 2. GLYCOL RECOVERY DATA

Analyte	LOD (µg/sample)	LOQ (µg/sample)	Desorption Efficiency Spikes[a]		$\bar{S}_r$[b]
			100 µg (% Recovery)	200 µg (% Recovery)	
Ethylene glycol	7	22	93.4	101	0.059
Propylene glycol	6	13	83.4	92.5	0.064
1,3-Butylene glycol	6	12	98.8	102	0.072
Diethylene glycol	16	48	94.6	114	0.041
Triethylene glycol	14	42	85.3	98.7	0.043
Tetraethylene glycol	14	42	111	141	0.092

[a] n = 6 for each spiking level
[b] Pooled Relative Standard Deviation

2,4-TDI: $CH_3C_6H_3(NCO)_2$	MW: 174.16	CAS: 584-84-9	RTECS: 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

METHOD: 5522, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**
Issue 2: 15 January 1998

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

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

SAMPLER: IMPINGER (tryptamine/DMSO; 20 mL)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L @ 35 µg/m³ TDI
-MAX: 360 L

SHIPMENT: ship in screw cap vial

SAMPLE STABILITY: at least 28 days in dark @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

BULK: isocyanate-based oligomers, 1 to 2 mL

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, FLUORESCENCE DETECTOR/ ELECTROCHEMICAL DETECTOR

ANALYTE: tryptamine derivatives of isocyanates

INJECTION VOLUME: 25 µL

MOBILE PHASE: acetonitrile (40 to 50%)/0.6% sodium acetate buffer (60 to 50%); 1 mL/min

COLUMN: 3.9-mm ID x 150 mm stainless steel packed with 10-µm µ-Bondapak C_{18}, or equivalent

DETECTOR: fluorescence: ex 275 nm; em 320 nm (electrochemical, +0.80V - confirmatory)

CALIBRATION: tryptamine derivatives in sampling medium

RANGE:
2,4-TDI: 0.3 to 14.0 µg/sample
2,6-TDI: 0.6 to 14.0 µg/sample
MDI: 1.0 to 10.0 µg/sample
HDI: 0.6 to 20.0 µg/sample [1]

ESTIMATED LOD:
2,4-TDI: 0.1 µg/sample
2,6-TDI: 0.2 µg/sample
MDI: 0.3 µg/sample
HDI: 0.2 µg/sample [1]

PRECISION ($\hat{S}_r$): 2,4-TDI: 0.059 MDI: 0.029
2,6-TDI: 0.062 HDI: 0.045 [1]

APPLICABILITY: The working range for TDI is 10 to 250 µg/m³ for a 50-L air sample. This method determines the air concentration of monomers and estimates the concentration of oligomers of specific diisocyanates. It is applicable to vapors and aerosols, such as those produced in a spray-painting operation. The method is not applicable to mixtures of different isocyanates, nor to condensation aerosols from inefficient collection by impingers.
NOTE: This method should be used for area sampling only because of the potential exposure hazard from DMSO solutions.

INTERFERENCES: Any substance which elutes with the tryptamine derivatives and fluoresces will interfere with the analysis, e.g., some aromatic diamines. Mobile phase conditions can be adjusted to separate most co-eluting peaks.

OTHER METHODS: This method is a modification of a method developed by the Occupational Health Laboratory, Ontario Ministry of Labour [2]. NIOSH Method 5521 is an alternate method for the determination of monomers of 2,4-TDI, 2,6-TDI, MDI, and HDI.

REAGENTS:

1. Water, deionized, distilled.
2. Acetonitrile, HPLC grade.
3. Dimethyl sulfoxide (DMSO), HPLC grade.*
4. Sodium acetate trihydrate.
5. Glacial acetic acid, reagent grade.
6. Toluene, HPLC grade.
7. *n*-Propanol, reagent grade.
8. Heptane, reagent grade.
9. Buffer solution: Dissolve 20.4 g sodium acetate trihydrate in 2 L distilled-deionized water. Add glacial acetic acid to pH 5.5.
10. Mobile phase, acetonitrile and buffer solution.
11. Sampling medium, 450 µg/mL,
    (a) For sampling in ambient temperatures >60 °F: tryptamine, 99+% pure, in DMSO;
    (b) For ambient temperatures <60 °F: 80/20 (v/v) DMSO/ acetonitrile containing tryptamine, 99+% pure.
    NOTE: Recrystallize tryptamine in acetonitrile before use. (Stable up to 6 mo. in the dark at ambient temperature.)
12. Tryptamine derivatives of isocyanates* (See APPENDIX).
13. Helium. prepurified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Midget impinger containing 20 mL sampling medium.
2. Personal sampling pump, 1 to 2 L/min, with flexible tubing.
3. HPLC, fluorescence detector, ex 275 nm, em 320 nm; integrator and column (page 5522-1). (Electrochemical detector for confirmation of fluorescent peaks.)
4. Vials, 20-mL, scintillation, and 40-mL opaque, with PTFE-lined caps.
5. Pipets, 20-mL.
6. Cylinders, graduated, 25-mL.
7. Syringes, 25-µL, or fixed sample loop.
8. Volumetric flasks, 10-mL.
9. Fritted glass funnel.
10. Filtering flasks.
11. Sealing bands.

SPECIAL PRECAUTIONS: Isocyanates are known respiratory irritants. Prepare standards and derivatives in a fume hood. DMSO is readily absorbed into the skin. Wear neoprene latex gloves when handling the solvent, sampling media, and field samples [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 20 mL sampling medium to an impinger, and connect to sampling pump with flexible tubing.
   NOTE: Prepare field blank samples by transferring 20 mL sampling medium to 20-mL vials.
3. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 15 to 360 L.
4. Estimate final impinger volume to the nearest 0.5 mL. Record on sample submittal sheet.
   NOTE: DMSO is hygroscopic; therefore, final sampling volumes may be greater than 20 mL.
5. Transfer the sample solution to a 40-mL opaque vial for shipment. Secure screw cap with sealing band.
6. Obtain a bulk sample (1 to 2 mL) and the material safety data sheet for each component of the formulation.

SAMPLE PREPARATION:

7. Transfer an aliquot of each sample to a HPLC autosampler vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards in the range of interest.

a. Prepare working standards containing 0.05 to 10.0 µg/mL of the appropriate monomeric tryptamine derivative in the sampling medium.
b. Analyze together with samples, controls, and blanks (steps 10 through 12).
c. Prepare calibration graph (response vs. µg per mL monomeric diisocyanate-tryptamine derivative).

9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

10. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5522-1. Inject 25-µL sample aliquot with a syringe, a fixed volume sample loop, or an autosampler.
    NOTE: Field sample run time = 60 min.
11. To investigate any intrinsic fluorescence from the bulk components, add an aliquot of the bulk sample to 100% DMSO containing no tryptamine reagent and run a chromatogram (See Figure 1).
    NOTE: If the bulk sample is not soluble in DMSO, prepare a stock solution in an alternative solvent such as dichloromethane. Add aliquots of the stock solution to DMSO.
12. Measure fluorescent response for all peaks in the chromatogram that also give an electrochemical response (See Figure 2).
    NOTE: If peak response is above the linear range of the working standards, dilute with sampling medium, reanalyze, and apply the appropriate dilution factors in the calculations.

CALCULATIONS:

13. Determine solution concentration (µg/mL) of each monomer derivative in the sample, C_s, and average media blank, W_b, from calibration graph (step 8.c.). Sum the responses of all other confirmed peaks in the chromatogram that elute later than the monomer peak. Read solution concentration, C_s (µg/mL), from calibration graph, and report as oligomer diisocyanate-tryptamine derivative.
    NOTE: Report the results for each monomer separately and the isocyanate-based oligomers as a group.
14. Using the solution volumes (mL) of the samples, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of each monomer and oligomer in the volume of air sampled, V (L), applying the ratio of molecular weight of diisocyanate, MW_{DI} (see Table 1), to the molecular weight of diisocyanate-tryptamine derivative, MW_{DIT} (see APPENDIX):

$$C = \frac{(C_s V_s - C_b V_b)\,(MW_{DI} / MW_{DIT})}{V}, \ mg/m^3$$

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

During method development, the performance of the fluorescence detector was verified through the use of a second detector in series (an electrochemical detector).

Recovery studies were conducted by analyzing groups of five to six samples of each diisocyanate. Vapor spikes of 2,4-TDI, 2,6-TDI, and HDI were prepared. Because of the low vapor pressure of MDI, liquid spikes were prepared instead of vapor spikes. For 2,4-TDI, 3 concentrations ranging from 4.9 to 60 µg per sample yielded an average recovery of 90.5%. For 2,6-TDI, 3 concentrations ranging from 6.0 to 60 µg per sample yielded an average recovery of 102.8%. For HDI, 3 concentrations ranging from 5.0 to 47 µg per sample yielded an average recovery of 89.5%. For MDI, 3 concentrations ranging from 3.2 to 72 µg per sample yielded an average recovery of 96.4%. The recovery studies also were conducted in the presence of 17% water, since the DMSO solvent is known to be hygroscopic. The recoveries for 2,4-TDI, HDI, and MDI with

17% water present were measured at one concentration level with an average recovery of 94.5%.

Storage stability studies were conducted at one concentration level by spiking groups of five to six impinger samplers with each diisocyanate-tryptamine derivative and storing at room temperature in the dark. Since the DMSO solvent is hygroscopic, additional storage studies were conducted in the presence of 17% water for each of the four diisocyanate-tryptamine derivatives. The average recovery for the four diisocyanate-tryptamine derivatives measured at one level was 95.8% for a 28-day storage period. Some of the samples were stored over a period of several months. HDI derivative had a recovery of 96.4% after 4 months. MDI derivative was stable for 5 months with a 98.9% recovery.

No interference in the method was found from acetone, methyl ethyl ketone, benzaldehyde, acetophenone, or cyclohexanone. Aromatic diamines with the same retention times as the analytes are potential interferences. Therefore, the use of an electrochemical detector is recommended for confirmation of isocyanate peaks.

Because of the high solidification point of DMSO, the addition of a reagent to lower the freezing point was necessary for sampling in environments <60 °F. An 80:20 DMSO:acetonitrile solution containing the derivatizing reagent is recommended. Recovery studies were conducted in 80:20 DMSO:acetonitrile. For each diisocyanate, liquid spikes were prepared in groups of six samples at 3 concentration levels. The average recoveries were 84% for 2,4-TDI, 104% for 2,6-TDI, 85% for HDI, and 88% for MDI. Storage stability studies of six samples at one level for each diisocyanate-tryptamine derivative yielded an average recovery for the four diisocyanate-tryptamine derivatives of 96% for 7 days and 95% for 28 days.

For more detail, see the Backup Data Report for this method [1].

REFERENCES:

[1] Key-Schwartz RJ, Tucker SP [1994]. Backup data report for isocyanates, Method 5522, NIOSH/DPSE. Unpublished report.
[2] Wu WS, Stoyanoff RE, Szklar RS, Gaind VS, Rakanovic M [1990]. Application of tryptamine as a derivatising agent for airborne isocyanate determination. Analyst *115*: 801-807.
[3] Schwope AD, Randel MA, Broome MG [1981]. Dimethyl sulfoxide permeation through glove materials. Am Ind Hyg Assoc J *42*(10): 722-725.

METHOD WRITTEN BY:

Rosa J. Key-Schwartz, Ph.D. and Samuel P. Tucker, Ph.D., NIOSH/DPSE

TABLE 1: SYNONYMS, EXPOSURE LIMITS, AND PROPERTIES

Compounds (Synonyms)	MW	Exposure Limits, µg/m³*			Properties
	(g/mol)	(OSHA)	(NIOSH)	(ACGIH)	
2,4-TDI (toluene-2,4-diisocyanate)	174.16	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 to 21.5 °C
2,6-TDI (toluene-2,-6-diiocyanate)	174.16	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)	250.26	200 (ceiling)	50; 200/10 min (ceiling)	51	solid (fused); d 1.23 g/mL @ 25 °C; MP 37.2 °C; VP 0.19 Pa (0.00014 mm Hg) @ 25 °C
HDI (hexamethylene diisocyanate)	168.20	no PEL	35; 140/10 min (ceiling)	34	liquid; d 1.04 g/mL @ 20 °C; BP 255 °C; 7 Pa (0.05 mm Hg) @ 25 °C

* 1 ppm = 7100 µg/m³ TDI; 10208 µg/m³ MDI; 7350 µg/m³ HDI;
Ca = Carcinogen

APPENDIX: PREPARATION OF TRYPTAMINE DERIVATIVE

Dissolve 0.00250 mole (0.41 g) of tryptamine (>99% purity) in 300 mL of toluene. Heat the solution to 60°C while stirring until much of the tryptamine is dissolved. Dissolve 0.001 mole (150-300 mg) of isocyanate in 20 mL of toluene. Add the isocyanate solution to the tryptamine solution. The tryptamine derivative will precipitate as a white gel. Collect the precipitate in a fritted-glass funnel by suction filtration. For the tryptamine derivatives of HDI and MDI, dissolve the precipitate in 100 mL (for HDI) or 450 mL (for MDI) of hot n-propanol. Filter the solution and allow it to cool. Collect the crystals. For the tryptamine derivatives of 2,4- and 2,6-TDI, dissolve the precipitate in 50 mL of hot n-propanol. Filter the solution and allow to cool. Add heptane (175 mL for 2,4-TDI and 100 mL for 2,6-TDI) and collect the precipitate in a fritted-glass funnel by suction filtration. For all derivatives, dry in a vacuum oven at 60°C to remove solvent.

TRYPTAMINE DERIVATIVES

Diisocyanate	Tryptamine Derivative	MP (°C)	MW (g/mol)
2,4-TDI	2,4-TDI-tryptamine	216-219	494.60
2,6-TDI	2,6-TDI-tryptamine	298-301	494.60
MDI	MDI-tryptamine	~270	570.70
HDI	HDI-tryptamine	201-201.5	488.64

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/m³
NIOSH: <0.1 mg/m³; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m³

PROPERTIES: soft metal;
d 11.3 g/cm³; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm cellulose ester membrane)	**TECHNIQUE:**	ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	lead
VOL-MIN: -MAX:	200 L @ 0.05 mg/m³ 1500 L	**ASHING:**	conc. HNO_3, 6 mL + 30% H_2O_2, 1 mL; 140 °C
SHIPMENT:	routine	**FINAL SOLUTION:**	10% HNO_3, 10 mL
SAMPLE STABILITY:	stable	**FLAME:**	air-acetylene, oxidizing
BLANKS:	2 to 10 field blanks per set	**WAVELENGTH:**	283.3 nm
ACCURACY		**BACKGROUND CORRECTION:**	D_2 or H_2 lamp, or Zeeman
RANGE STUDIED:	0.13 to 0.4 mg/m³ [1]; 0.15 to 1.7 mg/m³ (fume) [2]	**CALIBRATION:**	Pb^{2+} in 10% HNO_3
BIAS:	- 3.1%	**RANGE**	10 to 200 µg per sample [2,3]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.072 [1]; 0.068 (fume) [2]	**ESTIMATED LOD:**	2.6 µg per sample [4]
ACCURACY:	± 17.6%	**PRECISION ($\hat{S}_r$):**	0.03 [1]

APPLICABILITY: The working range is 0.05 to >1 mg/m³ 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 ≥ 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: Concentrated 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):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

NOTE: µg/mL ≡ mg/m

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].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[2] Heavy Metal Aerosols: Collection and Dissolution Efficiencies, Final Report of NIOSH Contract 210-79-0058, W. F. Gutknecht, M. H. Ranade, P. M. Grohse, A. Damle, and D. O'Neal, Research Triangle Institute; available as Order No. PB 83-106740 from NTIS, Springfield, VA 22161 (1981).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1979).

[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, S341 (revised 3/25/81), U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Lead (Revised Criteria), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-158 (1978).

[7] NIOSH Manual of Analytical Methods, 2nd ed., P&CAM 191.

[8] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).

[9] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S341, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[10] DataChem Laboratories in-house procedure for microwave sample digestion.

[11] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, SW-846 (1986).

[12] Kingston, H.M. and L.B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory." Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, (1988).

[13] 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water; ASTM, Philadelphia, PA, D1193 - 77 (1985).

[14] Introduction to Microwave Sample Preparation: Theory and Practice; Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington DC (1988).

[15] Kingston, H.M. EPA IAG #DW1-393254-01-0 January 1 - March 31, 1988, Quarterly Report.

[16] Binstock, D.A., Yeager, W.M., Grohse, P.M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460 (November, 1989).

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 the following table.

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 GFAAS 7105

Pb MW: 207.19 (Pb); 223.19 (PbO) CAS: 7439-92-1 (Pb); 1317-36-8 (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/m³
NIOSH: <0.1 mg/m³; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m³

PROPERTIES: soft metal; d 11.3 g/cm³; 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/m³
-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

INJETION: 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/m³ 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: Concentrated 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):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

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	$HNO_3 + H_2O_2$
Pb	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.

REFERENCES:

[1] Backup Data Report for Method 7105 submitted to NIOSH by DataChem Laboratories, NIOSH (Unpublished, September, 1990).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 214, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation (1976).
[4] Fernandez, F.J. and D.C. Manning. Atomic Absorbtion Analyses of Metal Pollutants in Water Using a Heated Graphite Atomizer, Atomic Absorption Newsletter 10, 65 (1971).

METHOD REVISED BY:

James B. Perkins, Brent E. Stephens, and Michael P. Beesley, DataChem Laboratories, Salt Lake City, UT.

LEAD BY FIELD PORTABLE XRF 7702

Pb	MW: 207.19 (Pb) 223.19 (PbO)	CAS: 7439-92-1 (Pb) 1317-3608 (PbO)	RTECS: OF7525000 (Pb) OG1750000 (PbO)

METHOD: 7702, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA:	0.05 mg/m³	**PROPERTIES:**	soft metal; d 11.3 g/mL @ 20 °C; MP 327.5°C; BP 1740°C; valences +2, +4 in salts
NIOSH:	<0.1 mg/m³; blood lead ≤ 60 µg/100 g		
ACGIH:	0.05 mg/m³; BEI blood 30 µg/ 100 mL		

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING

SAMPLER:	FILTER (0.8-µm, 37-mm, mixed cellulose ester membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	570 L @ 30.0 µg/m³ [1]
-MAX:	1900 L @ 9.0 µg/m³
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	0.1 to 1514.6 µg/m³ (as Pb) (based upon lead mass loadings)
BIAS:	0.069 [1]
PRECISION ($\hat{S}_{rT}$):	0.054 @ 10.3 to 612 µg Pb per sample
ACCURACY:	±16.4%

MEASUREMENT

TECHNIQUE:	X-RAY FLUORESCENCE (XRF), PORTABLE, L-SHELL EXCITATION (e.g., ^{109}Cd source)
	NOTE: Performance parameters are based upon research conducted with the NITON® 700 XRF [1].
ANALYTE:	lead
CALIBRATION:	lead thin-film standards (Micromatter Co., or equivalent); internal instrument calibration
RANGE:	17 to 1500 µg of Pb per sample [1]
ESTIMATED LOD:	6 µg of Pb per sample [1]

APPLICABILITY: This method was evaluated for air samples on filters only. The working range of this method is 0.017 mg/m³ to 1.5 mg/m³. This is a field portable analytical method, particularly useful for the analysis of initial exposure assessment samples, or for applications where laboratory analysis is impractical. Additionally, the method is non-destructive; samples analyzed in the field can later be analyzed in a laboratory. The method is applicable to all elemental lead forms, including lead fume, and all other aerosols containing lead.

INTERFERENCES: The presence of bromine will cause XRF readings for lead to be elevated, resulting in a positive bias error. Other interferences may exist in other XRF instruments.

OTHER METHODS: Laboratory-based methods include atomic spectrophotometric methods following hot plate acid digestion: NIOSH methods 7082 (flame atomic absorption spectrophotometry) [2], 7105 (graphite furnace atomic absorption spectrophotometry) [3], and 7300 (inductively coupled plasma atomic emission spectrophotometry) [4]. A field-portable analytical method for lead air filter samples using ultrasound/ASV has been developed, NIOSH Method 7701[5]. A field-portable screening method by spot test kit has been developed, NIOSH Method 7700 [6].

REAGENTS:

1. None

EQUIPMENT:

1. Sampler: Mixed cellulose ester filter, 0.8-µm pore size, 37-mm diameter, with cellulose back-up pad, in a closed-faced cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Field portable, L-shell X-Ray Fluorescence (XRF) instrument with a Cadmium-109 source.
4. Filter sleeve: thin cardboard with 37-mm dia. cut out, and covered with a light adhesive between two pieces of acetate (Mylar™) (NITON, Bedford, MA, or equivalent).
   NOTE: Material must be transparent to X-ray.
5. Filter test platform to hold the filter (specific to instrument).
6. Forceps
7. Thin film standard reference materials from 15 µg/cm^2 to 150 µg/cm^2 (Micromatter Co., Deer Harbor, WA), or equivalent [7,8].

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate (1 to 4 L/min) for a total sample size of approximately 1000 L. Do not exceed a filter loading of 2 mg total dust.

SAMPLE PREPARATION:

3. With forceps, transfer the MCE filter without the backup pad to a filter sleeve. The sleeve material must be transparent to X-rays (see EQUIPMENT, Item 4).
   NOTE: Take special care when removing the filter from the backup pad to avoid loss of lead-containing dust.
4. Place the filter into 37-mm opening and seal with Mylar™ film to prevent losses and allow undisturbed analysis of the filter.
5. Place the sealed filter onto the filter test platform of the instrument for analysis.
   NOTE: The NITON® 700 Series XRF has a filter test platform that allows for three readings with no substrate effect.

CALIBRATION AND QUALITY CONTROL:

6. Start XRF and allow a 30-minute warm-up period. The instrument will conduct an internal self-calibration.
7. Using thin film standards [8], verify the internal calibration to within ± 5% of the calibration standard. Use a minimum of three standards at concentrations of 15 µg/cm^2, 150 µg/cm^2, and one standard concentration between these two values.
8. Restart the instrument as needed to assure instrument accuracy prior to sample analysis.
   NOTE: When the thin film standard measurements are not within the specified parameters, the instrument may need to be recalibrated at the factory.
9. Analyze one thin film standard every 2 hours to check for instrument drift.
10. Repeat step 7 when all analyses are completed as a post-calibration check.

MEASUREMENT:

11. Set instrument parameters and analyze filter samples as specified by the manufacturer. The following measurement technique is based upon the NITON® 700 XRF.
    a. Analyze the middle of the sample filter first (see Figure 1, M).
    b. Allow the instrument to take a one source-minute reading (This may take longer than one real-time minute, depending upon the source strength). A one source-minute reading will assure the accurate L-shell reading necessary for the analysis of lead air filter samples.
    c. Analyze the filter sample at the top of the filter for one source minute (see Figure 1, T).
    d. Analyze the filter sample at the bottom of the filter for one source minute (see Figure 1, B).
    e. The instrument software uses an algorithm that converts the three readings in $\mu g/cm^2$ to an analytical result in µg of lead per sample. This result will be displayed following the third filter reading [1].
    f. Analyze one standard every 2 hours (step 8).
    g. Repeat three-reading calibration check following completion of analyses (step 8).

CALCULATIONS:

12. Using the measured lead concentration, W (µg), calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{W}{V}, \; mg/m^3$$

NOTE: $\mu g/L \equiv mg/m^3$

EVALUATION OF METHOD:

This method was validated on field samples [1] by collecting lead particulate samples from bridge lead abatement projects. Airborne concentrations of lead within the containment of a sand blasting bridge lead abatement project ranged from 1 to 10 mg/m^3. Area samples were collected for periods of time ranging from 15 seconds to 2 hours. This sampling protocol yielded 61 filter samples with lead loadings ranging between 0.1 to 1514.6 µg of lead per sample. Four personal samples were collected from a hand-scraping bridge lead abatement project for a total sample size of 65. The samples were first analyzed using a non-destructive, field portable XRF method. Samples subsequently were subjected to confirmatory analysis by the laboratory based NIOSH method 7105, Lead by GFAAS [3]. The method was statistically evaluated according to the NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation [9]. The overall precision ($\hat{S}_{rT}$) of the XRF method was calculated at 0.054 with a 95% confidence interval (CI) of 0.035 to 0.073, and the bias was 0.069 with a 95% CI of 0.006 to 1.515. The XRF method accuracy was determined to be ± 16%; however, at the upper 90% CI, the accuracy is ± 27%. Since the confidence interval includes the ± 25%, meeting the NIOSH accuracy criteria of ± 25% is inconclusive. However, the samples used to evaluate this method were field samples. Laboratory prepared aerosol samples would be expected to give better precision. Additionally, the XRF method is non-destructive; samples analyzed in the field can subsequently be analyzed in a laboratory using a method with greater accuracy, as needed. The filter sleeve used with the NITON® 700 Series XRF used a Mylar film to cover and seal the 37-mm filter. The lead particulate on the surface of the filter came into contact with the Mylar™ film. Both the Mylar™ film and the filter were digested with nitric acid and hydrogen peroxide as is specified in NIOSH Method 7105 [3].

REFERENCES:

[1] Morley JC [1997]. Evaluation of a portable x-ray fluorescence instrument for the determination of lead in workplace air samples [Thesis]. Cincinnati, OH: University of Cincinnati, Department of Environmental Health, College of Medicine.

[2] NIOSH [1994]. Lead by FAAS: Method 7082. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1994]. Lead by GFAAS: Method 7105. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[4] NIOSH [1994]. Elements: Method 7300. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[5] NIOSH [1994]. Lead by ultrasound/ASV: Method 7701 (supplement issued 1/15/98). In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.

[6] NIOSH [1994]. Lead in air by chemical spot test: Method 7700 (supplement issued 5/15/96). In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 96-135.

[7] National Institute of Standards and Technology, Standard Reference Material Program, Standard Reference Material 2579, Lead paint film on Mylar sheet for portable X-ray fluorescence analyzers, Gaithersburg, MD 20899.

[8] Micromatter Co., XRF Calibration Standards, P.O. Box 123, Deer Harbor, Washington, 98243, Phone (360) 3 76-4007.

[9] NIOSH [1995]. Kennedy, E.R., Fishbach, T.J., Song, R., Eller, P.M., Shulman, S.S.. Guidelines for Air Sampling and Analytical Method Development and Evaluation. Cincinnati, Ohio: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

METHOD WRITTEN BY: J. Clinton Morley, MS, NIOSH/DSHEFS

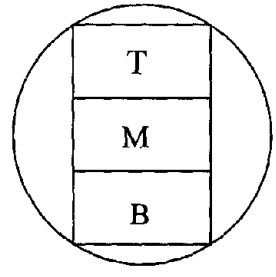


Figure 1: Analysis of a 37-mm filter using XRF
(XRF windows identified as M, T, and B are 2 cm x 1 cm)

LEAD BY ULTRASOUND/ASV 7701

Pb MW: 207.19 (Pb) 223.19 (PbO) CAS: 7439-92-1 (Pb) 1317-3608 (PbO) RTECS: OF7525000 (Pb) OG1750000 (PbO)

METHOD: 7701, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m^3

PROPERTIES: soft metal: d 11.3 g/cm^3@ 20 °C; MP 327.5 °C, BP1740 °C; valences +2, +4 in salts

SYNONYMS: elemental lead, lead compounds (except alkyl lead)

SAMPLING

SAMPLER:	FILTER (0.8-µm pore size, 37-mm dia., mixed cellulose ester membrane)
FLOW RATE:	1 to 4 L/min
VOL-MIN:	20 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:	0.025 to 0.150 mg/m^3 (as Pb) (based on Pb mass loadings) [4]
BIAS:	None identified [3,4]
OVERALL PRECISION ($\hat{S}_{rt}$):	0.087 (screen-printed electrodes); 0.094 (Hg film on glassy carbon electrodes) [4]
ACCURACY:	± 17.2 % (disposable electrodes); ± 19.3 % (renewable electrodes) [4]

MEASUREMENT

TECHNIQUE:	PORTABLE ANODIC STRIPPING VOLTAMMETRY
ANALYTE:	lead
EXTRACTION:	10% HNO_3, 10 mL; ultrasonication
FINAL SOLUTION:	50 mL 2% HNO_3
ANALYSIS ALIQUOT VOL.:	0.1 to 5 mL
DEPOSITION POTENTIAL:	-0.8 V to -1.0 V vs. Ag/AgCl
ANODIC SWEEP:	Deposition potential to 0.0 V vs. Ag/AgCl Sweep rate variable [1,2]
REFERENCE ELECTRODE:	Ag/AgCl or calomel
WORKING ELECTRODE:	mercury film on glassy carbon or screen-printed
SUPPORTING ELECTROLYTE:	Mixture of NaCl/NaOH or KCl/KOH, L-ascorbic acid
CALIBRATION:	Pb^{2+} in 5% HNO_3
RANGE:	0.31 to >1000 µg Pb per sample [3,4]
ESTIMATED LOD:	0.09 µg per sample [3]
PRECISION ($\hat{S}_r$):	0.068 @ 60 µg (as Pb) per sample [3]

APPLICABILITY: The working range is (at least) 0.20 to 5.00 mg/m^3 (as Pb) for a 120-L air sample. The lead determination by ultrasound/ASV method is applicable to the on-site, field-based determination of lead in air filter samples, and also may be used for laboratory-based air filter sample preparation and analysis.

INTERFERENCES: Thallium is a known interference, but its presence is unlikely in the vast majority of samples. Extremely high concentrations of copper may cause a positive bias. Surfactants can poison electrode surfaces, so if the presence of surfactants is suspected they must be eliminated during sample preparation [5].

OTHER METHODS: Laboratory-based methods include atomic spectrometric methods following concentrated acid hotplate digestion: NIOSH methods 7082 (flame AAS), 7105 (graphite furnace AAS), and 7300 (ICP-AES). ASTM standards based on NIOSH methods for sample collection, preparation and analysis have been published [6].

REAGENTS:

1. Nitric acid,* 10% (v/v) (Prepared from concentrated nitric acid, reagent grade; spectroscopic grade if trace analysis).
2. Distilled or deionized water (ASTM Type I or better [7]).
3. Calibration stock solution, 1000 µg/mL Pb. Commercial standard, or dissolve 1.00 g Pb metal in minimum of 10 mL of 50% HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable for at least one year.
4. Supporting electrolyte: Aqueous inert salt mixture such as 2.5 *M* NaCl and 0.25 *M* NaOH* (reagent grade or equivalent) [3,4].
5. Dissolved oxygen scavenger such as 0.25 *M* L-ascorbic acid (tissue culture grade or equivalent) [3,4].
6. Mercuric nitrate (reagent grade), if required (for Hg film electrodes).
7. Reference materials, primary or secondary.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Mixed 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. Field-portable anodic stripping voltammeter.
4. Disposable or renewable voltammetry electrodes.
5. Ultrasonic bath, 50 watts minimum power.
6. Power source for ultrasonic bath.
7. Plastic centrifuge tubes, 50-mL, with screw caps.
8. Test tube rack (size to fit in ultrasonic bath).
9. Plastic sample cell container.
10. Mechanical pipets (class A equivalent), 0.1-mL to 10-mL, as needed.
11. Pipet tips for mechanical pipets.
12. Forceps
13. Bottles, polyethylene, 100- to 1000-mL.
14. Volumetric flasks, 100-mL (for preparatory lab work).
15. Plastic rods.

NOTE: Clean all glassware and reusable plasticware with diluted nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Nitric acid and sodium hydroxide are irritants and may burn skin. Perform extractions in a well-ventilated area. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in the 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 20 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and, with forceps, transfer the samples and blanks to separate 50-mL centrifuge tubes. Push the filters to the bottom of the tubes with plastic rods.
4. Add 10 mL of 10% HNO_3 and cap the centrifuge tubes.
5. Place centrifuge tubes in ultrasonic bath, and agitate at room temperature for 30 min.
   NOTE 1: The water level in the bath should be at least 2.5 cm above the level of liquid within the centrifuge tubes.
   NOTE 2: Proper performance of the ultrasonic bath should be demonstrated before use. This can be accomplished by checking recoveries of lead from performance evaluation materials.
6. Uncap centrifuge tubes and dilute each ultrasonicated sample to 50-mL mark with distilled or deionized water. Cap tubes, shake for 5 to 10 sec, and allow to settle.

CALIBRATION AND QUALITY CONTROL:

7. Prior to field work, prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (12.5 to 1000 µg Pb per 50-mL sample).
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks, and dilute to volume with 10% HNO_3. Store and transport the working standards in polyethylene bottles, and prepare fresh weekly.
   b. Analyze the working standards together with the blanks and samples.
   c. Prepare a calibration graph of instrumental response vs. lead concentration (µg/mL Pb).
      NOTE: Some portable instruments read concentration directly. Calibrate according to manufacturer's directions.
8. Analyze a standard for every 10 samples to check for instrument drift (steps 11 through 14).
9. Check recoveries with at least one spiked media blank per 10 samples. Use primary or secondary reference materials to substantiate recoveries. Use method of standard additions to check for matrix effects or interferences.
10. Check for lead contamination by analyzing at least one reagent and one media blank per 10 samples (steps 11 through 14).

MEASUREMENT:

11. Set instrument parameters as specified by the manufacturer, or use conditions specified on page 7701-1.
    NOTE: If renewable electrodes are used, clean the glassy carbon electrode and deposit a fresh mercury film prior to conducting analyses.
12. Transfer sample aliquot (1 to 5 mL) to analytical cell, and dilute with 10% HNO_3, if necessary.
    NOTE: High concentrations of lead may require analysis of diluted analyte solutions.
13. Add supporting electrolyte and oxygen scavenger to sample cell. Ensure final volume of the cell is 5 mL (disposable electrodes) or 10 mL (renewable electrodes) by diluting with distilled or deionized water.
14. Measure lead content of the sample aliquot (µg/sample or µg/mL), and record the result.
    NOTE 1: For renewable electrodes, rinse and drain electrochemical sample cell three times with distilled or deionized water between sample runs. For disposable electrodes, use a fresh plastic sample cell container for each sample analyzed.
    NOTE 2: If the measured value is above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Using measured lead contents, calculate the corresponding concentrations (µg/mL) of lead in the original extracted sample, C_s, and average media blank, C_b, from the calibration graph.
    NOTE: Be sure to account for dilution factors.
16. Using solution volumes (mL) of the samples, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3$$

NOTE: µg/mL = mg/m^3

EVALUATION OF METHOD:

This method was evaluated with lead fume samples generated in the laboratory (40 to 80 µg Pb per filter) [3], and with air particulate samples collected from workplaces where abrasive blasting of leaded paint on highway bridges was being conducted [4]. For the latter, lead loadings cover the range from below the detection limit of 0.09 µg Pb per filter to loadings in excess of 1500 µg Pb per filter [4]. The method also has been evaluated with performance evaluation materials, National Institute of Standards and Technology Standard Reference Materials (NIST SRMs) [3,4]. Lead recoveries from NIST SRMs were found to be quantitative (≥90%) and equivalent to recoveries obtained using confirmatory analytical methods (NIOSH 7082, 7105, 7300 [8]).

REFERENCES:

[1] Wang J [1985]. Stripping analysis. New York: VCH Publishers.
[2] Wang J [1996]. Electrochemical preconcentration. In: Kissinger PT, Heineman WR, Eds. Laboratory Techniques in Electroanalytical Chemistry. 2nd ed. New York: Marcel Dekker.
[3] Ashley K [1995]. Ultrasonic extraction and field-portable anodic stripping voltammetry of lead from environmental samples. Electroanalysis 7: 1189-1192.
[4] Ashley K, Mapp KJ, Millson M [In press]. Ultrasonic extraction and field-portable anodic stripping voltammetry for the determination of lead in workplace air samples. Submitted to AIHAJ.
[5] Ashley K [1994]. Electroanalytical applications in occupational and environmental health. Electroanalysis 6: 805-820.
[6] ASTM [1996]. Standard Nos. E1553, E1613, E1741, E1775. In Annual Book of ASTM Standards, Vol. 04.07. W. Conshohocken, PA: American Society for Testing and Materials.
[7] ASTM [1997]. Standard No. D1193: Specification for reagent water. In Annual Book of ASTM Standards, Vol. 11.01. W. Conshohocken, PA: American Society for Testing and Materials.
[8] NIOSH [1994]. Lead: Method 7082, Lead by GFAAS: Method 7105, Elements: Method 7300. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM). 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health.

METHOD WRITTEN BY:

Kevin Ashley, Ph.D., NIOSH/DPSE

METHANOL 2000

CH_3OH MW: 32.04 CAS: 67-56-1 RTECS: PC1400000

METHOD: 2000, Issue 3 **EVALUATION: FULL** **Issue 1: 15 August 1984**
Issue 3: 15 January 1998

OSHA : 200 ppm
NIOSH: 200 ppm (skin); STEL 250 ppm (skin)
ACGIH: 200 ppm (skin); STEL 250 ppm (skin)
(1 ppm = 1.310 mg/m³ @ NTP)

PROPERTIES: liquid; d = 0.792 g/ml @ 20 C; BP = 64.5 C; VP = 15.3 kPa (115 mm Hg; 15.1% v/v) @ 20 C; explosive range is 6 to 36% (v/v) in air

SYNONYMS: Methyl alcohol, wood alcohol, carbinol, wood naphtha, wood spirit

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 100/50 mg)

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 1 L @ 200 ppm
-MAX: 5 L

SHIPMENT: pack securely for shipment; store at 5°C.

SAMPLE STABILITY : at least 30 days at 5°C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 140 to 540 mg/m³ [2]

BIAS: -4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.074 [1, 2]

ACCURACY: ±16.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methanol

DESORPTION: 1 mL water/isopropanol (95:5) [1]

INJECTION VOLUME: 1 µL

TEMPERATURE- INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 50 to 90 °C (8 °C/min) [1]
(Split Ratio 10:1)

CARRIER GAS: He, 2.6 mL/min

COLUMN: capillary, 30 m x 0.53-mm ID; 3-µm film 35% diphenyl-65% dimethyl polysilozane, Rtx™-35 or equivalent [1]

CALIBRATION: standard solutions of methanol in water/isopropanol (95:5)

RANGE: 2.2 to 6000 µg per sample [1,2]

ESTIMATED LOD: 0.7 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.030 [1]

APPLICABILITY: Under the GC parameters stated in the method, methanol may be identified based upon retention time and quantified. The working range is 0.4 to 1200 mg/m³ (0.3 to 916.0 ppm) for a 5-L air sample [1]. At high concentrations of methanol or under conditions of high relative humidity, a large silica gel tube (700 mg) is required [2].

INTERFERENCES: No specific interferences were identified. However, any compound with a similiar retention time may interfere. Positive identification can be confirmed by dual column chromatography with a 100% PEG capillary column. Mass spectrometry can also be used as a confirmation aid.

OTHER METHODS: This method updates and replaces NMAM 2000 (August 15, 1994), which combined and replaced Method S59 [3] and P&CAM 247 [4].

REAGENTS:

1. Methanol, chromatographic grade. *
2. Water, distilled and prepurified.
3. Isopropanol (IPA), chromatographic grade.*
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.
7. Desorbing solution, 5% isopropanol in 95% distilled water.
8. Calibration stock solution, 2µg/µL. Add 25.3µL Methanol to 10 mL of desorbing solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: silica gel tube, 7 cm long, 4-mm ID, containing two sections of 20/40 mesh silica gel (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section. A 4-mm foam plug follows the back section. Samplers are commercially available.
   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, flame ionization detection, integrator, and Rtx-35 capillary column, or equivalent (page 2000-1).
4. Utrasonic bath.
5 Vials, autosampler, with PTFE-lined caps.
6. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
7. Flasks, volumetric, various sizes.
8. Pipets, various sizes.

SPECIAL PRECAUTIONS: Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation. Isopropanol is flammable and a fire risk. Wear appropriate protective clothing and work with these compounds in a well ventilated 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 0.02 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap the samplers with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front (include glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard foam plugs.
6. Add 1 mL of water/IPA (95/5) to each vial and attach crimp caps.
7. Place vials in an ultrasonic bath for 30 to 60 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to water/isopropanol (95/5) 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. µg methanol).

9. Determine desorption efficiency (DE) at least once for each lot of silica gel tubes used for sampling in the calibration range (step 8). Prepare three samplers at each of six levels plus three media blanks.
   a. Remove and discard back sorbent sections of samplers and media blanks.
   b. Inject a known amount of calibration stock solution directly onto the front sorbent bed of each silica gel tube.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
   d. Desorb the samples (steps 5 through 7) and analyze together with working standards and blanks (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 ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2000-1. Inject a 1-µL 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 with water/IPA (95/5), reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for 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)

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

The method was reevaluated and revised. Improvements were made to enhance the recovery of methanol from silica gel, to improve baseline resolution, and to improve the precision of the method. Desorption efficiency (DE) was determined for three levels using the improved analytical parameters stated on page 2000-1. The average DE for methanol was determined at 20 µg (0.942), 40 µg (0.945), and 79 µg (0.942) [1]. The LOD was determined to be 0.7 µg/sample [1]. The precision, as determined from the pooled relative standard deviation ($\hat{S}_r$) was determined to be 0.030 [1].

The original method S59 [3] was issued on January 17, 1975 and was validated over the range of 140 to 540 mg/m^3 at 25 °C and 758 mm Hg with 5-L sample volumes [2]. The estimated LOD determined for a user check was 0.010 mg/sample [5]. Overall precision ($\hat{S}_{rT}$) was determined to be 0.063 with an average recovery for 18 samples of 94.2%, representing non-significant bias. The atmospheres were generated by calibrated syringe pump. Desorption efficiency (DE) was determined to be 0.92 at 1.3 mg methanol and 0.84 at 0.65 mg methanol per sample. The breakthrough volume was 10.4 L (5% on back section) when sampling a methanol atmosphere containing 541 mg/m^3 in dry air at 0.2 L/min for 52 min.

Data gathered using larger silica gel tubes (700 mg front section) under conditions of high humidity were

published in P&CAM 247 [4]. The data are consistent with a recommended maximum sample volume of 5 L.

REFERENCES:

[1] Pendergrass, SM [1996]. Backup data report for methanol method development. Cincinnati, OH: National Institute for Occupational Safety and Health, DPSE/NIOSH (unpublished May).
[2] NIOSH [1977]. Documentation of the NIOSH validation tests. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-185.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods (NMAM), V. 2, S59. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-B.
[4] NIOSH [1977]. NIOSH Manual of Analytical Methods (NMAM), V. 1, P&CAM 247. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A (1977).
[5] NIOSH [1983]. User Check, UBTL, NIOSH Sequence # 4121-K (unpublished November 3).

METHOD WRITTEN BY:

Stephanie M. Pendergrass, NIOSH/DPSE

METHYLENE CHLORIDE 1005

CH_2Cl_2 MW: 84.94 CAS: 75-09-2 RTECS: PA8050000

METHOD: 1005, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 August 1984 **Issue 3:** 15 January 1998

OSHA : 25 ppm; STEL 125 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m³)

PROPERTIES: liquids, d 1.323 g/mL @ 20 °C; BP 40 °C; MP -95 °C; VP 47 kPa (349 mm Hg) @ 25 °C, nonflammable

SYNONYMS: dichloromethane, methylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT
(2 coconut shell charcoal tubes, 100/50 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 back tubes

SAMPLE STABILITY: ca. 30 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1700 to 7097 mg/m³ [2]

BIAS: - 4.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1, 2]

ACCURACY: ±15.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylene chloride

DESORPTION: 1 mL CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 80 to150 °C at 10 °C/min

CARRIER GAS: Helium, 2.4 mL/min

COLUMN: capillary, 30 m x 0.32-mm ID, 0.25-µm film polyethylene glycol, Stabilwax, or equivalent

CALIBRATION: solutions of methylene chloride in CS_2

RANGE: 1.4 to 2600 µg per sample [1]

ESTIMATED LOD: 0.4 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.026 [1]

APPLICABILITY: The working range for GC-FID analysis is 0.4 to 749 ppm (1.4 to 2600 mg/m³) for a 1-L air sample [1]. An electron capture detector (ECD) also may be used to obtain lowest feasible level of detection and quantitation [3]. Conditions for using an ECD are listed in the APPENDIX.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time may interfere. Alternate chromatographic columns are Carbowax-PEG and DB-1 fused silica capillary columns. The capacity of the charcoal is greatly reduced when sampling in high humidity [4].

OTHER METHODS: This revises NMAM 1005 (dated 8/15/94) [5]. If sampling in an atmosphere with high relative humidity (≥ 80%), a tube with larger bed of charcoal is recommended. OSHA Method 59 uses a sampler with three sorbent sections, each containing 350 mg of charcoal, and has been evaluated for a 10-L air sample at 1 ppm of methylene chloride with 80% relative humidity [4]. OSHA Method 80 uses a carbon molecular sieve sampler and GC-FID analysis, and has been evaluated at 10 ppm and 500 ppm [6].

REAGENTS:

1. Methylene chloride, chromatographic grade.*
2. Carbon disulfide, chromatographic grade. *
3. 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 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 plug follows the back section. Tubes are commercially available (SKC #226-01, Supelco ORBO-32s, 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 (page 1005-1).
4. Vials, autosampler, with PTFE-lined caps.
5. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
6. Flasks, volumetric, various sizes.
7. Pipets, various sizes.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Methylene chloride is a suspected carcinogen. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampling tubes immediately before sampling. Attach sampler train 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 to prevent migration of methylene chloride between tubes. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front (along with first glass wool plug) and back sorbent sections of each tube in separate vials. Discard the foam plugs.
6. Add 1 mL of desorption solvent, CS_2, to each vial and attach crimp caps.
   NOTE: Significant heat is generated when the desorbing solution is added to the charcoal. To minimize sample loss, chill the desorbing solution before adding to the charcoal [4].
7. Allow to stand 30 min with occasional agitation to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from the LOD to LOQ.

a. Add known amounts of methylene chloride to CS_2 in 10-mL volumetric flasks and dilute to the mark.
NOTE: An internal standard such as 2-butanol or hexane can be added to the CS_2.
b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak area or height vs. µg methylene chloride).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal tubes used for sampling in the calibration range (step 8). Prepare three samplers at each of 6 levels plus three media blanks.
a. Remove and discard back sorbent sections of sampler and media blanks.
b. Inject a known amount of methylene chloride directly onto the front sorbent bed of each charcoal tube.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb the samples (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg methylene chloride recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1005-1. Inject a 1-µL 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 with appropriate solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for 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):

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

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

The method was originally evaluated for methylene chloride (Method S329) and validated over the range 1700 to 7100 mg/m^3 at 25 °C and 763 mm Hg using a 1-L sample [2, 7]. Overall precision ($\hat{S}_{rT}$) using flame ionization detection was 0.073 with a recovery of 95.3% (non-significant bias). The concentration of methylene chloride was independently verified by calibrated syringe pump. Desorption efficiency was 0.97 over the range of 1.3 mg to 5.3 mg methylene chloride per sample. Breakthrough (5% on backup 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 in the original method development.

Method 1005 was evaluated for methylene chloride using electron capture detection (ECD)[3]. Toluene was determined to be the best desorption solvent for use with ECD. Desorption efficiency was determined to be 75% at a 230 ng spiking level. After 30 days storage at 5 °C, the stability of 320 ng methylene chloride samples was determined to be 87.3% [3]. The NIOSH storage stability criterion of ≥90% recovery was within

the 95% confidence interval of 80.9 to 93.7%.

REFERENCES:

[1] Pendergrass SM [1997]. Backup Data Report for Methylene Chloride by ECD. Cincinnati, OH: National Institute for Occupational and Health, DPSE (NIOSH)(unpublished report).
[2] NIOSH [1977]. Documentation of the NIOSH Validation Tests. S329. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-185.
[3] NIOSH [1997]. Analytical Report for Methylene Chloride, Data Chem, NIOSH Sequence #8799-L (unpublished report).
[4] OSHA [1986]. Methylene Chloride: Method 59. OSHA Analytical Methods Manual. Salt Lake City, Utah: DOL, Occupational Safety and Health Administration.
[5] NIOSH [1994]. Methylene Chloride: Method 1005. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[6] OSHA [1990]. Methylene Chloride: Method 80. OSHA Analytical Methods Manual. Salt Lake City, Utah: DOL, Occupational Safety and Health Administration.
[7] NIOSH [1977]. Method S329: Methylene Chloride. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., V3. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A.

METHOD REVISED BY:

Stephanie M. Pendergrass, NIOSH/DPSE

APPENDIX. MEASUREMENT CONDITIONS FOR METHYLENE CHLORIDE BY GC-ECD.

Desorption: 1 mL toluene, 30 min with agitation
Calibration: Solutions of methylene chloride in toluene
Range: 0.23 to 1.0 µg per sample (instrumental) [1]
Estimated LOD: 0.002 µg per sample [1]
Precision ($\bar{S}_r$): 0.050 at 320 µg

Analytical column, GC temperature program, and injection volume are the same as on page 1005-1.

N-METHYL-2-PYRROLIDINONE 1302

C_5H_9NO MW: 99.13 CAS: 872-50-4 RTECS: UY5790000

METHOD: 1302, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA: None
NIOSH: None
ACGIH: None
(1 ppm = 4.05 mg/m³ @ NTP)

PROPERTIES: Clear liquid, amine-like odor; d = 1.027 g/mL@ 25 °C; BP = 202 °C @ 760 mm Hg; FP = -24.4 °C; VP = 0.29 mm Hg (0.039 kPa) @ 20 °C; explosive limits = 1.3% to 9.5% (v/v).

SYNONYMS: 1-methyl-2-pyrrolidone, *N*-methyl-γ-pyrrolidone, *N*-methyl-γ-butyrolactone, NMP, 1-methylazacyclopentan-2-one, MP, M-Pyrol

SAMPLING

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

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 0.5 L
-MAX: 125 L

SHIPMENT: Keep cold. Protect from prolonged exposure to light.

SAMPLE STABILITY: 14 days at 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NPD or FID

ANALYTE: *N*-methyl-2-pyrrolidinone (NMP)

DESORPTION: 1 mL methylene chloride/methanol (95:5)

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 60 to 200 °C (10 °C/min)

CARRIER GAS: Helium, 2.4 mL/min

COLUMN: amine capillary, 30 m, 0.32-mm ID, 1-µm film, crossbonded® 5% diphenyl-95% dimethyl polysiloxane

CALIBRATION: solutions of NMP in solvent

RANGE: 0.063 to 25.8 µg/sample (NPD) [1]
0.662 to 2066 µg/sample (FID) [1]

ESTIMATED LOD: 0.02 µg/sample (NPD) [1]
0.3 µg/sample (FID) [1]

PRECISION ($\bar{S}_r$): 0.05 (NPD) [1]
0.01 (FID) [1]

APPLICABILITY: Under the GC parameters given in the method *N*-methyl-2-pyrrolidinone can be identified based upon retention time and quantified.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time may interfere.

OTHER METHODS: This method represents an improvement over an OSHA In-House method for *N*-methyl-2-pyrrolidone [2]. Method 1302 employs a shorter capillary column, improved sensitivity and recovery at lower sample levels, and a choice of two detection systems.

REAGENTS:

1. *N*-methyl-2-pyrrolidinone, reagent grade.*
2. Methanol, chromatographic grade. *
3. Methylene chloride, chromatographic grade*
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, filtered.
7. Desorption Solvent. 5% methanol in 95% methylene chloride.
8. Calibration Stock Solution. Add *N*-methyl-2-pyrrolidinone to desorption solvent in a 10-mL volumetric flask. Protect from light.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass tube, 70 mm, 6-mm OD, containing two sections of coconut shell charcoal (100 mg front, 50 mg back section) separated by polyurethane foam plug. A glass wool plug precedes the front section and a polyurethane foam plug follows the back section. Tubes are commercially available (SKC 226-01, Supelco ORBO-32).
2. Personal sampling pump, 0.05 to 2 mL/min, with flexible connecting tubing.
3. Gas chromatograph, nitrogen phosphorous detector and/or flame ionization detector, integrator, and amine capillary column, Restek Rtx-5 or equivalent (page 1302 -1).
4. Vials, autosampler, with PTFE-lined caps.
5. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
6. Flasks, volumetric, various sizes.
7. Pipets, various sizes.

SPECIAL PRECAUTIONS: *N*-methyl-2-pyrrolidinone is an irritant with possible teratogenic properties. Methanol is flammable and a dangerous fire risk. Methylene chloride is a potential occupational carcinogen. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.05 to 0.2 L/min for a total sample size of 0.5 to 125 L.
4. Cap the samplers and pack securely for shipment. Protect samplers from prolonged exposure to light.

SAMPLE PREPARATION:

5. Place front sorbent section including glass wool plug and back sorbent section in separate autosampler vials. Discard foam plugs.
6. Add 1 mL desorption solvent to each vial and cap.
7. Let each vial stand with occasional agitation for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range from below the LOD to 10 times the LOQ. The calibration graph may be extended if sample concentrations dictate.
   a. Add known amounts of calibration stock solution to solvent in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution. Prepare fresh daily.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. µg *N*-methyl-2-pyrrolidinone).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal tubes used for sampling in the calibration range (step 8).
   a. Prepare three samplers at each of six levels plus three media blanks.
   b. Remove the back section of the charcoal tubes. Inject a known amount of calibration stock

solution directly onto the front sorbent bed of each charcoal tube.

c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with standards and blanks (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 ensure that the calibration and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1302-1. Inject a 1-µL 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 with desorption solvent, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for *N*-methyl-2-pyrrolidinone 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*-methyl-2-pyrrolidinone in the air volume sampled, V (L):

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

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

The method was evaluated for *N*-methyl-2-pyrrolidinone using GC-NPD and GC-FID over a range of 0.662 to 2066 µg/sample. Precision was determined to be 0.05 using GC-NPD and 0.01 using GC-FID. For GC-NPD, a DE graph was developed over a range of 0.310 µg to 10.8 µg. GC-FID was used to verify the results. The mean recovery was determined to be 98.8% with a pooled relative standard deviation ($\hat{S}_r$) of 0.051. An extended DE graph of the upper level of the method (0.103 to 2.07 mg) was previously determined by OSHA [2]. When spiked onto charcoal tubes at the 10.8 µg level and stored at ambient temperature, N-methyl-2- pyrrolidinone was stable on the charcoal tube for 7 days. OSHA reported that *N*-methyl-2-pyrrolidinone, when spiked at the 2070 µg level, was stable for 15 days at ambient temperature [2]. Refrigerated storage is recommended.

REFERENCES:

[1] Pendergrass, SM [1997]. Backup data report for N-methyl-2-pyrrolidinone (unpublished). Cincinnati, OH: National Institute for Occupational Safety and Health.
[2] Eide M [1991]. OSHA Stopgap Method for N-methyl-2-pyrrolidinone. Salt Lake City, UT: OSHA Salt Lake City Technical Center.

METHOD WRITTEN BY: Stephanie M. Pendergrass, DPSE, NIOSH

MYCOBACTERIUM TUBERCULOSIS, AIRBORNE 0900

METHOD: 0900, Issue 1 **EVALUATION: N/A** **Issue 1: 15 January 1998**

BIOLOGICAL INDICATOR OF: exposure to *M. tuberculosis*

SYNONYMS: TB, tubercle bacilli

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (PFTE filter, 37-mm)	**TECHNIQUE:**	POLYMERASE CHAIN REACTION (PCR)/ MICROPLATE READER [2]
FLOW RATE-RANGE:	4 L/min or higher [1]	**ANALYTE:**	*M. tuberculosis*
RECOMMENDATION:	if the airborne particle concentration is low, sample for at least 8 hours and/or use high volume sampling; in the laboratory studies, sampling times were 10 min	**WAVELENGTH:**	450 nm
		QUALITY CONTROL:	3 laboratory negative PCR controls, all should read less than 0.25 absorbance units, 2 laboratory positive controls, both should read 2.0 absorbance units or greater
PRESERVATIVE:	none		
SHIPMENT:	follow CDC guidelines for interstate shipment of human pathogen (42 CFR Part 72); may ship at ambient temperature	**RANGE:**	purified *M. tuberculosis* H37Ra DNA, 1-300 copies; H37Ra mycobacteria, approximately 4 to 1950 particles (all higher ranges will test positive)
SAMPLE STABILITY:	1 week or more @ ambient temperature; indefinitely @ -20 ° C	**ESTIMATED LOD:**	approximately 20 mycobacteria particles (from air samples)
CONTROLS:	2 or more field blanks		

APPLICABILITY: This is a qualitative method which permits the detection of airborne *M. tuberculosis* particles. It will detect approximately 20 or greater *M. tuberculosis* particles. This method does not indicate how many particles were detected.

INTERFERENCES: Positive interferences, *M. bovis, M. bovis BCG;* negative interferences, metals, and other unknown airborne particulate matter (note: to detect suspected negative interferences, spike field samples which resulted in negative readings with *M. tuberculosis* H37Ra DNA or H37Ra particles and re-run assay. Alternately, the Roche positive control may be used instead of H37Ra).

OTHER METHODS: The measurement technique was originally developed by Roche Diagnostic Systems for the analysis of clinical samples [2]. Various other *M. tuberculosis* detection methods are now available, such as Gen-Probe [3,4] and Digene [5].

REAGENTS:

1. Filter stripping solution containing 1% Triton X-100 in 10 mM Tris-HCl, pH 8.0. Alternately, the Sputum Wash solution (Roche) may be used.
2. Roche reagent kit, the AMPLICOR *Mycobacterium tuberculosis* test, containing various solutions and controls.
3. Bleach (5.25% sodium hypochlorite)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: polytetrafluoroethylene (PTFE) filter, 37-mm, 1.0-µm pore size, with cellulose support pad in plastic, three-piece filter cassette. (Costar #130810).
2. Sampling pump, 4 L/min or greater, with flexible connecting tubing.
3. Petri dishes, Polystyrene, 50-mm (Gelman #7242, or equivalent).
4. Forceps and/or tweezers.
5. Disposable gloves.
6. Platform clinical rotator.
7. Serological pipets, sterile, disposable, 2.0-mL.
8. Microcentrifuge tubes, 2.0-mL.
9. Microcentrifuge.
10. Heating block or water bath.
11. PCR thermocycler and accessories.
12. Microplate reader.
13. Microplate washer.
14 Microplate incubator.
15. Aerosol barrier pipettor tips or positive displacement micropipettors.
16. Sample bags, size 10.2 X 15.2 cm.

SPECIAL PRECAUTIONS: Entering rooms contaminated with airborne TB is a health risk. Appropriate respiratory protection should be worn [6]. Filter samples should be opened in a biosafety cabinet. Once the samples are heated for the specified time period, there is little risk to the laboratory worker conducting the analysis. The TB PCR method is extremely sensitive. Therefore, segregation of the various laboratory activities is essential in order to prevent the generation of false positives.

SAMPLER ASSEMBLY:

1. Assemble each filter cassette in a clean environment wearing disposable, preferably powder free or low powder, gloves.
   a. With forceps, insert support pad and PTFE filter into lower section of cassette.
   b. Attach middle and top cassette sections and insert plugs.
   c. Place shrinkable sealing band around cassette and air dry.
   d. Place each filter cassette into a sample bag for transport (one sampler/bag).

SAMPLING:

2. Calibrate each pump with a representative filter cassette in line.
3. Sample closed-face at a flow rate of 4 L/min or greater. The sampling time period depends on the suspected concentration. If the concentration is unknown, sample for long time periods (hours).
   NOTE: If the airborne particle concentration is unknown, assume the particles are present at a low concentration.
4. Reinsert cassette plugs, place each filter cassette in a sample bag (one cassette /bag), and pack securely for shipment. Ship at ambient temperatures, according to CDC guidelines for shipment of human pathogens (42 CFR Part 72).

SAMPLE PREPARATION:

5. Place 2.0 mL of filter stripping solution in a 50-mm Petri dish.
6. Remove the PTFE filter with a forceps or tweezers.
7. Wet both sides of the filter by touching each side of the filter to the stripping solution and then place the filter (one filter/dish), sample side up, in the dish. Cover tightly.
8. Place the dishes on the platform clinical rotator and strip the filters for 30 min. The stripping solution should move back and forth across the surface of the filter.
9. Transfer the stripping solution from each filter to a 2.0-mL microcentrifuge tube.
10. Centrifuge at 12,500 X g for 10 min and decant the supernatant into a beaker containing bleach. (Residual stripping solution should be removed from the microcentrifuge tubes).
11. Add 100 µL Roche lysis reagent to each microcentrifuge tube, close lids tightly and heat at 60°C for 45 min.
12. Follow steps described in the AMPLICOR *Mycobacterium tuberculosis* test booklet contained in the Roche reagent kit.

CALIBRATION AND QUALITY CONTROL:

13. Calibrate the PCR thermocycler and microplate reader according to the manufacturer's instructions.
14. Prepare positive and negative controls as described in the Roche reagent booklet.
    NOTE: Negative and positive controls are included in the Roche reagent kit.
    Include 3 negative controls and 2 positive controls each time the test is performed, randomizing the positions of these samples in the test.
    Discard the run:
    a. If one or more of the negative control values exceeds 0.25 absorbance units.
    b. If either of the positive control values falls below 2.0 absorbance units.

MEASUREMENT:

15. *Mycobacterium tuberculosis* is considered present in the sample if the absorbance of the unknown sample is equal to or greater than 0.35 absorbance units. A sample yielding an absorbance value less than 0.35 absorbance units is considered negative for *Mycobacterium tuberculosis*.

CALCULATIONS:

16. Since this is a qualitative method (positive/negative), no special calculations are required.

REFERENCES:

[1] Schafer MP, Fernback JE, Jensen PA [in press]. Sampling and analytical method development for qualitative assessment of airborne mycobacterial species of the *Mycobacterium tuberculosis* complex. Am Ind Hyg Assoc J (submitted).

[2] Devallois A, Legrand E, Rastogi N [1996]. Evaluation of Amplicor MTB test as adjunct to smears and culture for direct detection of *Mycobacterium tuberculosis* in the French Caribbean. J Clin Microbiol *34*:1065 -1068.

[3] Pfyffer GE, Kissling P, Wirth R, Weber R [1994]. Direct detection of *Mycobacterium tuberculosis* complex in respiratory specimens by a target-amplified test system. J Clin Microbiol *32*:918-923.

[4] Bodmer T, Gurtner A, Schopfer K, Matter L [1994]. Screening of respiratory tract specimens for the presence of *Mycobacterium tuberculosis* by using the Gen-Probe amplified *Mycobacterium tuberculosis* direct test. J Clin Microbiol *32*:1483-1487.

[5] Huang T-S, Liu Y-C, Lin H-H, Huang W-K, Cheng D-L [1996]. Comparison of the Roche AMPLICOR

MYCOBACTERIUM Assay and Digene SHARP signal system with in-house PCR and culture for detection of *Mycobacterium tuberculosis* in respiratory specimens. J Clin Microbiol *34*:3092-3096.

[6] NIOSH [1996]. Protect yourself against tuberculosis - a respiratory protection guide for health care workers. DHHS (NIOSH) Publication No. 96-102.

METHOD WRITTEN BY:

Millie P. Schafer, Ph.D., NIOSH/DPSE

$C_{10}H_{14}N_2$ MW: 162.2 CAS: 54-11-5 RTECS: QS5250000

METHOD: 2551, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : 0.5 mg/m³
NIOSH: 0.5 mg/m³, group I pesticide
ACGIH: 0.5 mg/m³
(1 ppm = 6.74 mg/m³ @ NTP)

PROPERTIES: liquid; d = 1.009 g/mL @ 20 °C; BP = 245.5 °C; VP = 0.08 mm Hg; FP = -29 °C; range of explosive limits: 0.7 to 4.0% in air.

SYNONYMS: 3-(1-methyl-2-pyrrolidyl)-pyridine

SAMPLING

SAMPLER: SORBENT TUBE (XAD-4, 80/40 mg)

FLOW RATE: 0.1 to 1.0 L/min [1-3]

VOL-MIN: 0.5 L
-MAX: 600 L

SHIPMENT: Keep cold. Protect from prolonged exposure to light.

SAMPLE STABILITY : 14 days at 5 °C in dark [4]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined.

BIAS: not determined.

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

ACCURACY: not determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NPD

ANALYTE: nicotine

DESORPTION: 1 mL ethyl acetate with 0.01% triethylamine

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 60 to 200 °C (20 °C/min); hold @ 200 °C for 3 min

CARRIER GAS: helium, 2.4 mL/min

COLUMN: capillary column, 30 m, x 0.32-mm ID, 1.0-µm film, crossbond® 5% diphenyl 95% dimethyl polysiloxane, Rtx-5® or equivalent

CALIBRATION: solutions of nicotine in desorbing solution

RANGE: 0.050 to 20 µg/sample [4]

ESTIMATED LOD: 0.013 µg/sample (instrumental) [4]

PRECISION ($\hat{S}_r$): 0.024

APPLICABILITY: Under the GC parameters stated in the method, nicotine can be identified based upon retention time. Nicotine is quantified using quinoline as an internal standard [1]. At high sample concentration, XAD-4 sorbent tube capacity (300 µg) may be exceeded and breakthrough may occur [1].

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time may interfere. Positive identification can be confirmed by dual column chromatography with an appropriate alternative capillary column. In this method development a Rtx-1 capillary column was used. Mass spectrometry also may be used as a confirmation aid.

OTHER METHODS: Other methods for nicotine are NMAM 2544 (August 15,1994) [2] and Method S293 [5] on which it was based. This method replaces the XAD-2 sorbent with XAD-4, and uses a capillary column in place of a packed GC column. The ethyl acetate desorption solvent was modified to improve nicotine recovery from sides of glass sorbent tube, and to improve recoveries for the lower DE levels.

REAGENTS:

1. Ethyl acetate, chromatographic grade.*
2. Triethylamine, reagent grade.*
3. Desorbing solution (modified ethyl acetate solution). 0.01% triethylamine in ethyl acetate.
4. Nicotine* primary stock solution (1.0 mg/mL). Dilute 100 mg nicotine to 100 mL with desorbing solution.
5. Nicotine* secondary stock solution (10 µg/mL). Dilute 1.0 mL nicotine primary stock solution to 100 mL with desorbing solution.
6. Quinoline* (Internal standard) primary stock solution (1.0 mg/mL). Dilute 100 mg quinoline to 100 mL with desorbing solution.
7. Quinoline* secondary stock solution (100 µg/mL). Dilute 10.0 mL quinoline primary stock solution to 100 mL with desorbing solution.
8. Helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass tube, 70 mm, 7-mm OD, containing two sections of XAD-4 (front = 80 mg, back = 40 mg) separated by a silylated glass wool. A silylated glass wool plug precedes the front section and follows the back section. (Glass wool plugs must be specified when ordering XAD-4 tubes.) Tubes are commercially available (SKC, Inc., Cat. No. 226-93, or equivalent).
2. Personal sampling pump, 0.1 to 1.0 L/min, with flexible connecting tubing.
3. Gas chromatograph, nitrogen-phosphorous detector, integrator, and Rtx-5® capillary column or equivalent (page 2551-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
7. Flasks, volumetric, various sizes.
8. Pipets, various sizes.
9. Refrigerant packs.

SPECIAL PRECAUTIONS: Nicotine is classified as a neurotoxin and possible teratogen [6]. Avoid inhalation, skin contact, and ingestion. Quinoline is classified as moderately toxic, a severe eye irritant, and possible carcinogen [6]. Avoid skin contact (readily adsorbed), inhalation, and ingestion. Ethyl acetate is flammable and a fire hazard. Triethylamine is an eye, skin, and respiratory irritant. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of tubes immediately before sampling. Attach tubes to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 1.0 L/min for a total sample size of 0.5 to 600 L.
4. Cap the tubes with plastic caps and pack securely for shipment. Protect from exposure to light. Ship with refrigerant packs to keep samples cold.

SAMPLE PREPARATION:

5. Place front (include glass wool plug) and back sorbent sections of the sampler in separate vials. Discard middle and back glass wool plugs.
6. Add 1 mL of desorbing solution (modified ethyl acetate) to each vial.
7. Add aliquots (10 to 50 µL) of the quinoline secondary stock internal standard solution to both the calibration standards and sample vials and attach PTFE-lined crimp caps.
   NOTE: Determine the approximate level of nicotine that will be in the samples and add a similar amount of quinoline. Environmental tobacco smoke usually has low nicotine levels. Pesticide operations usually have relatively high levels.
8. Place vials in an ultrasonic bath for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range of interest.
   a. Add known amounts of the nicotine stock solution to 1.0 mL of desorbing solution in separate vials.
   b. Add amount of quinoline secondary stock solution equal to amount used in Step 7 to each vial.
   c. Seal vials with PTFE-lined crimp caps.
   d. Analyze together with samples and blanks (steps 12 through 14).
   e. Prepare calibration graph (ratio of nicotine/quinoline areas vs. µg nicotine).
10. Determine desorption efficiency (DE) at least once for each lot of XAD-4 tubes used for sampling in the calibration range (step 9). Prepare three samplers at each of six levels plus three media blanks.
   a. Remove and discard the back sorbent section of the sampler.
   b. Inject a known volume of calibration stock solution directly onto the front sorbent bed of each XAD-4 tube.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
   d. Desorb (steps 6 through 8) and analyze together with standards and blanks (steps 12 through 14).
   e. Prepare a graph of DE vs. µg nicotine recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2551-1.
13. Inject a 1-µL 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 with desorbing solution, reanalyze, and apply the appropriate dilution factor in the calculations.
14. Measure peak areas and calculate ratio of nicotine peak area to quinoline peak area.

CALCULATIONS:

15. Determine the mass, µg (corrected for DE), for nicotine 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 nicotine in the air volume sampled, V (L):

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

This method development was based upon a request to measure nicotine in environmental tobacco smoke and an HHE request to measure nicotine in a greenhouse pesticide application. Desorption efficiency (DE) was determined for 5 levels: 2 x LOQ; 0.1, 0.5, 1.0, and 2.0 x Recommended Exposure Limit (REL) using the analytical parameters stated on page 2551-1. The average DE for nicotine was determined to be 0.924. The instrumental LOD was determined at 0.013 µg/sample. The precision, as determined from the pooled relative standard deviation ($\bar{S}_r$) was 0.024. Nicotine storage stability at 5 °C and at a concentration of 0.5 x REL was acceptable after 14 days with a mean recovery of 91%.

This method was employed to analyze nicotine that was used as a greenhouse pesticide and applied by a fogging procedure. In addition to XAD-4 sorbent tubes, nicotine was collected on glass fiber filters, gauze wipes, and cotton gloves. Nicotine was not stable on these media for more than 1 h. Recovery data for nicotine spiked on these media is contained in the method backup data report [4].

The maximum sampling volume of 600 L was calculated based on the XAD-4 sampling tube capacity of 300 µg nicotine [7] and the NIOSH REL of 0.5 mg/m^3. Concentrations of environmental tobacco smoke (ETS) typically range from 1 to 100 µg/m^3 [1]. At the highest ETS concentration and a sampling rate of 1 L/min, over 3000 L of air would need to be sampled to reach the sampling tube capacity. Sampling rates and times typically employed in field studies would almost never exceed the capacity of the XAD-4 sampling tube.

When sampling for nicotine in ETS, only the XAD-4 sampling tube is employed. However, when sampling for nicotine where particulate matter is present, such as in the greenhouse study, it may be necessary to use a glass fiber filter (GFF) in series with the XAD-4 sorbent tube. When a GFF is used, it also should be analyzed for nicotine as studies have indicated that nicotine can be adsorbed on particulate matter.

REFERENCES:

[1] ASTM [1990]. ASTM standard test method for nicotine in indoor air, Method D 5075-90a, ASTM Committee D-22, November 1990.
[2] NIOSH [1994]. Nicotine: Method 2544. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed., Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[3] EPA [1988]. Determination of nicotine in indoor air using XAD-4 for active sampling and treated filter cassettes for active and passive sampling with gas chromatographic and nitrogen-selective detection. Compendium Method IA-02, Design and Reports Branch, Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, N.C., May 1988.
[4] Pendergrass SM [1997]. Backup data report for nicotine (unpublished report). NIOSH/DPSE.
[5] NIOSH [1977]. Nicotine: Method S293. In: Taylor DG, ed. NIOSH manual of analytical methods, 2nd ed., V. 3, DHHS NIOSH) Publication No. 77-157-C.
[6] The Merck Index, 12 ed. [1996]. Nicotine, Quinoline. Whitehouse Station, NJ: Merck and Co.
[7] OSHA [1995]. Draft Method for Nicotine. Salt Lake City, UT: OSHA Salt Lake Technical Center.

METHOD WRITTEN BY:

Stephanie M. Pendergrass and Larry B. Jaycox, Ph.D. , NIOSH/DPSE

(1) Nitrobenzene: $C_6H_5NO_2$	MW: (1) 123.11	CAS: (1) 98-95-3	RTECS: (1)	DA6475000
(2) *o*-Nitrotoluene: $CH_3C_6H_4NO_2$	(2) 137.14	(2) 88-72-2	(2)	XT3150000
m-Nitrotoluene:		99-08-1		XT2975000
p-Nitrotoluene:		99-99-0		XT3325000
(3) 4-Chloronitrobenzene: $C_6H_4ClNO_2$	(3) 157.56	(3) 100-00-5	(3)	CZ1050000

METHOD: 2005, Issue 3 **EVALUATION: Table 1** **Issue 1: 15 August 1990**
Issue 3: 15 January 1998

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

PROPERTIES: Table 1

SYNONYMS:
(1) Nitrobenzol, oil of mirbane
(2) *o*- Methylnitrobenzene, 2-Methylnitrobenzene, 2-Nitrotoluene
m-Methylnitrobenzene, 3-Methylnitrobenzene, 3-Nitrotoluene
p-Methylnitrobenzene, 4-Methylnitrobenzene, 4-Nitrotoluene
(3) *p*-Chloronitrobenzene, 1-Chloro-4-nitrobenzene, 4-Nitrochlorobenzene, PCNB, PNCB

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 0.02 L/min

	(1)	(2)	(3)
VOL-MIN:	10 L	1 L	1 L
-MAX:	150 L	30 L	150 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 1

BIAS: Table 1

OVERALL PRECISION ($\hat{S}_{rT}$): Table 1

ACCURACY: Table 1

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: nitrobenzene, nitrotoluene isomers, 4-chloronitrobenzene

DESORPTION: 1 mL methanol in ultrasonic bath for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE -INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 80 °C, 1 min; 8 °C/min to 180 °C

CARRIER GAS: He, 2.5 to 3.0 mL/min

COLUMN: capillary, 30 m x 0.53-mm ID; µm film crossbonded 5% diphenyl 95% dimethylpolysiloxane, Rtx®-5 Amine or equivalent

CALIBRATION: analytes in methanol

RANGE: Table 1

ESTIMATED LOD: Table 1

PRECISION ($\hat{S}_r$): Table 1

APPLICABILITY: The working ranges for a 30-L air samples are 0.396 to 1.92 ppm (1.98 to 9.60 mg/m^3) for nitrobenzene; 0.346 to 1.73 ppm (1.97 to 9.86 mg/m^3) for *o*-nitrotoluene; 0.344 to 1.72 ppm (1.96 to 9.81 mg/m^3) for *m*-nitrotoluene; 0.303 to 1.52 ppm (1.73 to 8.67 mg/m^3) for *p*-nitrotoluene; and 0.308 to 1.54 ppm (1.98 to 9.92 mg/m^3) for 4-chloronitrobenzene [1,2].

INTERFERENCES: Any compounds with retention times similar to the analytes of interest will interfere. During sampling, high humidity may greatly decrease breakthrough volume.

OTHER METHODS: This method is an update of NMAM 2005, Nitrobenzenes, issued 15 August 1994, which combined and replaced methods S217, S218, and S223 [2,3].

REAGENTS:

1. Methanol, HPLC chromatographic grade.
2. Nitrobenzene*, reagent grade.
3. *o*-,*m*-,*p*-nitrotoluene isomers,* reagent grade.
4. 4-chloronitrobenzene*, reagent grade.
5. Calibration stock solution, 500 µg/mL. Prepare each analyte in methanol.
6. Helium, purified and filtered.
7. Hydrogen, purified and filtered.
8. Air, purified and 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.
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. Autosampler vials, glass, 2-mL, with PTFE-lined crimp caps.
5. Volumetric flasks, 10-mL.
6. Pipets, 5-mL and 3-mL, with pipet bulb.
7. Syringes, 10-µL, 100-µL, and 1-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: These analytes are severe poisons and irritants. Prevent contact with eyes, skin, or clothing by wearing eye protection, chemically resistant gloves, and a lab coat. Avoid inhalation. Nitrobenzene and *m*-nitrotoluene are absorbed through contact with skin and can cause methemoglobinemia [5,6]. 4-Chloronitrobenzene is a carcinogen. Methanol is highly flammable.

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. Note the maximum and minimum sample volumes on page 2005-1.
4. Cap both ends of the sampler. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (include the glass wool plug) and back sorbent sections of each sample tube in separate vials. Discard the foam plugs.
6. Add 1.0 mL of methanol to each vial. Attach crimp cap securely to each vial.
7. Allow to desorb 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range of the method. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of calibration stock 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 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).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each silica gel tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with standards and blanks (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 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 a 1-µL sample aliquot manually using the solvent flush technique or with an 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 the calculations.
12. Measure peak areas.

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):

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

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

The update of this method included the use of capillary column chromatography that lowered the LOD/LOQ values, a lower 5-level desorption efficiency study, and a 30-day storage stability study for each analyte [1]. The method evaluation data for these compounds are listed in Table 2. Methods S217, Nitrobenzene, and S218, 4-nitrochlorobenzene, were initially issued on November 21, 1975 [4]. Method S223, *o*-nitrotoluene was issued on December 19, 1975 [4]. The analytes *m*-nitrotoluene and *p*-nitrotoluene were added on May 15, 1984 [3]. In the original method development work, sample tube capacity, or breakthrough, was determined as 5% of the generated atmosphere concentration as measured in the effluent of the sample tubes. Capacity was measured at >2.8 mg/sample for nitrobenzene; >2.5 mg/sample for nitotoluene isomers; and >2.2 mg/sample for 4-chlorobenzene [2.]

REFERENCES:

[1] Pendergrass SM [1997]. Backup data report for nitroaromatic compounds method development. Cincinnati, OH: National Institute for Occupational Safety and Health, DPSE/NIOSH (unpublished December).

[2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S217, S218, and S223, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.

[3] NIOSH [1994]. *m*-Nitrotoluene and *p*-Nitrotoluene: Method 2005. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[4] NIOSH [1978]. Nitrobenzene: Method S217; *p*-Chloronitrobenzene: Method S218; and Nitrotoluene: Method S223. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Publ. (NIOSH) 77-157-C.

[5] NIOSH [1977]. Occupational diseases, a guide to their recognition, revised ed., 235-238, 280-281, U.S. Department of Health, Education, and Welfare, DHEW (NIOSH) Publication No. 77-157-C.

[6] NIOSH [1981]. 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.

METHOD WRITTEN BY: Stephanie M. Pendergrass, NIOSH/DPSE

TABLE 1. GENERAL INFORMATION

Chemical	TWA OSHA NIOSH ACGIH	Physical Properties	Method Evaluation
Nitrobenzene	1 ppm (5.0 mg/m^3) (skin) 1 ppm (5.0 mg/m^3) (skin) 1 ppm (5.0 mg/m^3) (skin)	Colorless oily liquid, almond odor; d=1.196 g/mL @ 20°C; MP 6°C; BP 210-211°C; VP=37 Pa (0.30 mm Hg) @ 20°C	Full
o-Nitrotoluene	5 ppm (28.5 mg/m^3) (skin) 2 ppm (11.7 mg/m^3) 2 ppm (11.7 mg/m^3)	yellowish liquid; d=1.163 g/mL @ 20°C; MP -4°C; BP 222°C; VP=20 Pa (0.15 mm Hg) @ 20°C	Full
m-Nitrotoluene	5 ppm (28.5 mg/m^3) 2 ppm (11.7 mg/m^3) 2 ppm (11.7 mg/m^3)	liquid; d=1.157 g/mL @ 20°C; MP 16°C; BP 232°C; VP=20 Pa (0.15 mm Hg) @ 20°C	Partial
p-Nitrotoluene	5 ppm (28.5 mg/m^3) 2 ppm (11.7 mg/m^3) 2 ppm (11.7 mg/m^3)	yellow crystals; d=1.163 g/mL @ 20°C; MP 52°C; BP 238°C; VP=17 Pa (0.12 mm Hg) @ 20°C	Partial
4-Chloronitro-benzene	0.16 ppm (1.03 mg/m^3) Ca* 0.1 ppm (0.644 mg/m^3)	yellow crystals; d=1.298 g/mL @ 20°C; MP 83°C; BP 242°C; VP=28 Pa (0.2 mm Hg) @ 30°C	Partial

* - Cancer suspect agent

TABLE 2. METHOD SUMMARY

Chemical	Range Studied[a] (mg/m³)	$\hat{S}_{rT}$	Bias	Accuracy (±%)	Analytical Range (µg/sample)	LOD (µg/sample)	$\bar{S}_r$	Desorption Efficiency (%)	30-Day Storage (% Rec)
Nitrobenzene	1.98 to 9.60	0.0590	0.0186	12.3	2 to 598	0.6	0.012	98.7	100.2
o-Nitrotoluene	1.97 to 9.86	0.0142	-0.120	21.1	3 to 582	0.8	0.028	98.2	101.2
m-Nitrotoluene	not studied	nd[b]	nd	nd	3 to 579	1.0	0.042	97.5	99.4
p-Nitrotoluene	not studied	nd	nd	nd	9 to 511	2.6	0.061	96.9	99.4
4-Chloro-nitrobenzene	1.98 to 9.92	0.1034	0.0869	27.3[c]	8 to 595	2.5	0.063	100.3	97.6

[a] 30-L air sample
[b] Not determined
[c] Exceeds the NIOSH accuracy criterion of ± 25% at the 95% confidence level

NITROGEN DIOXIDE (Diffusive sampler) 6700

NO_2 MW: 46.01 CAS: 10102-44-0 RTECS: QW9805000

METHOD: 6700, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 January 1998

OSHA : C 5 ppm
NIOSH: STEL 1 ppm/15 min
ACGIH: 3ppm; STEL 5 ppm
(1 ppm = 1.881 mg/m³ @ NTP)

PROPERTIES: yellowish-brown fuming liquid or reddish-brown gas; BP 21 °C; MP -9.3 °C; d 1.448 @ 20 °C; vap density (air=1) 1.59

SYNONYMS: nitrogen peroxide, dinitrogen tetroxide, Azote

SAMPLING

SAMPLER: DIFFUSIVE SAMPLER (Palmes tube with three triethanolamine-treated screens) [1]

SAMPLING TIME - **MIN:** 15 min @ 5 ppm
- **MAX:** 8 h @ 10 ppm

SHIPMENT: routine

SAMPLE STABILITY: use sampler within 1 month after preparation; analyze within 1 month after sampling

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.2 to 80 ppm-h (0.13 to 8.5 µg NO_2 per sample) [2]

BIAS: - 6.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [3]

ACCURACY: ± 16.0%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: nitrite ion (NO_2^-)

REAGENT: aqueous solution of sulfanilamide, H_3PO_4, and N-1-naphthylethylenediamine dihydrochloride

WAVELENGTH: 540 nm

PATHLENGTH: 1 cm

CALIBRATION: solutions of $NaNO_2$ in reagent

RANGE: 0.13 to 8.5 µg NO_2 per sample [2]

ESTIMATED LOD: 0.01 µg NO_2 per sample

PRECISION ($\bar{S}_r$): 0.05 [2]

APPLICABILITY: The working range is 1.2 to 80 ppm-h [2]. The method is applicable for ceiling and short-term exposure measurements. In the development of this passive sampler, it was assumed that NO_2 was completely converted to nitrite ion [1]. Incomplete conversion of NO_2 to nitrite ion (Saltzman factor <1) will cause a negative bias [1]. Diffusive samplers have a lower collection efficiency at lower pressure (-7% @ 5500 m altitude) [4].

INTERFERENCES: In very dusty environments, particles may deposit on the inside surface of the sampler. Resuspension of the dust in analytical reagent can give a positive bias in the spectrophotometric reading.

OTHER METHODS: Short-term and long-term detector tubes, passive indicator tubes, and various other diffusive samplers and electrochemical instruments have been used to sample for NO_2. NMAM Method 6014 [5] also uses an active solid sorbent sampling method with similar color development .

REAGENTS:

1. Absorbing reagent. Combine 1 part reagent grade triethanolamine (TEA) with 7 parts analytical grade acetone.*
2. Sulfanilamide solution. Combine 2 g sulfanilamide and 5 mL conc. H_3PO_4, and dilute to 100 mL with distilled water.
3. N-1-naphthylethylenediamine dihydrochloride (NEDA) solution. Dissolve 70 mg NEDA in 50 mL distilled water.
4. Combined reagent. Combine 1 part sulfanilamide solution, 1 part water, and 0.1 part NEDA solution. Protect from light and refrigerate. Stable ~ 1 month .
5. Sodium nitrite stock solution, 0.05 *M*. Accurately weigh 0.345 g $NaNO_2$ (reagent grade). Dissolve in 100 mL deionized water. Protect from light and refrigerate. Stable 90 days.
6. Calibration stock solution. Dilute an aliquot of $NaNO_2$ stock solution with distilled water (e.g.,1:50 dilution yields 1 nanomole NO_2^-/µL). Prepare fresh immediately before use.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: See APPENDIX (Potential sources of equipment given in reference [1]):
   a. Acrylic tubing, 3/8-inch (9.5-mm) ID.
   b. Stainless steel screen, 40x40 mesh/inch (16x16 mesh/cm).
   c. Polyethylene cap, unflanged, ½-inch (12.7-mm).
   d. Polyethylene cap, flanged, ½-inch (12.7-mm).
   e. Pen clips, 0.48-inch (12.2-mm).
   f. Electrical tape, plastic.
   g. Stopcock grease.
2. Spectrophotometer, 540 nm, with 1-cm cuvettes.
3. Volumetric flasks and pipets for preparation of standards.
4. Mixer, vibration or vortex (optional).
5. Forceps.

SPECIAL PRECAUTIONS: Acetone is a fire hazard.

SAMPLING:

1. Attach the sampler with flanged cap down. Start sampling by removing flanged cap. Estimate appropriate sampling time such that the amount of NO_2 collected is in the range 1.2 to 80 ppm-h (0.13 to 8.5 µg NO_2).
2. Terminate sampling by replacing flanged cap.

CALIBRATION AND QUALITY CONTROL:

3. Calibrate daily with at least six working standards over the range 0 to 40 nanomoles (0 to 1.84 µg) NO_2^- per 2.1 mL combined reagent.
   a. Prepare working standards from calibration stock solution immediately before use.
   b. Allow 10 min for color development.
   c. Transfer an aliquot of the working standard to a cuvette and analyze (steps 6 through 8).
4. Prepare a calibration graph (absorbance at 540 nm vs. NO_2^- mass in nanomoles.
   NOTE: The absorbance of 40 nanomoles NO_2^- is approximately 1 absorbance unit.
5. Check dimensions of the sampler. If cross-sectional area divided by length (A_t/L) of the sampler tube differs significantly from 0.10 cm, recalculate the diffusive collection rate (step 9).

MEASUREMENT:

6. Remove flanged cap from samplers. Add 2.1 mL combined reagent directly into samplers.

NOTE: If 2.1 mL is not sufficient to completely cover the exit slit of the spectrophotometer, a larger volume can be used provided the same volume is used for both standards and unknowns.

7. Recap the samplers and mix manually or with a mixer. Allow 10 min for the color to develop.
8. Transfer the solution to a cuvette and read the absorbance at 540 nm within 30 min from time reagent was added.

   NOTE: If sample reads beyond calibration graph, dilute sample with combined reagent or extend calibration range.

CALCULATIONS:

9. From calibration graph, read nanomoles nitrite ion (NO_2^-) collected by the sampler. Divide by 2.3 nanomoles/ppm-h (the diffusive collection rate [1]) and the sample exposure time, t (h), to obtain time-weighted average concentration, C (ppm NO_2), of NO_2:

$$C = \frac{\text{nanomoles } NO_2^-}{2.3\ t}$$

NOTE 1: If sampler dimensions are different from those specified in the APPENDIX, use 2.3•(actual A_f/L [cm]÷ 0.1 cm) nanomoles/ppm-h as the diffusive collection rate.

NOTE 2: The assumption is made that NO_2 is completely converted to NO_2^-, because of the small quantity collected [1].

EVALUATION OF METHOD:

This method is based on a method developed by E. D. Palmes *et al* at New York University [1]. Analytical precision and useful range were estimated from a laboratory evaluation conducted by NIOSH (1982) [2]. Overall precision ($\hat{S}_{rT}$ = 0.06) was estimated from side-by-side replicate samples collected in an underground salt mine [3]. In a laboratory study, this method gave results averaging 94 ± 4% (mean ± s_r) of a reference method over the range 1.3 to 79 ppm-h [2]. A field study found results for this method of 109 ± 9% (mean ± s_r) vs. a reference method in the range 12 to 19 ppm-h [3]. Sampling errors may exist in this method when the concentration is not constant in time and the sampling period is short [6, 7]. For example, the value of s_r associated with estimating the TWA of an isolated random 10-sec concentration pulse within a 15-min sampling period may be calculated [6] to equal 0.5. Secondly, reference [6] reports a specific set of real-time concentration data measured in an industrial environment. For these data, the error s_r in making 15-min TWA estimates is calculated to equal 0.12. Although these values are large, similar sampling errors due to time variations are expected to be better controlled for longer sampling periods as the variance of the sampling error varies inversely with the sampling period.

REFERENCES:

[1] Palmes ED, Gunnison AF, DeMattio J, Tomczyk C [1976]. Personal sampler for nitrogen dioxide. Am Ind Hyg Assoc J *37*:570-577.

[2] Woebkenberg ML [1982]. A comparison of three personal passive sampling methods for NO_2. Am Ind Hyg Assoc J *43*:553-561.

[3] Jones W, Palmes ED, Tomczyk C, Millson M [1979]. Field comparison of two methods for the determination of NO_2 concentration in air. Am Ind Hyg Assoc J *40*:437-438.

[4] Lindenboom R, Palmes ED [1983]. Effect of reduced atmospheric pressure on a diffusional sampler. Am Ind Hyg Assoc J *44*:105-108.

[5] NIOSH [1994]. Nitric oxide and nitrogen dioxide: Method 6014. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[6] Bartley DL, Doemeny LJ, Taylor DG [1983]. Diffusive monitoring of fluctuating concentrations. Am Ind Hyg Assoc J *44*:241-247.
[7] Hearl FJ, Manning MP [1980]. Transient response of diffusive dosimeters. Am Ind Hyg Assoc J *41*:778-783.

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APPENDIX: PREPARATION OF SAMPLER

1. Measure the average cross-sectional area of a length of 3/8 inch (9.5 mm) ID acrylic tubing.
   a. Cap one end of the tubing. Pour in a known volume, v (mL), of water to nearly fill the tubing (e.g., 100 mL water for a 180-cm (6-foot) length of tubing).
   b. Measure the height, h (cm), of the water column in the tubing.
   c. Determine the average cross-sectional area, A_t (cm^2), of the tubing.

$$A_t = \frac{v}{h}$$

2. Cut the tubing into lengths, L (ca. 7.1 cm), such that A_t / L = exactly 0.1 cm.
   NOTE: The collection rate is directly proportional to A_t / L. For $A_t / L = 0.1$ cm, the collection rate is 2.3 nanomoles/ppm-h [2].
3. Cut circular portions, 13/32 inch (10.3 mm) to 7/16 inch (11.1 mm) in diameter, from stainless steel screen using a 13/32 inch (10.3 mm) paper punch or other suitable means.
4. Clean the tubes, screens and caps with detergent solution in an ultrasonic bath. Rinse with distilled water. Air dry.
5. Dip the screens in absorbing reagent.
6. Using forceps, place the screens on absorbent paper. Press the screens momentarily with the forceps tips to blot. Allow the acetone to evaporate.
7. Stack three treated screens in the bottom of an unflanged cap. Insert the acrylic tube into the unflanged cap securing the screens (see the figures).
8. Slide the pen clip onto the acrylic tube touching the unflanged cap. Secure the pen clip and unflanged cap with a piece of electrical tape.
9. Apply a small amount of stopcock grease to the outside of the uncapped end of the acrylic tube and slide the flanged cap into place.

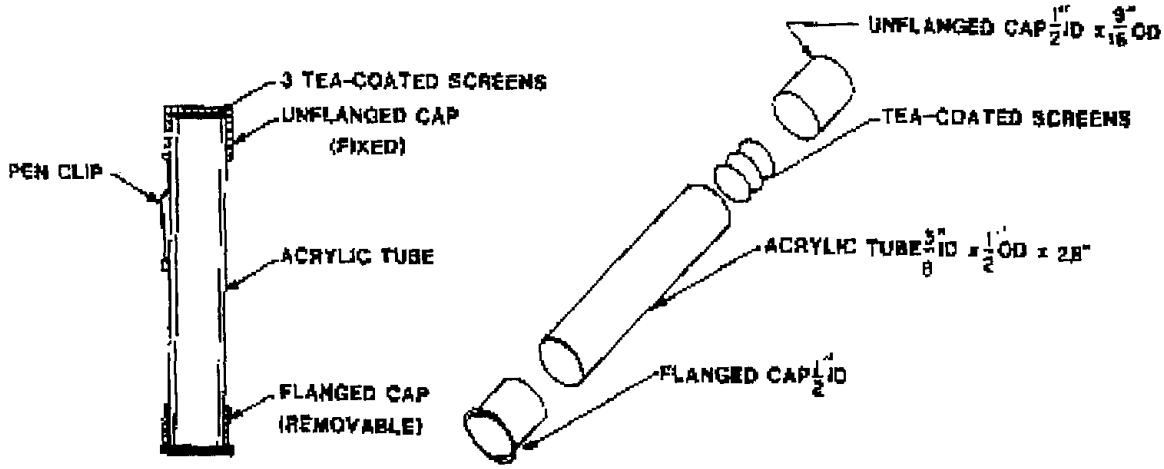


Figure 1. Assembled view (left) and exploded view (right) of sampler.

FORMULAE: Figure 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5601, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

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

PROPERTIES: Table 1

NAMES and SYNONYMS: (Table 1) Aldicarb, Benomyl, Captan, Carbaryl, Carbendazim, Carbofuran, Chlorprophan, Diuron, Formetanate, Methiocarb, Methomyl, Oxamyl, Propham, Propoxur, Thiobencarb

SAMPLING

SAMPLER: FILTER/SOLID SORBENT TUBE (OVS-2 Tube: 13-mm quartz fiber filter; XAD-2, 270 mg/140 mg)

FLOW RATE: 0.1 to 1 L/min [1]

VOL-MIN: variable (see Table 2)
-MAX: 480 L

SHIPMENT: routine

SAMPLE STABILITY: at least 30 days @ -12 °C [1]
at least 7 days @ 24 °C [1]

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: HPLC, UV detection

ANALYTE: organonitrogen pesticides (Table 1)

EXTRACTION: 2 mL extraction solution (0.2% V/V 0.1 *M* aqueous triethylamine phosphate buffer in acetonitrile, pH 6.9 to 7.1)

INJECTION VOLUME: 5 µL

MOBILE PHASE A: 2% 1-propanol in aqueous 0.02 *M* triethylamine phosphate (pH 6.9 to 7.1)

MOBILE PHASE B: 2% 1-propanol in acetonitrile

PROGRAM: mobile phase B, 3 to 95% in 30 min, hold 95% 5 min

COLUMN: NOVA-PAK® C-18, 30 cm x 3.9-mm ID, or equivalent; ambient temperature (Table 3)

DETECTOR: UV absorption at 200 and 225 nm

CALIBRATION: solutions of analytes in extraction fluid

RANGE: Table 2

ESTIMATED LOD: Table 2

PRECISION ($\hat{S}_r$): Table 2

APPLICABILITY: The working ranges (Table 2) for aldicarb, carbofuran, and oxamyl range from 0.5 to 10 times the OSHA PEL. Others cover 0.1 to 2 times the OSHA PELs with appropriate dilutions [1].This method may be applicable to the determination of other organonitrogen compounds after evaluation, and to a broad range of pesticides having UV chromophores, e.g., acetanilides, acid herbicides, organophosphates, phenols, pyrethroids, sulfonyl ureas, sulfonamides, triazines, and uracil pesticides.

INTERFERENCES: Because of the broad response of the UV detector at shorter wavelengths, there are many potential interferences. Those tested include solvents (chloroform and toluene), antioxidants (BHT), plasticizers (dialkyl phthalates), nitrogen compounds (nicotine and caffeine), impurities in HPLC reagents (e.g., in triethylamine), other pesticides (2,4-D, atrazine, parathion, etc.), and pesticide hydrolysis products (1-naphthol). Retention times are given in Table 4. Confirmation techniques are recommended when analyte identity is uncertain.

OTHER METHODS: This method may be used to replace previous related pesticide methods: S273 Carbaryl [2]; 5006 Carbaryl [3]; OSHA 63 Carbaryl and 74 Aldicarb [4]; OSHA Stopgap methods for several pesticides [5]; and EPA TO-10 for captan, Folpet, and Mexacarbate [6]. The OVS-2 Tube is similar in concept to the device of Hill and Arnold [7], but offers convenience and lower flow resistance.

REAGENTS:

1. Carbamate, urea, and sulfenimide analytes listed in Table 1; internal standards acetanilide and acetophenone, analytical grade.*
2. Acetonitrile, UV grade.*
3. Methanol, HPLC grade.*
4. Deionized water, ASTM Type II.
5. 1-Propanol, UV grade.*
6. n-Butyl isocyanate.*
7. Triethylamine (TEA), HPLC grade.* Keep refrigerated (0 to 4 °C) and store under nitrogen for longer shelf life [1,8].
8. Ortho-phosphoric acid, >85% by weight, ACS grade or better.*
9. Extraction solution. Prepare separate triethylamine phosphate ($TEA\text{-}PO_4$) preservative and internal standard solutions.
   a. $TEA\text{-}PO_4$ preservative, 0.1 *M*. Dissolve 1.4 mL of TEA in 90 mL of deionized water. Add phosphoric acid to lower pH to 7.0 (± 0.1) as indicated by a calibrated pH meter. Bring volume to 100 mL. Keep tightly capped and refrigerated.
      NOTE: Do not use chloroacetic acid as a preservative [9]. Formetanate, at least, is unstable with chloroacetic acid.
   b. Internal standard stock solution, 5mg/mL. Add 100 mg of each internal standard of choice for each 20 mL of solution required. Dissolve in acetonitrile. Store capped at −12 ± 1 °C.
   c. Final extraction solution. Add 1 mL of the $TEA\text{-}PO_4$ solution and 12 mL of the internal standard stock solution to a 500-mL volumetric flask. Dilute to volume with acetonitrile. Concentration of TEA = 0.2 m*M*, water = 0.2%, and internal standards = 120 µg/mL. Stable up to 30 days at 0 to 4 °C.
10. Individual analyte stock solutions, 5 mg/mL. Add each analyte to acetonitrile in separate volumetric flasks. Use methylene chloride for benomyl and carbendazim. Use 50/50 v/v methanol/acetonitrile for formetanate. Store at −12 ± 1 °C. (Solutions are stable up to 30 days.)
11. Calibration stock solution. Combine stock solutions of analytes of interest in a volumetric flask to produce the highest concentration standard (suggest 120 to 480 µg/mL).
    NOTE: Do not combine benomyl and carbendazim in the same standard

EQUIPMENT:

1. Sampler: OSHA Versatile Sampler (OVS-2 tube), 13-mm OD inlet, 6-mm OD outlet. Front section contains 270 mg 20/60 mesh XAD-2 sorbent held in place by an 11-mm diameter quartz fiber filter and Teflon® ring, separated from the back section of 140 mg XAD-2 sorbent by a short plug of polyurethane foam. The back section is held in place with a plug of polyurethane foam (See Figure 2). The tube is available commercially (SKC #226-58). OVS-2 tubes with glass fiber filters have equivalent desorption efficiencies and are available from SKC (#226-30-16) and Supelco (#ORBO-49P).
2. Personal sampling pump: 0.1 to 1 L/min with flexible and inert connecting tubing.
3. High Performance Liquid Chromatograph capable of mixing two mobile phases in a linear gradient. Must be capable of pumping up to 4000 psi, to accommodate 300 mm long columns.
4. Autosampler, low dead-volume, capable of 5-µL injections. Preservative ($TEA\text{-}PO_4$) in the desorbing solution may be eliminated if a refrigerated autosampler tray is available.**
5. Analytical columns.
   a. Primary column: Base-deactivated octadecylsilyl (C_{18}) column, *e.g.*, NOVA-PAK® C18, 3.9-mm ID X 300 mm, 5-µm particle size or equivalent.
   b. Secondary column: Cyanopropyl silica column, *e.g.*, Supelco LC-CN® 4.6 X 250-mm, 5-µm particle size or equivalent.
6. Guard column, low dead-volume, containing analytical column packing material.**
7. Ultraviolet detector, low dead-volume, with 1-cm path length cell capable of monitoring two wavelengths (200- and 225-nm) simultaneously.
8. Vials: 4-mL with PTFE-lined caps; 2-mL HPLC autosampler vials with PTFE- or polyethylene-lined snap caps.
9. Syringes: 0.01-, 0.05-, 0.1-, 1.0- and 2.5-mL; Luer lock, 1- or 2.5-mL for sample filtering.
10. Volumetric flasks: 2-, 5-, 10-, 25-, 50-, 100-, 500-, and 1000-mL.
11. PTFE syringe filter: 0.45-µm. (Gelman Acrodisc® CR PTFE 0.45-µm filter, Product #4472, Gelman Sciences, Ann Arbor, MI or equivalent.)
12. Forceps.
13. Small vial/tube tumbler capable of 5 to 10 RPM
14. pH meter.
15. Graduated cylinders, 10-mL, 25-mL.

REAGENTS (contd)

solution. [10-12]. See APPENDIX.

12. Quality control spiking solutions: Add analyte stock solutions to acetonitrile at concentrations in the analytical range of the samples. Store in the freezer at −12 ± 1 °C until immediately before spiking.
    NOTE: Spiking solutions must not contain internal standard.
13. Mobile phase A. Combine 20 mL of 1-propanol and 2.8 mL of TEA in a 1-L volumetric flask and bring to volume with deionized water. Adjust pH to 7.0 (± 0.1) with phosphoric acid using a pH meter. Final concentrations: 2% 1-Propanol, 0.02 *M* TEA-PO_4. Degas prior to use.
14. Mobile phase B. Add 20 mL of 1-propanol to acetonitrile in a 1-L volumetric flask and bring to volume. Degas prior to use.

* See SPECIAL PRECAUTIONS

EQUIPMENT (contd)

16. Pipettes, glass, disposable.

** Low dead volumes will give lower dwell volumes [13,14] and better resolution [15].

SPECIAL PRECAUTIONS: Pesticides: Avoid inhaling vapors or dust; avoid skin contact. Wear gloves and suitable clothing when handling pure material. Solvents: Avoid skin contact and open flame. Use in a hood. Phosphoric acid: Avoid skin contact. n-Butyl isocyanate may act as a sensitizer. Avoid skin contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to the personal sampling pump with flexible tubing. Place sampler vertically, with the large end down, in the worker's breathing zone.
3. Sample at an accurately known flow rate between 0.1 and 1 L/min for a total sampling volume up to 480 L. Record volume, and document presence of any known or potential interferences.
4. Cap both ends of the sampler with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end. Transfer filter, PTFE retainer ring, and front XAD-2 resin section to a 4-mL vial. Transfer the polyurethane foam divider plug along with the back-up XAD-2 resin bed to a second 4-mL vial.
6. Add 2.0 mL of desorbing solvent with internal standards to each vial using a 2.5- or 5-mL syringe or 2-mL pipette; cap each vial.
7. Mix by rotating the vials end-over-end at 5 to 10 RPM for approximately 45 minutes.
8. Filter an aliquot into a 2-mL autosampler vial through a 0.45-µm PTFE filter.

CALIBRATION AND QUALITY CONTROL:

9. Determine retention times for the analytes of interest using the column and chromatographic conditions of choice for the analysis.
10. Calibrate daily with at least six working standards covering the analytical range for individual analytes.
    a. Prepare working standards by diluting aliquots of the high-level calibration standard with desorbing

solution containing internal standard in a volumetric flask. Include an unspiked desorption solution calibration blank.

b. Filter aliquots of standards and blanks for analysis (See Step 8).
c. Analyze together with samples, blanks, and laboratory control samples (Steps 12 through 14).
d. Prepare a calibration graph (ratio of peak area of analyte over peak area of internal standard vs. µg analyte).

NOTE: Use of an internal standard is recommended [1,16], but optional if the precision of the injection device and HPLC system are known to be adequate.

11. Prepare desorption efficiency (DE) samples and Laboratory Control Samples (LCS) with each sample set at a rate of 10% of samples.
    a. Remove cap and the PTFE retainer ring from large end of sampler tube (to prevent wicking behind the ring). Apply known volume of calibration solution to face of quartz fiber filter.

    NOTE: Spike no more than 15 to 30 µL at a time. If more needs to be applied, connect the sampler to a vacuum pump with a flow ≤1 L/min, then apply spiking solution in 15- to 30-µL aliquots. Allow several minutes for the solvent to evaporate between each aliquot, to prevent wicking along the sides of the tube into the back-up section (5% or more may deposit on the walls of the tube).

    b. Cap and allow to stand a minimum of one hour.

    NOTE: Prepare LCS when samples arrive and store with field samples until analyzed.

    c. Include an unspiked sampler as a media (method) blank.
    d. Analyze with the field samples, blanks, and the liquid standards (Steps 12 through 14).

MEASUREMENT:

12. Set liquid chromatograph according to manufacturer's recommendations and to conditions listed in Table 3. Select two wavelengths for detection with 200 and 225 nm for general-purpose screens. For selected analytes, chose a more specific wavelength {from Table 10 or} from UV spectra where available.
13. Inject sample aliquot with autosampler. See Table 4 for approximate retention times of selected analytes.

    NOTE: If peak area is greater than the area of the highest standard, dilute with desorbing solution containing internal standards and reanalyze. Apply the appropriate dilution factor in calculations.

14. Measure peak area of analyte(s) and internal standard(s). Divide peak area of analyte by peak area of internal standard on same chromatogram.

CALCULATIONS:

15. Determine the mass, µg, (corrected for DE) of analyte found in the sample filter and front sorbent section (W_f), back sorbent section (W_b), and the media blank front (B_f) and back (B_b) sorbent sections from a standard curve.
16. Calculate concentration, C (mg/m ^{3}), of each analyte in the air volume sampled, V (L).

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

NOTE: µg/mL ≡ mg/m^3

CONFIRMATION:

Retention Times with Alternate Conditions. Whenever the identity of an analyte is uncertain, confirmation may be achieved by analysis on an alternate column. If primary analysis was performed on a base-deactivated octadecylsilyl (C18) column, identity may confirmed by reanalysis on a cyanopropyl silica column, or by changing to a water/methanol mobile phase (see Table 9 for recommended alternative conditions). See Table 4 for approximate retention times for each column type and condition. Relative

retention times (retention indices for a particular set of conditions) are more convenient for the identification of unknown analytes.

UV or Mass Spectra. Confirmation may be achieved through comparison of unknown spectra with reference spectra where available. Relative response ratios (See Table 10 for ratio of absorbances at 225 nm/200 nm for selected analytes) wiil give a moderate level of confirmation. Some analytes (O-aryl carbamates especially) can be confirmed by GC/MS using highly deactivated injection ports and analytical GC columns, or by HPLC/MS.

EVALUATION OF METHOD:

This method was evaluated over the ranges specified in Table 2 at 25 °C with 240-L air samples. Samplers were tested at 15 and 80% relative humidity and 10 and 30 °C. In these experiments, test atmospheres were not generated; instead, analytes were fortified on the face of the sampler filters. The conditioned air was pulled through the samplers at 1 L/min for four hours. No significant difference in sampler performance was noted at any of these temperature/humidity combinations. Evaluation of sampler precision and stability was conducted at ambient conditions of temperature and relative humidity. Overall sampling and measurement precision, bias, accuracy, and average percent recovery after long-term storage are presented in Table 2. No breakthrough was detected with samplers fortified with 480 µg per analyte per tube after sampling eight hours at 1 L/min. For the estimation of LOD/LOQ, a series of media-spiked standards were prepared in triplicate, analyzed, and responses fitted to a quadratic curve. The Limit of Detection (LOD) and Limit of Quantitation (LOQ), given in Table 2, were estimated according to NIOSH SOP 018 [1, 17]. Criteria established by NIOSH were met [1].

REFERENCES:

[1] Back-up Data Report [1995, unpublished] Carbamate, urea, and sulfenimide pesticides, prepared under NIOSH Contract 200-88-2618.
[2] NIOSH [1977]. NIOSH Manual of Analytical Methods (NMAM), 2nd ed., v. 3, s273, U.S. Dept. Health, Education, and Welfare, National Institute for Occupational Safety and Health (NIOSH) Publ. 77-157-C.
[3] NIOSH [1994]. Method 5006. In: Cassinelli ME, Ed. NIOSH Manual of Analytical Methods(NMAM),4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publ. 94-113.
[4] OSHA Methods 63 and 74, OSHA Analytical Methods Manual, Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, UT.
[5] OSHA Stopgap Methods for individual pesticides (Refer to by compound name), Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, UT.
[6] EPA [1986]. EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, US EPA, Publ. EPA/600/4-87/006.
[7] Hill RH Jr., Arnold JE [1979]. A personal air sampler for pesticides. Arch Environ Contam Toxicol 8:621-628.
[8] Dolan JW [1993]. LC troubleshooting. LC-GC *11*(7):500.
[9] EPA [1988]. EPA Method 531.1, Rev. 3.0, Methods for the determination of organic compounds in drinking water, US EPA. Publ. EPA 600 4-88 039.
[10] Chibia, Mikio, Doornbos F [1974]. Instability of benomyl in various conditions. Bulletin of Environ Contami Toxicol *11*(3):273-274.
[11] Calmon, Jean-Pierre, Sayag DR [1976]. Kinetics and mechanism of conversion of methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate (benomyl) to methyl 2-benzimidazolecarbamate (MBC). J Agric Food Chem *24*(2):311-314.
[12] Calmon, Jean-Pierre, Sayag DR [1993]. Instability of methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate (benomyl) in various solvents, Ibid. 426-428.
[13] Dolan JW [1993]. LC troubleshooting. LC-GC *11*(12):858-860.
[14] Dolan JW [1993]. LC troubleshooting. LC-GC *11*(6):412-314.
[15] Dolan JW [1993]. LC troubleshooting. LC-GC *12*(4):298.
[16] Gere DR [1993]. Column watch. LC-GC *11*(10):710-712.

[17] Kennedy ER, Fischbach TJ, Song R, Eller PM, Schulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117:65-67.
[18] NIOSH [1987]. In: Sweet, DV Ed.. Registry of Toxic Effects of Chemical Substances. National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 87-114.
[19] *Merck Index* [1989]. 11th Ed., S. Budavari, Ed., Merck and Co., Rahway, NJ.
[20] *Farm Chemicals Handbook* [1995], Meister Publishing Co., Willoughby, OH.
[21] Wise, Stephen A, May WE [1983]. Effect of C18 surface coverage on selectivity in reversed-phase liquid chromatography of polycyclic aromatic hydrocarbons. Anal Chem *55*(9):1479.
[22] Cole, Lynn A, Dorsey JG [1992]. Temperature dependence of retention in reversed-phase liquid chromatography. 1. Stationary-phase considerations. Anal Chem *64*(13):1317-1323.
[23] Wirth, Mary J [1994]. Column watch. LC-GC *12*(9):656-664.
[24] Cole, Lynn A, Dorsey JG [1990]. Reduction of reequilibration time following gradient elution reversed-phase liquid chromatography. Anal Chem *62*(1):16-21.
[25] Foley, Joe P, May WE [1987]. Optimization of secondary chemical equilibria in liquid chromatography: variables influencing the self-selectivity, retention, and efficiency in acid-base systems. Anal Chem *59*(1):110-115.
[26] Dolan, John M [1993]. LC troubleshooting. LC-GC *11*(2):94.
[27] Roos, Robert W, Lau-Cam CA [1986]. General reversed-phase high-performance liquid chromatographic method for the separation of drugs using triethylamine as a competing base. Journal of Chromatography *370*:403-418.
[28] Kirkland JJ, Boyes BE, and DeStefano JJ [1994]. Changing band spacing in reversed-phase HPLC. American Laboratory *Sept*:36-42.
[29] Seaver, Sadek P, Sadek C [1994]. LC troubleshooting. LC-GC *12*(10):742-746.
[30] Zweig, Gunter, Ru-yu Gao [1983]. Determination of benomyl by reversed-phase liquid chromatography. Anal Chem *55*(8):1448-1451.
[31] Dolan, John W [1992]. LC troubleshooting. LC-GC *10*(10):746.
[32] Evans, Christine E, Victoria L, McGuffin [1991]. Direct examination of the injection process in liquid chromatographic separations. Anal Chem *63*(14):1393-1402.
[33] Steffeck RJ, Woo SL, Weigand RJ, Anderson JM [1995]. A comparison of silica-based C18 and C8 HPLC columns to aid column selection. LC-GC*13*(9):720-726.

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TABLE 1. GENERAL INFORMATION

Name / Synonym	Empirical Formula	MW	Properties	Solubility in H_2O (g/L)	Exposure Limit (mg/m^3)
Aldicarb CAS# 116-06-3 RTECS UE2275000	$C_7H_{14}N_2O_2S$	190.3	MP 99-100 °C; vp 3.9 mPa ($2.9x10^{-5}$ mm Hg) @ 25 °C; LD_{50} 1 mg/kg	6 @ 25 °C	
Benomyl CAS# 17804-35-2 RTECS DD6475000	$C_{14}H_{18}N_4O_3$	290.36	MP decomposes; vp <1.3 mPa (<$1x10^{-5}$ mm Hg) @ 20 °C; LD_{50} >9590 mg/kg	0.002 @ 25 °C	OSHA 5.0 (resp) ACGIH 10
Captan CAS# 133-06-2 RTECS GW5075000	$C_9H_8Cl_3NO_2S$	300.6	MP 178 °C; vp <1.3 mPa (<$1x10^{-5}$ mm Hg) @ 20 °C; LD_{50} 9000 mg/kg	<0.005 @ ~25 °C	NIOSH 5 ACGIH 5
Carbaryl CAS# 63-25-2 RTECS FC5950000	$C_{12}H_{11}NO_2$	201.24	MP 142 °C; vp <5.3 mPa (<$4x10^{-5}$ mm Hg) @ 25 °C; LD_{50} 250 mg/kg	0.12 @ 30 °C	OSHA 5 NIOSH 5 ACGIH 5
Carbendazim CAS# 10605-21-7 RTECS DD6500000	$C_9H_9N_3O_2$	191.21	MP 302-307 °C (decomposes); LD_{50} 6400 mg/kg	0.008/pH 7 @ 24 °C	
Carbofuran CAS# 1563-66-2 RTECS FB9450000	$C_{12}H_{15}NO_3$	221.28	MP 150-153; vp 0.031 mPa ($2.3x10^{-7}$ mm Hg) @ 20 °C; LD_{50} 5.3 mg/kg	0.70 @ 25 °C	NIOSH 0.1 ACGIH 0.1
Chlorpropham CAS# 101-21-3 RTECS FD8050000	$C_{10}H_{12}ClNO_2$	213.68	MP 40.7-41.1 °C; vp 2.7 mPa ($2x10^{-5}$ mm Hg) @ 33 °C;LD_{50} 1200 mg/kg	slightly soluble	
Diuron CAS# 330-54-1 RTECS YS8925000	$C_9H_{10}Cl_2N_2O$	233.11	MP 158-159 °C; vp 0.41 mPa ($3.1x10^{-6}$ mm Hg) @ 50 °C; LD_{50} 437 mg/kg	0.042 @ 25 °C	NIOSH 10 ACGIH 10
Formetanate.HCl CAS# 23422-53-9 RTECS FC2800000	$C_{11}H_{16}ClN_3O_2$	257.75	MP 200-202 (decomposes); LD_{50} 20 mg/kg	>50% as hydrochlor-ide	
Methiocarb CAS# 2032-65-7 RTECS FC5775000	$C_{11}H_{15}NO_2S$	225.34	MP 121.5 °C; vp 0.036 mPa ($2.7x10^{-7}$ mm Hg) @ 25 °C; LD_{50} 60 mg/kg	insoluble	
Methomyl CAS# 16752-77-5 RTECS AK2975000	$C_5H_{10}N_2O_2S$	162.24	MP 78-79 °C; vp 6.7mPa ($5x10^{-5}$ mm Hg) @ 25 °C; LD_{50} 17 mg/kg	58 @ 25 °C	NIOSH 2.5 ACGIH 2.5
Oxamyl CAS# 23135-22-0 RTECS RP2300000	$C_7H_{13}N_3O_3S$	219.3	MP 100-102 °C; vp 31 mPa ($2.4x10^{-4}$ mm Hg) @ 20 °C; LD_{50} 5 mg/kg	280 @ 25 °C	
Propham CAS# 122-42-9 RTECS FD9100000	$C_{10}H_{13}NO_2$	179.24	MP 90 °C; vp 18 mPa ($1.35x10^{-4}$ mm Hg); LD_{50} 3724 mg/kg	0.25 @ 25 °C	
Propoxur CAS# 114-26-1 RTECS FC3150000	$C_{11}H_{15}NO_3$	209.27	MP 91.5 °C; vp 1.3 mPa (9.75 mm Hg) @ 20 °C; LD_{50} 83 mg/kg	2 @ 20 °C	NIOSH 0.5 ACGIH 0.5
Thiobencarb CAS# 28249-77-6 RTECS EZ7260000	$C_{12}H_{16}ClNOS$	257.81	Not available; LD_{50} 1130 mg/kg	~0.03 @ 20 °C	

Abbreviations: MW=molecular weight (Daltons); RTECS=Registry of Toxic Effects of Chemical Substances[18]; LD_{50}=lethal dose 50% [19,20]; mPa=milliPascals

TABLE 2. METHOD EVALUATION

Compound	Min. Sample Vol (L)	Range Studied (µg/samp)	LOD (µg/samp)	Mean Bias	Overall Precision ($\hat{S}_{rT}$)	Accuracy	Storage Stability 31-Day %Rec. 24 °C	-12 °C
Aldicarb	240	12.0-240	1.2	-0.009	0.066	± 0.131	93.2	95.6
Benomyl	6	12.0-120	0.6	[A]	[A]	[A]	[A]	[A]
Captan	30	48.0-960	4.8	-0.036	0.061	± 0.142	98.7	102.2
Carbaryl	6	12.0-240	0.06	+0.012	0.061	± 0.123	88.2	91.8
Carbendazim	6	[B]	0.6	+0.006	0.061	± 0.121	92.1	89.3
Carbofuran	240	12.0-240	0.6	-0.020	0.060	± 0.126	89.1	92.4
Chlorpropham	6	12.0-240	0.6	-0.017	0.068	± 0.140	84.3	85.9
Diuron	3	12.0-240	0.6	-0.062	0.060	± 0.167	86.0	87.1
Formetanate.	60	12.0-240	0.6	+0.032	0.056	± 0.129	89.8	93.0
Methiocarb	60	12.0-240	0.6	+0.009	0.061	± 0.122	85.1	89.1
Methomyl	12	12.0-120	0.6	-0.002	0.063	± 0.124	90.5	95.2
Oxamyl	240	12.0-240	0.6	+0.037	0.055	± 0.132	94.8	95.9
Propham	3	12.0-240	0.8	-0.053	0.066	± 0.168	88.5	92.5
Propoxur	60	12.0-240	0.6	+0.007	0.079	± 0.156	91.4	95.4
Thiobencarb	6	12.0-240	0.6	-0.068	0.073	± 0.197	75.0	79.8

[A] Results calculated as carbendazim, the primary breakdown product of benomyl.
[B] See range for benomyl, a precursor for carbendazim.

TABLE 3. RECOMMENDED LIQUID CHROMATOGRAPHIC COLUMNS AND CONDITIONS

PARAMETER	HPLC COLUMN AND CONDITIONS			
Column:	C_{18}	C_{18}	Cyano	Cyano
Solvent:	Acetonitrile	Methanol	Acetonitrile	Methanol
Application:	Primary Analysis	Confirmation	Confirmation	Confirmation
Column parameters:				
Column	NOVA-PAK C18	NOVA-PAK C18	Supelcosil LC-CN	Supelcosil LC-CN
Stationary phase	octadecyl	octadecyl	cyanopropyl	cyanopropyl
Length (mm)	300	150	250	250
ID (mm)	3.9	3.9	4.6	4.6
Particle size (µm)	4	4	5	5
Ligand density[A]	2.7	2.7	5.2	5.2
Mobile Phase A:				
Solvent	water	water	water	water
Organic modifier[B]	2% 1-propanol	none	none	none
Buffer[C]	TEA-PO_4	none	TEA-PO_4	TEA-PO_4
Concentration (Molarity)	0.02 *M*	none	0.02 *M*	0.02 *M*
Mobile Phase B:				
Solvent[D]	acetonitrile	methanol	acetonitrile	methanol
Organic modifier	2% 1-propanol	none	none	none
Mobile Phase Program:				
Initial hold time (min)	0	0	0	0
Program rate	3-95% B	10-80% B	3-60% B	3-95% B
Program time (min)	30	30	30	30
Program type	linear	linear	linear	linear
Final hold time (min)	5	5	5	5
Flow rate (mL/min)	1.00	1.00	1.00	1.00
Column temperature (°C)	ambient(~24)	ambient(~24)	ambient(~24)	ambient(~24)
Dwell volume (mL)	0.6-0.8	3.5-3.8	0.6-0.8	0.6-0.8
Injection volume (µL)	5	30	5	5
Injection solvent	acetonitrile	1:3 acetonitrile:H_2O	acetonitrile	acetonitrile

[A] Ligand density (micromole/m^2) is a better description of surface coverage than % carbon loading [22,23].
[B] Choice of alcohol modifier is not critical. Percentages may be varied to adjust retention times and peak shapes for early eluting analytes. Reequilibration time may be shorter with 1-propanol [24-26].
[C] Buffer is very essential for basic analytes such as Formetanate, Carbendazim, and Benomyl [12,27,28]. Formentate is cationic at about pH 7, and its actual elution time is sensitive to small changes in pH and ionic strength of the buffer in mobile phase A.
[D] Acetonitrile is the better choice when monitoring compounds at UV absorptions below 210 nm [20,29].

TABLE 4. APPROXIMATE RETENTION TIMES AND INDICES FOR ORGANONITROGEN PESTICIDES AND POTENTIALLY INTERFERING COMPOUNDS

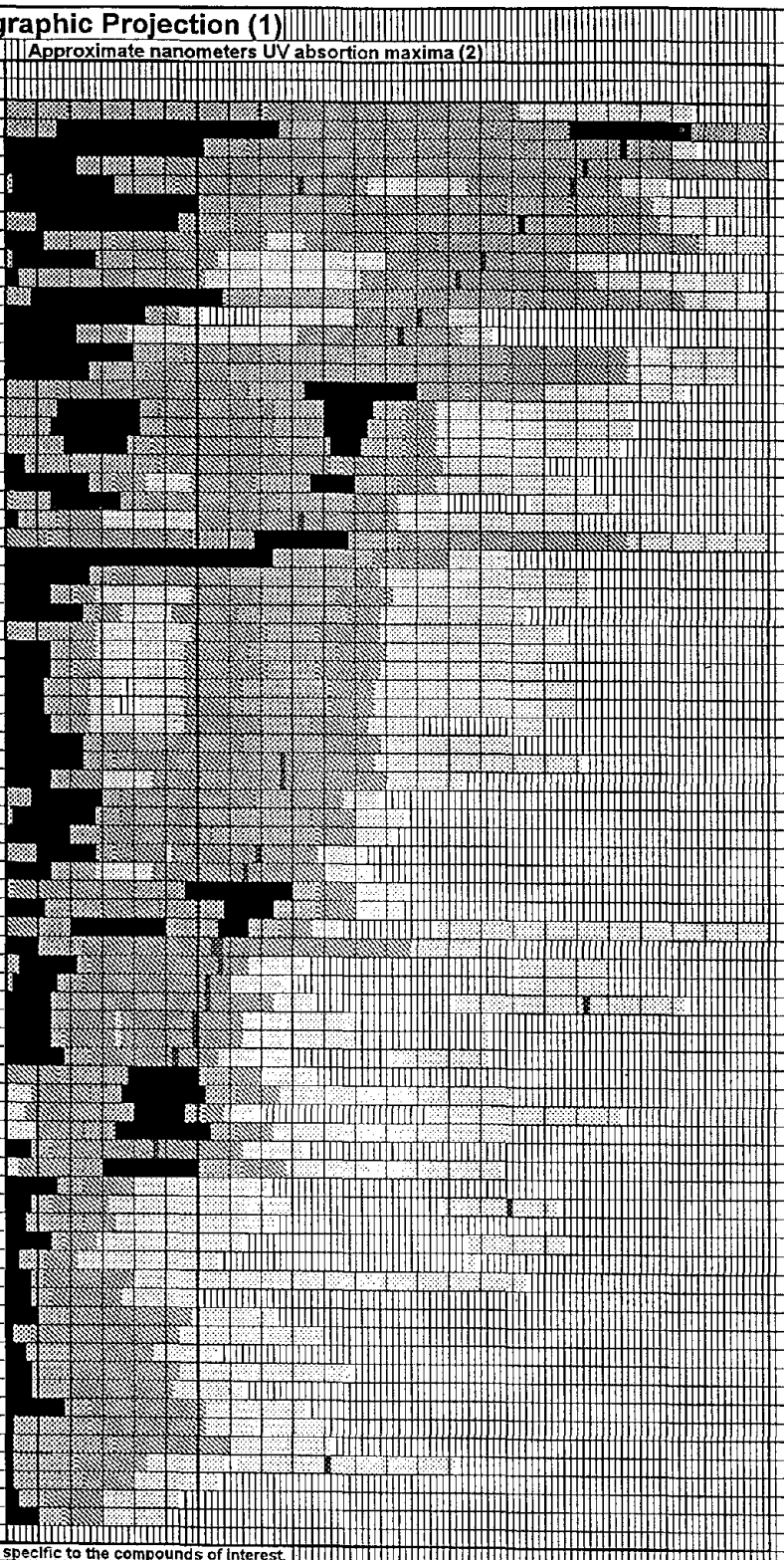
	HPLC COLUMNS AND CONDITIONS					
Column:	C18			Cyano		
Solvent:		MeCN	MeOH		MeCN	MeOH
COMPOUND[A] (by retention time)	Retention Index[B]	Ret. Time (min)	Ret. Time (min)	Retention Index	Ret. Time (min)	Ret. Time (min)
Solvent void volume	**0.000**	**2.3**	**1.4**	**0.000**	**3.0**	**3.2**
Asulam	0.004	2.3				
Imazapyr	0.372	3.2				
Acetaminophen *//S*	**1.000**	**4.7**		**1.000**		
Oxamyl	1.269	6.1	9.9	1.865	7.0	6.4
Caffeine	1.397	6.8				
Methomyl	1.445	7.0	10.7	1.915	7.4	6.6
Formetanate	1.573	7.7	[C]	2.574	12.8	11.3
Sulfometuron methyl	1.868	9.3				
Acetanilide *//S*	**2.000**	**9.9**		**2.000**	**8.1**	**7.7**
Fenuron	2.053	10.2				
2,4-D acid	2.064	10.2				
Nicotine	2.179	10.8				
Carbendazim	2.192	10.8	[C]	4.274	13.6	12.9
Chlorimuron ethyl	2.422	11.9				
Aldicarb	2.755	13.5	19.9	3.000	10.5	10.1
Tebuthiuron	2.817	13.8	23.9			
m-Cresol	2.866	14.0				
Bromacil	2.902	14.2				
Hexazinone	2.921	14.3				
Dinoseb	2.928	14.3				
Simazine	2.938	14.3				
Monuron	2.981	14.5				
Acetophenone *//S*	**3.000**	**14.6**		**3.000**	**10.5**	**9.9**
Cyanazine	3.003	14.6				
Metribuzin	3.115	15.0				
Thiodicarb	3.247	15.5				
Aminocarb	3.301	15.7				
Propoxur	3.317	15.8	22.9	3.675	13.1	11.9
Bendiocarb	3.376	16.0	23.3			
Carbofuran	3.399	16.1	23.2	4.018	14.4	14.1
Fluometuron	3.551	16.6	25.2			
Chloroform	3.601	16.8				
Carbaryl	3.654	17.0	24.5	5.236	19.1	18.2
Atrazine	3.688	17.1				
Metalaxyl	3.837	17.6				
Diuron	3.843	17.6	27.0	5.751	21.1	19.9
DEET	3.851	17.7				
alpha-Naphthol	3.893	17.8				
Propiophenone *//S*	**4.000**	**18.2**		**4.000**	14.4	
Propachlor	4.241	18.8				
Thiophanate	4.241	18.8	27.6			
Propham	4.267	18.9	25.9	5.092	17.7	17.3
Diethyl phthalate	4.367	19.2				
Clomazone	4.459	19.4				
Siduron	4.615	19.9				
Desmedipham	4.696	20.1				
Phenmedipham	4.700	20.1	>33			
Methiocarb	4.744	20.2	29.3	6.680	22.5	21.8

	HPLC COLUMNS AND CONDITIONS					
Column:	C18			Cyano		
Solvent:		MeCN	MeOH		MeCN	MeOH
COMPOUND[A] (by retention time)	Retention Index[B]	Ret. Time (min)	Ret. Time (min)	Retention Index	Ret. Time (min)	Ret. Time (min)
Linuron	4.848	20.5	28.9			
BDMC */IS*	4.904	20.6				
SWEP	4.919	20.7				
Captan	4.926	20.7	27.7	6.172	20.9	21.6
Promecarb	4.981	20.8	20.4			
Butyrophenone */IS*	**5.000**	**20.9**		**5.000**	17.4	
Mexacarbate	5.186	21.3				
Toluene	5.269	21.5				
Chlorpropham	5.504	22.1	30.1	6.700	23.4	23.3
Folpet	5.537	22.2	>33			
Barban	5.566	22.3	>33			
Malathion	5.731	22.7				
Fenitrothion	5.802	22.8				
Benomyl	5.822	22.9	[C]	7.391	25.8	23.9
Oryzalin	5.860	23.0				
Metolachlor	5.876	23.0				
Alachlor	5.979	23.3				
Acetochlor	5.983	23.3				
Valerophenone */IS*	**6.000**	**23.3**		**6.000**	20.9	
Captafol	6.018	23.4	30.1			
Neburon	6.045	23.4				
Parathion	6.640	24.7				
Hexanophenone */IS*	**7.000**	**25.5**		**7.000**	**24.0**	
Thiobencarb	7.148	25.8	33.4	7.916	26.2	26.8
Heptanophenone */IS*	**8.000**	**27.6**		**8.000**	**26.4**	
Di-n-butyl phthalate	8.016	27.6				
Chlorpyrifos	8.701	28.9				
Pendimethalin	8.724	28.9				
2,4-D butoxyethyl ester	8.892	29.2				
Octanophenone */IS*	**9.000**	**29.4**		**9.000**	**29.0**	
BHT	9.488	30.2				
Amitraz	9.886	30.9				
Nonanophenone */IS*	**10.000**	**31.1**				
2,4-D ethylhexyl ester	10.545	31.9				
Decanophenone */IS*	**11.000**	**32.5**				

[A] Organonitrogen pesticides are in bold letters.
[B] Estimated (~) retention times are extrapolated from shorter columns using relative retention times.
[C] Without TEA-PO_4 buffer, basic compounds had irregular peak shapes and retention times, or were not detected.
Abbreviations: MeCN=acetonitrile; MeOH=methanol; *IS*=internal standard.

Table 5. UV Spectra, Orthographic Projection (1)

	Compound (by UV maxima) (3)	max. (3)	Ratio (4) 225/200
1	Dinoseb	373	
2	Metribuzin	293	
3	Benomyl	292	1.074
4	Amitraz	287	
5	Carbendazim	284	0.503
6	Oryzalin	279	
7	Bromacil	277	
8	Parathion	273	
9	Caffeine	270	
10	Fenitrothion	267	
11	Thiophanate	266	
12	Toluene	260	
13	Nicotine	257	
14	Formetanate	254	0.505
15	Asulam	254	
16	Tebuthiuron	251	
17	Neburon	249	
18	Linuron	249	
19	Diuron	248	0.437
20	Chlorimuron ethyl	247	
21	Monuron	246	
22	SWEP	245	
23	Acetaminophen IS	243	
24	Pendimethalin	242	
25	Oxamyl	242	0.867
26	Fluometuron	242	
27	Acetophenone IS	242	
28	Siduron	240	
29	Propiophenone IS	240	
30	Butyrophenone IS	240	
31	Valerophenone IS	240	
32	Hexanophenone IS	239	
33	Heptanophenone IS	239	
34	Octanophenone IS	239	
35	Fenuron	239	
36	Aminocarb	238	
37	Acetanilide IS	238	
38	Chlorpropham	237	0.312
39	Phenmedipham	236	
40	Desmedipham	236	
41	Barban	235	
42	Propham	233	0.383
43	Methomyl	233	1.944
44	Thiodicarb	232	
45	alpha-Naphthol	231	
46	Chlorsulfuron	228	
47	2,4-D acid	228	
48	2,4-D ethylhexyl ester	228	
49	Chlorpyrifos	227	
50	Di-n-butyl phthalate	225	
51	Diethyl phthalate	224	
52	Methiocarb	222	0.269
53	Folpet	221	
54	Atrazine	220	
55	Carbaryl	219	2.595
56	Simazine	219	
57	Thiobencarb	219	0.484
58	Cyanazine	219	
59	BDMC IS		
60	Bendiocarb		
61	BHT		
62	Carbofuran		0.148
63	Propoxur		0.209
64	Mexacarbate		
65	Promecarb		
66	Acetochor		
67	Clomazone	211	
68	Metalaxyl		
69	DEET		
70	Alachlor		
71	Metolachlor		
72	Propachlor		
73	Malathion		
74	Aldicarb		0.169
75	Captan		0.135
76	Captafol		
77	Chloroform		



(1) This table may be used to select wavelengths specific to the compounds of interest.

(2) Approximate UV absorbance: 80-100% | 50-80% | 20-50% | 5-20% | 0-5%

Slight variations in the boundaries should be expected for different scanning UV detectors, compound concentrations, and variations in background subtraction technique. Spectra were obtained at approximately 60ug/mL under analytical conditions on a C18 column. Spectra are scaled independantly to 100% and absolute absorbance may vary significantly.

(3) Compounds are sorted by the longest wavelength of a peak or shoulder with an absorbance greater than about 20% of the maximum absorbance between 195 and 400 nm. For peaks at wavelengths less than 210nm, sorting is only approximate due to possible background subtraction errors.

(4) Ratio of UV absorbance, 225 nm/ 200 nm, is a semiqualitative number derived from the average absorbance of 7 replicates analyzed at 60 ug/mL.

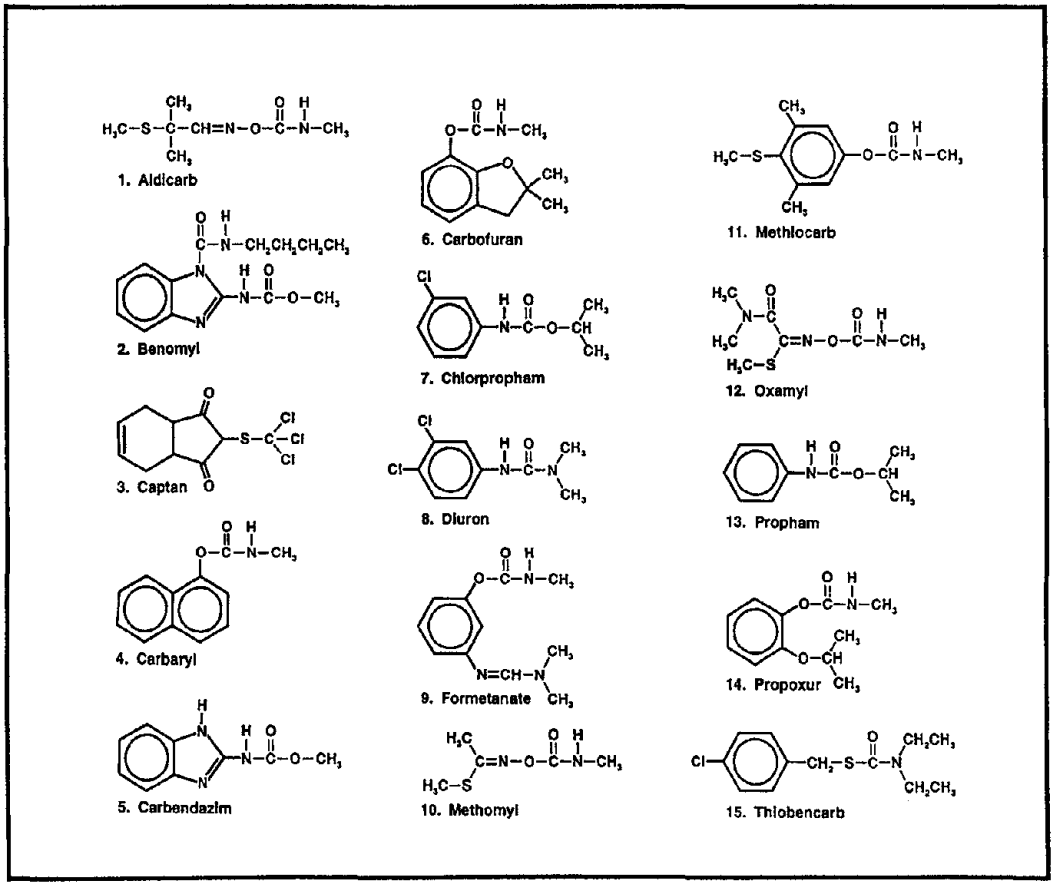


FIGURE 1. STRUCTURE OF CARBAMATE, UREA, AND SULFENIMIDE PESTICIDES

NOTES ON HPLC ANALYSIS OF CARBAMATE, UREA, AND SULFENIMIDE PESTICIDES

It is expected that the analyst will have a well-founded background in the analytical practices and principles that are required for any method to work. The following list of cautions and reminders is provided for convenience; most will impact the success or failure of this method.

A. ANALYTES

1. Aldicarb
   a. The UV response for aldicarb passes through a minimum at approximately 225 nm. If only two wavelength channels are used (225 nm and 200 nm), the response for aldicarb at 200 nm should be monitored (refer to UV spectrum for aldicarb). At 205 nm the signal will be smaller, but the signal-to- noise ratio may be better on particular instruments. An alternative but lesser maximum is at approximately 245 to 246 nm. This latter maximum, though small, may have less background noise and interferences from coelutants.
   b. Aldicarb is a highly toxic pesticide. Care should be exercised in handling pure stock material.

2. Benomyl (see also Carbendazim)
   a. Benomyl breaks down rapidly by either hydrolysis in protic solvents (*e.g.*, water or methanol) or solvolysis in nonprotic solvents (*e.g.*, methylene chloride or acetonitrile) to carbendazim. The breakdown of benomyl can be so rapid that no benomyl will be detected at all after approximately 4 to 24 hours at room temperature. The rate of solvolysis is slower in the less polar methylene chloride and very rapid in acetonitrile, even exceeding the rate of hydrolysis [10-12]. Benomyl standards in these nonprotic solvents can be stabilized with the addition of 1% n-butyl isocyanate [30]. The preservative effect is lost as soon as the solution is diluted in solvents that contain or consist of protic solvents, since protic solvents also react with the isocyanates. It is generally unnecessary to add any preservative to the benomyl standard solution (it breaks down anyway). The carbendazim produced can precipitate out, if the solutions are too concentrated. In such an event, the addition of 1% n-butyl isocyanate is essential.
   b. Since benomyl breaks down to carbendazim, do not include both benomyl and carbendazim in the same standard mixture.
   c. When analyzing for benomyl, both benomyl and carbendazim must be determined. The results can be reported as either benomyl or carbendazim by converting the response of one to the equivalent response for the other at any particular wavelength. The relative response of benomyl to carbendazim at 225 nm has been determined to be approximately 1.0738, (adsorption-benomyl/ adsorption-carbendazim). This ratio should be determined for individual instruments with equimolar solutions analyzed separately, and with the benomyl injection solution being preserved with 1% n-butyl isocyanate. To convert carbendazim response to the equivalent benomyl response so that the values can be summed, multiply the carbendazim response by 1.0738 and add this to the benomyl response. Report results as benomyl. Alternately, to report results as carbendazim, divide benomyl response by 1.0738 and then add this to the carbendazim response. Report as total carbendazim.
   d. See notes for carbendazim.

3. Captan
   a. Captan is not stable in methanol or in aqueous mixtures of methanol or acetonitrile at temperatures greater than –12 °C. Therefore, do not dilute desorbing solutions with water or methanol to weaken the injection solvent. Instead, use small injection volumes of acetonitrile solutions.
   b. Use methylene chloride for making stock standard solutions. See Note A16 of this Appendix.
   c. Captan has low absorption at 225 nm (see UV spectrum for captan). If only two wavelength channels are used (225 and 200 nm), the response for captan at 200 nm should be monitored. Although a lesser response may be obtained at approximately 205 or 210 nm, this can be accompanied by a proportionately better signal-to-noise response and may be an optional choice of wavelength if it is compatible with other analytical objectives.

4. Carbaryl (see also Diuron): Carbaryl tends to break down to 1-naphthol. Chloroacetic acid in methanol will inhibit this reaction [9], but this reagent is deleterious to other analytes. Carbaryl is stabilized in acetonitrile desorbing solutions containing the TEA-PO_4 preservative for at least 24 hours at room temperature, long enough to permit HPLC analysis. Any 1-naphthol that is detected may represent breakdown of carbaryl prior to desorption or may come from another source. Carbaryl has been stabilized with the TEA-PO_4 buffer/preservative for up to three weeks at room temperature.

5. Carbendazim
   a. See notes for benomyl.
   b. Carbendazim can break down to 4-aminobenzimidazole and other compounds. In acetonitrile containing TEA-PO_4 preservative, this breakdown appears to be inhibited for up to 24 hours at room temperature, long enough to permit analysis of desorbates.
   c. Carbendazim is itself used as a pesticide. There are also other analytes such as thiophanate methyl that can break down to carbendazim. Therefore, any carbendazim should not automatically be assumed to represent benomyl.

6. Carbofuran
   a. In most instances carbofuran and bendiocarb coeluted under all conditions tested. Their UV spectra are so nearly alike as to be practically indistinguishable. Any positive identification for carbofuran must be tempered by this knowledge and would require an alternate confirmation such as by mass spectrometry or a knowledge of the history of the sample.
   b. Propoxur and carbofuran elute very close together. The separation of the two compounds with nearly baseline resolution is a good test of resolving power of the HPLC system for neutral compounds on a C18 HPLC column. If they cannot be resolved, there may be problems with large dead volumes in the system, analytical column quality, or injection quality.

7. Chlorpropham: No serious problems are expected to be encountered.

8. Diuron: The breakdown product of carbaryl, 1-naphthol, elutes immediately after diuron under the conditions given. On certain columns, it may coelute with diuron, giving false positive responses. The retention time of 1-naphthol relative to diuron must be determined for any particular column if carbaryl is anticipated to have been present in the sample.

9. Formetanate
   a. At analytical concentrations formetanate is not stable either in methanol or in aqueous mixtures of methanol or acetonitrile with or without chloroacetic acid. Therefore, do not dilute desorbing solutions with methanol or water to weaken the injection solvent. Do not use chloroacetic acid as a preservative. Use only small injection volumes of acetonitrile solutions.
   b. The breakdown of formetanate in analytical solutions is inhibited in acetonitrile containing TEA-PO_4 preservative at room temperature for up to 24 hours, long enough to permit analysis.
   c. At stock standard concentrations, formetanate dissolves better in 50:50 mixtures of methanol: acetonitrile and is stable if kept in freezer at -12 ± 1 °C.
   d. Formetanate is basic and possesses a single positive charge in solution at neutral pH (6.9 – 7.1). The use of TEA-PO_4 buffer and/or base-deactivated HPLC columns is essential for the analysis for this compound.
   e. The exact retention time of formetanate is more affected by exact pH and ionic strength of the buffer (or any other electrolytes) than are the noncharged analytes. Day-to-day inconsistencies in the preparation of mobile phases will cause differences in retention time. If the analyte is eluting too close to methomyl (which just precedes it under the specified conditions), its retention time may be delayed by either raising the pH slightly (by 0.1 to 0.2 units), or by lowering the ionic strength of mobile phase A.

10. Methiocarb: Methiocarb has the same problems as carbaryl, only to a lesser extent. As methiocarb breaks down, there are several other peaks that arise. These have been shown to be alkylthiophenol and/or oxidation products.

11. Methomyl: Attention should be placed on the problem of methomyl as it relates to its early elution time. Refer to Notes B1a and B4 of this Appendix.

12. Oxamyl: Attention should be placed on the problem of oxamyl as it relates to its early elution time. Refer to Notes B1a and B4 of this Appendix.

13. Propham: No problems are expected with propham.

14. Propoxur
    a. With prolonged standing in desorbing solutions at room temperature without preservative, propoxur has been observed to break down to some degree, although much less than carbaryl.
    b. Propoxur elutes very close to carbofuran. See comments under carbofuran.

15. Thiobencarb: Thiobencarb is relatively nonpolar and has lower (but acceptable) recoveries from the XAD-2 resin than the other analytes.

16. Solvent for Analyte Standard Solutions: Most of the analytes (Table 1) are soluble in acetonitrile at stock standard concentrations. The exceptions are benomyl, captan, and formetanate. Appropriate solvents are described under headings for these compounds. In each of the solvents mentioned, analytes are stable at –12 ± 1 °C for at least 30 days.

17. Desorption Solvent and Preservative for Analytes: All analytes (except benomyl) were stable in acetonitrile at –12 °C for at least 48 hours. If refrigerated HPLC autosampler trays are available and all desorbing and tumbling operations are carried out in subambient conditions, no preservative should be needed. At room temperature, several analytes (*e.g.*, carbaryl, methiocarb, and oxamyl especially) degraded unpredictably over 24 to 48 hours. The addition of as little as 0.2% v/v of aqueous 0.1 *M* triethylamine phosphate (TEA-PO_4) buffer, pH 6.9 to 7.1, to the acetonitrile desorption solvent stabilizes all analytes (except benomyl) from hydrolysis or solvolysis for at least 48 hours at room temperature. Methanol, isopropanol, aqueous methanol, and acetonitrile containing any of these alcohols promote degradation of several analytes (especially captan and formetanate) and poor desorption efficiencies. The use of chloroacetic acid, as is required for aqueous samples in EPA Method 531.1 [9], is destructive to at least formetanate. Since the desorption solvent is also the HPLC injection solvent, refer to note on Injection Solvent (B1) for additional comments.

B. HPLC CONDITIONS

1. Injection Solvent
    a. Normally a solvent producing equal or lower capacity factors than the mobile phase is desirable as an injection solvent in order to produce sharp peaks for early eluting analytes (*e.g.*, oxamyl and methomyl) [31,32]. Since the initial mobile phase mixture of this method is mostly water, the only way to achieve this would be to dilute the samples with water. Water, however, is deleterious to several of the analytes specified in this method (see note A17 above). Therefore, an acceptable alternative is to inject very small volumes, not greater than 5 µL [31], of the desorption solvent (acetonitrile in this method) on a high-resolution HPLC column. If it is known that only analytes that are stable in aqueous solutions are to be determined (*e.g.*, oxamyl and methomyl, but not formetanate or captan), the desorbates may be diluted with water and larger volumes injected. By diluting with water, sharper peaks may be obtained for early eluting compounds with accelerated elution conditions such as the use of shorter HPLC columns, higher percentages of organic modifier, or higher percentages of mobile phase B in the initial conditions.
    b. All sample extracts must be filtered through individual 0.45-micron PTFE filters in order to prolong guard column lifetimes and to protect the injection system valving.

    c. The accidental or intentional inclusion of significant amounts of solvents less polar than acetonitrile in the injection solvent, such as tetrahydrofuran or acetone, may shorten retention times and adversely affect the peak shapes of early eluites (*e.g.*, oxamyl and methomyl) [31].

2. Guard Columns: Guard columns are essential to the long life and reproducibility of results on the main analytical column. There are several on the market. Those giving the lowest possible dead volume preserve good peak shapes and resolution of quality analytical columns and are preferred.

3. Analytical Columns
   a. General: The main analytical column specified in this method is a C18 reverse-phase column. Other columns known to perform well also may be used, following manufacturer recommendations. There are many good columns available [28,33].
   b. Base Deactivation: The basic compounds (benomyl, carbendazim, and formetanate) present special challenges that are easily overcome with highly inert or base-deactivated columns [26]. The addition of TEA-PO_4 buffer to mobile phase A also greatly improves performance for these compounds [16, 26, 27].
   c. Dimensions: A longer column (300 mm) was used in this method in order to improve resolution for a large number of analytes and interferences, expected and unexpected. Long columns have higher operating pressures; therefore, necessary steps should be taken to provide for them, such as thicker-walled (narrower-bore) transfer lines (if polymer tubing is used), *etc.* Shorter columns may work well if a limited number of analytes or interferences are expected. The diameter (3.9-mm) is not necessarily critical and should be governed by user preference and equipment, adjusting flow rates and other parameters as necessary. Diameters from 2.0 to 4.6 mm should be expected to perform similarly, as long as the columns are stable and rugged.
   d. Packing Density: Packing (or ligand) density is a better parameter than carbon loading for comparing columns [21,22]. A column with a ligand density near that of the one used in this method should be expected to perform similarly.

4. Mobile Phase Composition
   a. Modifier: Because of the high percentage of water in the initial mobile phase, a condition referred to as hydrophobic collapse of the C18 phase occurs [23,24], which results in poor reequilibration and irreproducible retention times and peak shapes for early eluting analytes such as oxamyl and methomyl. The addition of a constant amount of an alcohol to both mobile phases A and B has been reported and found to improve column performance under these conditions The method specifies 2% 1-propanol to be added to both mobile phases A and B. A concentration of 1-propanol between 3% and 4% has been reported as optimum [24,25]; 2% is a compromise made in order to generate retention (capacity) factors for the earliest eluites, oxamyl and methomyl, of greater than 5, as suggested in the literature [26]. Also, 1-propanol has been reported (and found) to reduce the time required for reequilibration at the end of the run [24]. Other alcohols may be used at higher concentrations (except for reducing reequilibration times) [1]. These are isopropanol (at 3% to 5%) and methanol (at 5% to 10%). If early-eluting analytes are to be determined, or if a column is found that gives sufficiently long retention times for the earliest expected eluite with an initial mobile phase composition as high as 5% to 10% acetonitrile in water, the alcohol could be eliminated (from both phases). Table 4 would not apply if such changes are made.
   b. Mobile Phase B: Pure methanol as mobile phase B results in a steep rise in the baseline UV response, making automatic integrations difficult and UV scanning for confirmation spectra nearly impossible. For this reason acetonitrile has been chosen [28,29]. Methanol is acceptable if these conditions are tolerable and is recommended as an alternate solvent system on a C18 column for confirmation (Section F3); however, precision and LOD values reported in Table 2 would not be applicable.
   c. Solvent Programming: One of the most serious concerns that may be encountered in trying to make adaptations of this method is an attempt to shorten retention times by using higher concentrations of organic modifier in mobile phase A, higher percentages of mobile phase B in the initial solvent program condition, or faster solvent programming. In any case, these changes will seriously affect the peak shape, sensitivity, and retention time reproducibility of early eluting analytes. There is also a greater possibility of false positives from potential interferences because of poor resolution in the early region of the chromatogram. Retention times for the earliest eluting analyte should be kept at 3 to 6 times the retention time of the solvent front *(i.e.*, of an unretained analyte), which is equivalent to a capacity factor of 2 to 5 [5].

The retention or capacity factor for any analyte can be calculated as follows:

Retention or capacity factor = $(t_r - t_o) / t_o$
where t_r = the retention time of the compound
and t_o = the retention time of an unretained analyte (the mobile phase holdup time).

The value of keeping analytes from eluting too close to the solvent front cannot be overemphasized.

d. Buffer: For the compounds evaluated, formetanate, carbendazim, and benomyl required a buffer in order to obtain good peak shapes. Of several pHs tested, pH 6.8 to 7.1 gave the best results. Buffer concentration should be 0.01 to 0.05 *M*. The concentration and pH of the buffer had a great effect on exact retention time of formetanate.

5. Dwell Volumes: Dwell volumes can affect the retention times and peak shapes of analytes. This is internal volume of the system from the point of mixture of the mobile phases A and B to the head of the column. It includes the volume of the transfer lines; any in-line filters (which should be between the pump and the sample injector if at all, and definitely not after the sample injector); the sample injector; the guard column; and the head of the analytical column. This volume can range from approximately 0.6 to 3.8 mL. At a flow rate of 1 mL/minute, each mL dwell volume represents a minute delay between the time that the pump produces a given change in a mixture of solvent and the time when the analytical column experiences that change. In effect, it is equivalent to a solvent program delay [13,14]. For this method, lower dwell volumes and no program delays gave better peak shapes for the early eluites.

6. Dead Volumes: Dead volumes can cause the method to fail seriously. Important areas to look for are larger bore and longer-than-necessary transfer lines between the sample injector and the analytical column [15]. Another area of potential large dead volumes are poorly designed or connected guard columns and sample injectors.

7. UV Wavelength Selection
   a. The wavelengths specified in this method are a best compromise for all of the analytes listed in Table 1. There are maxima for each of the pesticides that would give greater sensitivity and/or signal-to-noise ratio. If only a selected few of the pesticides in Table 1 are to be determined, other wavelengths may be considered. For this purpose, Table , an orthographic projection of the UV absorbances, is provided. From this table, a wavelength can be selected in the vertical column that intersects the zones of greater UV absorbance for the compounds of interest. For example, if only ureas are to be determined, the selection of an absorbance band of 240 to 250 nm would give greater sensitivity for these compounds and less interference from others.
   b. Spectra are also provided in the Backup Data Report [1] for many analytes and potential interferences. These were obtained under actual operating conditions. Because of unavoidable errors in background subtractions, the profiles of these spectra are subject to errors at the low wavelength ends of the spectra (190 nm to 210 nm). This could be attributed to the absorbance from the alcohol modifier to the mobile phases, which, in spite of efforts to add an equal amount to both phases, produces a slight baseline rise near the end of the chromatograms.
   c. Many of the O-aryl carbamates and the sulfenimides absorb well only in the low UV range (<215 nm). This is generally an area of great background noise. Many contaminants (plasticizers and solvents) also absorb in this range better than at higher wavelengths. Selecting a longer wavelength that is not at the absorption maximum may give a better signal-to-noise ratio and thus actually increase sensitivity. This should be determined by experimentation for selected analytes.
   d. Bandwidth: A bandwidth of 15 nm was used for evaluation of this method.

C. INTERNAL STANDARDS

1. Calibration Internal Standards: Internal standards are essential for obtaining the precisions listed

in Table 2 [1,16]. Acetanilide was found to be unretained by the media during desorption, and therefore, could be added to the extraction fluid. It was also found to be relatively stable and not to interfere with the retention times of other analytes. A second compound, acetophenone, may be added as a back-up internal standard. It is also unretained by all media except XAD-2, on which it has about a 95% recovery. It may be used whenever the acetanilide is interfered with by coeluting analytes or contaminants. It also serves to indicate, by monitoring relative response between the two internal standards, when the first internal standard has a coeluting interference.

2. Alternate Calibration Internal Standards: It may be wise, especially under isocratic conditions, to select other internal standards having capacity factors closer to particular analytes of interest. There is a wide range of alkyl phenones available for late-eluting analytes, and 4-hydroxy-acetanilide (acetaminophen) for earlier eluting analytes. Their retention times are listed in Table 4. Since these longer alkyl chain phenones have increasingly lower recoveries from the XAD-2 resin, they should not be added to the extraction solutions until after the resin is removed.

3. Retention Index Reference Standards:These are optional standards and are used to establish relative retention times for qualitative purposes. These are highlighted in Table 4 and include a homologous series of alkyl phenones and acetanilides. Establishing retention times between two nearest-eluting reference standards gives a more consistent retention value than retention time alone or relative retention time using a single internal standard alone. This value, the Retention Index, varies according to column and analytical conditions, but should be relatively consistent for any one set of conditions and more reliable as a qualitative tool over a long period of time. This value is calculated as follows:

$RI_{(A)}$ = Retention Index of Analyte "A"

$$\frac{Tr_{(A)} - Tr_{(RS-P)}}{Tr_{(RS-F)} - Tr_{(RS-P)}} + N_{(RS-P)}$$

where $Tr_{(A)}$ = retention time of analyte A
$Tr_{(RS-P)}$ = retention time of preceding reference standard
$Tr_{(RS-F)}$ = retention time of following reference standard
$N_{(RS-P)}$ = a number assigned to preceding reference standard, with zero assigned to the first peak in the series.

(Numerical assignments for the acetanilide and phenone series are suggested in Table 4.)

In order to avoid confusion in the chromatograms, the retention index reference standards are analyzed periodically as external standards and not added to the analytical samples themselves. The use of these reference standards is optional but is suggested where application of this method is expected to encounter consistently a broad range of unknown analytes and to augment other confirmatory techniques.

D. INTERFERENCES:

The UV detector responds to many compounds. Retention times of some common potential interferences are provided in Table 4. Interfering compounds that may be encountered are discussed below.

1. Impurities in Mobile Phases and Additives: Only HPLC-grade solvents should be used. Triethylamine (TEA) was found to develop unidentified impurities over time which contributed to significant irregularities in the baseline. This degradation was reduced or eliminated by storing the TEA under nitrogen in a small desiccator at 0 to 4 °C [8].

2. Organic Solvents or Fuels
   a. Chloroform showed a response that nearly coelutes with carbaryl (Table 4). Benomyl and

captan, therefore, are made up in methylene chloride, which is more UV transparent than chloroform.
b. Toluene (Table 4).
c. Blends of solvents having ketones, ester, or any of the above compounds, such as lacquer solvents, gasoline, paint stripper, and cleaning solvents, are to be avoided or documented during sample collection and handling.

3. Industrial Chemicals (Plastic and Rubber Additives)
   a. Several plasticizers might elute in the window of interest depending upon the selection of column and conditions. These include diethyl and dibutyl phthalates. Dibutyl phthalate is typically found in polyvinyl gloves, flexible tubing, and in coatings on bottles and tool handles. Contact with these materials should be avoided or documented. Other plasticizers, such as dioctyl phthalate and bis-ethylhexyl adipate, have late elution times and will elute after about 30 minutes under the conditions specified. However, if the run times are shortened, these may be carried over on-column to subsequent analyses, causing interferences.
   b. Common antioxidants such as BHT (2,6-di-tert-butyl-4-methyl phenol) also elute late and may be carried over on-column, creating interferences in subsequent analyses.

4. Other Pesticides: Spray mixtures very often contain a mixture of pesticides. It is not uncommon to find chlorpyrifos, an organophosphate, or a pyrethroid pesticide in combination with propoxur, for example. Both of these noncarbamate pesticides can be detected under the conditions of the method. The retention time and spectra of chlorpyrifos is included for qualitative purposes. Most pyrethroids elute later than most of the carbamates; if present, they may elute in a subsequent run if run times are too short. It is also not uncommon to mix herbicides of different classes such as diuron with bromacil, atrazine, or 2,4-D. Because of this possibility, retention times and spectra of other common herbicides are also provided in Table 4 for qualitative purposes.

5. Miscellaneous Chemicals: There are a number of chemicals which elute in the retention time window of interest for carbamates and urea pesticides and may, with particular columns or conditions, interfere with analytes of interest. The presence or the known use of these compounds or their sources should be documented as part of the sample history. Table 4 lists a few of the compounds, which include the following.
   a. The common insect repellent, DEET (N,N-diethyl-meta-toluamide). Since DEET may be heavily used by outdoor workers, its presence on exposed areas of the skin or clothing may contribute to sampler contamination either through direct contact with the face of the sampler or through collection of vapors if the sampler is in close proximity to areas of application or is exposed to overspray during application from a spray can or bottle.
   b. Inadvertent collection of tobacco side-stream smoke may introduce potentially interfering compounds, one of which is nicotine.
   c. Compounds in beverages used during work periods, which include at least caffeine.

E. SAMPLER

1. The OVS-2 Sampler. The OVS-2 (OSHA Versatile Sampler with XAD-2) combines both filter and XAD-2 sorbent in one unit. The filter is necessary to trap submicron aerosols that would pass through the XAD-2 bed. Substitutions should not be made.

2. Quartz Fiber and Glass Fiber Filters (GFF). The OVS-2 tubes are available with either glass or quartz fiber filters. OSHA Methods specify GFF. This method specifies a quartz fiber filter. For analytes being desorbed with acetonitrile, no difference in desorption efficiency was observed between glass fiber and quartz fiber filters. Therefore, the tubes may be interchanged for the analytes specified in this method.

3. Flow Rates. The OVS-2 sampler is designed for a flow rate of 1 L/min. At slower flow rates, 0.1 to 0.2 L/min, there may not be enough capture velocity for aerosols.

4. Applying Liquid Spikes. The Teflon ® retainer ring should be removed when spiking the face of the

OVS-2 tubes with more than approximately 10 µL, in order to prevent wicking of the carrier solvent behind the ring and consequent loss of standard. Volumes of spiking fluid greater than 15 to 30 µL will flood the XAD-2 section and possibly wick into the back-up section. Whenever more than 15 to 30 µL is to be applied to the tubes, air must be drawn through the tubes at approximately 1 L/min during the spiking procedure and the solvent added in 15- to 30-µL increments with a few minutes between each addition allowed for drying of the solvent.

F. CONFIRMATION

1. By Relative Retention Times (Retention Index). The Retention Index (RI) may vary considerably from column to column and from one set of conditions to another. But it will be reasonably consistent once a set of conditions has been chosen and will be much more reliable for day-to-day comparisons than will absolute retention times. Actual RIs need to be established for each set of conditions. Compounds that are ionic under elution conditions or that interact strongly with polar sites on the column will have the most variable retention times and retention indices.

2. By Second Column. The cyanopropyl stationary phase strongly induces some exchanges in elution orders and alters relative spacings between adjacent analytes in the chromatogram that may be useful in confirmations.

3. By Alternate Solvent. As mentioned earlier (Section B1), methanol as the mobile phase B solvent on a C18 column can be used just as effectively to establish confirmations because methanol interacts differently with the stationary phase than acetonitrile, and so different molecular forces come into play. Significant alterations in retention order are thus obtained; for some analytes this is more dramatic than with a cyanopropyl column.

4. By Ratio of Two UV Absorption Bands. As long as the UV absorption channels are not saturated, there should be a consistent ratio between the background-corrected absorption bands that is characteristic of each analyte and should reflect the ratio of relative heights of the absorption spectra at their respective UV bands in the UV spectra. This ratio is dependent, however, on the bandwidth of the adsorption bands employed, and consistent bandwidths must be used. The consistency of the ratio of absorption across the HPLC peak is also indicative of the purity of the peak. A constantly changing ratio indicates that the peak may have multiple components.

5. By Matching to Reference UV Spectra. Unknown spectra should not be oversaturated in any portion. They need to be background-corrected properly. If the baseline is rising, a background selected from the backside of the peak may induce losses of absorption in the region below 210 nm. Conversely, one selected from in front of the unknown HPLC peak may add to this region of the spectra. It is better to get an averaged background first. Spectra maxima should match within a few nanometers. Relative absorbance at each maxima may vary, even after background subtraction, depending upon the concentration of the analytes and the characteristics of different scanning UV detectors.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-µm median cut point

CAS: None RTECS: None

METHOD: 0600, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 January 1998

OSHA : 5 mg/m³
NIOSH: no REL
ACGIH: 3 mg/m³

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates non-ciliated portions of respiratory system

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell [HD] cyclone, or Aluminum cyclone + tared 5-µm PVC membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 L/min
Al cyclone: 2.5 L/min

VOL-MIN: 20 L @ 5 mg/m³
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m³ (lab and field)

BIAS: dependent on dust size distribution [1]

OVERALL PRECISION ($\hat{S}_{rT}$): dependent on size distribution [1,2]

ACCURACY: dependent on size distribution [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; <70 µg with 0.01 mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. In addition to 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., ≈ +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 samples 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).
   b. Cyclone: 10-mm nylon(Mine Safety Appliance Co., Instrument Division, P. O. Box 427, Pittsburgh, PA 15230), Higgins-Dewell(BGI Inc., 58 Guinan St., Waltham, MA 02154)[7], aluminum cyclone (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330), or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone, 2.2 L/min ± 5% for HD cyclone, or 2.5 L/min ± 5% for the Al 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. Weights, NIST Class S-1.1, or ASTM Class 1.
5. Static neutralizer, e.g., Po-210; replace nine months after the production date.
6. Forceps (preferably nylon).
7. 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 anti-static 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.
4. Remove the cyclone's grit cap 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 1: Because of their inlet designs, nylon and aluminum cyclones are calibrated within a large vessel with inlet and outlet ports. The inlet is connected to a calibrator (e.g., a bubble meter). The cyclone outlet is connected to the outlet port within the vessel, and the vessel outlet is attached to the pump. See APPENDIX for alternate calibration procedure. (The calibrator can be connected directly to the HD cyclone.)
   NOTE 2: 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 2 mg dust loading on the filter. Take 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).
   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:

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 convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention 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 magnitude 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(Omega Specialty Instrument Co., 4 Kidder Road, Chelmsford, MA 01824) 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 0.006 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] 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:

[1] Bartley DL, Chen CC, Song R, Fischbach TJ [1994]. Respirable aerosol sampler performance testing. Am. Ind. Hyg. Assoc. J., *55*(11): 1036-1046.
[2] Bowman JD, Bartley DL, Breuer GM, Shulman SA [1985]. The precision of coal mine dust sampling. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Pub. No. 85-220721.
[3] Parobeck P, Tomb TF, Ku H, Cameron J [1981]. Measurement assurance program for the weighings of respirable coal mine dust samples. J Qual Tech 13:157.
[4] ACGIH [1996]. 1996 Threshold limit values (TLVs™) for chemical substances and physical agents and biological exposure indices (BEIs™). Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
[5] American Conference of Governmental Industrial Hygienists [1991]. Notice of intended change - appendix D - particle size-selective sampling criteria for airborne particulate matter. Appl Occup Env Hyg *6*(9): 817-818.
[6] NIOSH [1977]. NIOSH Manual of sampling data sheets. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-159.
[7] Higgins RI, Dewell P [1967]. A gravimetric size selecting personal dust sampler. In: Davies CN, Ed. Inhaled particles and vapors II. Oxford: Pergammon Press, pp. 575-586.
[8] Bowman JD, Bartley DL, Breuer GM, Doemeny LJ, Murdock DJ [1984]. Accuracy criteria recommended for the certification of gravimetric coal mine dust personal samplers. NTIS Pub. No. PB 85-222446 (1984).
[9] Breslin, JA, Page SJ, Jankowski RA [1983]. Precision of personal sampling of respirable dust in coal mines. U.S. Bureau of Mines Report of Investigations #8740.
[10] Bartley DL, Breuer GM [1982]. Analysis and optimization of the performance of the 10-mm cyclone. Am Ind Hyg Assoc J *43:* 520-528.
[11] Caplan KJ, Doemeny LJ, Sorenson S [1973]. Evaluation of coal mine dust personal sampler performance, Final Report. NIOSH Contract No. PH CPE-r-70-0036.
[12] Bartley DL, Breuer GM, Baron PA, Bowman JD [1984]. Pump fluctuations and their effect on cyclone performance. Am Ind Hyg Assoc J *45*(1): 10-18.
[13] Briant JK, Moss OR [1983]. The influence of electrostatic charge on the performance of 10-mm nylon cyclones. Unpublished paper presented at the American Industrial Hygiene Conference, Philadelphia, PA, May 1983.
[14] Koqut J [1994]. Private Communication from MSHA, May 12, 1994.

[15] Vaughn NP, Chalmers CP,Botham [1990]. Field comparison of personal samplers for inhalable dust. Ann Occup Hyg *34*: 553-573.

METHOD REVISED BY: David L. Bartley, Ph.D., NIOSH/DPSE/ARDB and Ray Feldman, OSHA.

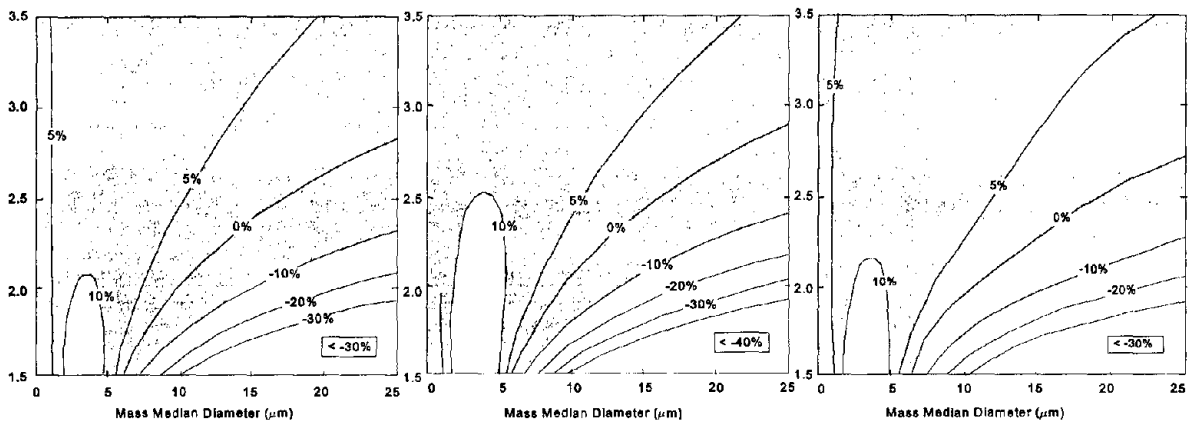


Figure 1. Bias of three cyclone types relative to the international respirable dust sampling convention.

APPENDIX: Jarless Method for Calibration of Cyclone Assemblies

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter "calibration jar".

(1) Connect the pump to a pressure gauge or water manometer and a light load (adjustable valve or 5-μm filter) equal to 2" to 5" H_2O with a "TEE" connector and flexible tubing. Connect other end of valve to an electronic bubble meter or standard bubble tube with flexible tubing (See Fig. 2.1).
NOTE: A light load can be a 5-μm filter and/or an adjustable valve. A heavy load can be several 0.8-μm filters and/or adjustable valve.

(2) Adjust the pump to 1.7 L/min, as indicated on the bubble meter/tube, under the light load conditions (2" to 5" H_2O) as indicated on the pressure gauge or manometer.

(3) Increase the load until the pressure gauge or water manometer indicates between 25" and 35" H_2O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min ± 5%.

(4) Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed (Fig. 2.2). If the loading caused by the cyclone assembly is between 2" and 5" H_2O, the calibration is complete and the pump and cyclone are ready for sampling.

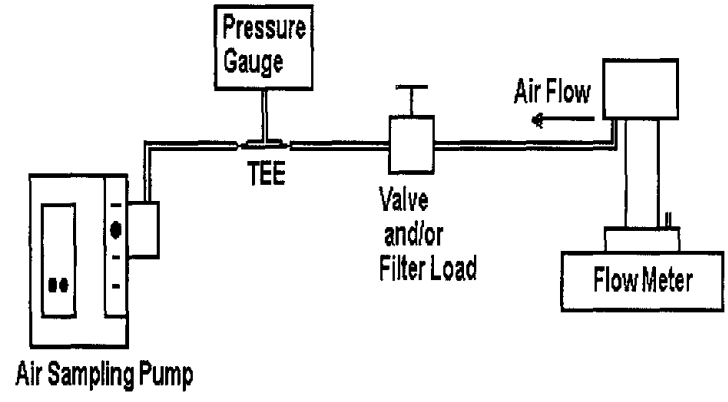


Figure 2.1 Block Diagram of Pump/Load/Flow Meter Set-up.

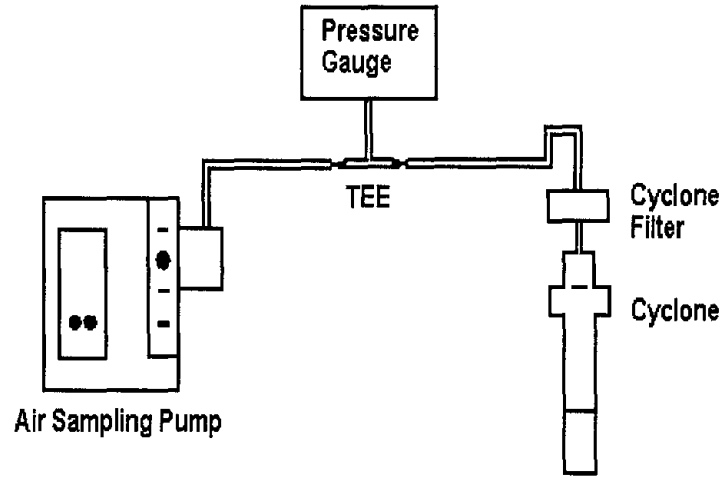


Figure 2.2. Block Diagram with Cyclone as the Test Load.

PERCHLOROETHYLENE (portable GC) in exhaled breath and air

3704

C_2Cl_4 MW: 165.8 CAS: 127-18-4 RTECS: KX3850000

METHOD: 3704, Issue 1 **EVALUATION: FULL** **Issue 1: 15 January 1998**

OSHA : 100 ppm; C 200 ppm; P 300 ppm (5 min. max peak in any 3 h)
NIOSH: Ca; lowest feasible
ACGIH: 25 ppm, 100 ppm STEL; 10 ppm BEI, end-exhaled air
(1 ppm = 6.8 mg/m³ @ NTP)

PROPERTIES: colorless liquid with mild chloroform-like odor; d 1.62 g/mL @ 20 °C; BP 121 °C; VP 14 kPa (13 mm Hg) @ 22 °C; I. P 9.32 eV

SYNONYMS: tetrachloroethylene; perc

SAMPLING

SAMPLER: AIR BAG (Tedlar™) or direct injection

FLOW RATE: 0.02 to 5 L/min
sufficient volume in bag (greater than approximately 0.5 L) during sampling period of interest; fill bag ≤80% capacity

SAMPLE STABILITY: 8 h in Tedlar bags

BLANKS: clean air in bag from non-work area

ACCURACY

RANGE STUDIED: 0.1 to 100 ppm
0.05 to 0.3 ppm field validation [1]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): ≤0.115

ACCURACY: ± 22.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE) / PHOTOIONIZATION DETECTOR (PID)

ANALYTE: perchloroethylene (perc)

INJECTION VOLUME: 0.5 mL (greater volume will increase sensitivity, smaller volume will extend upper range)

TEMPERATURE-INJECTION: ambient
-DETECTOR: ambient
-COLUMN: 40 °C

CARRIER GAS: air, ultra-pure @ 10 to 20 mL/min

COLUMN: macrobore capillary, 10 m, 0.53-mm ID, 2-µm polymethyl siloxane film, (CPSil 5CB™or equivalent)

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.1 to 1000 ppm [1]

ESTIMATED LOD: 0.01 ppm

PRECISION ($\hat{S}_r$): ≤0.115

APPLICABILITY: The working range is from 0.1 to 100 ppm for both air and exhaled breath samples by direct on-site analysis or by collection into inert sampling bags. Collection of exhaled breath into sample bags requires the use of a desiccant (see SAMPLING section) to remove humidity which may condense on the bag.

INTERFERENCES: Any compounds having similar retention times as perchloroethylene are potential positive interferences. The presence of a large number of compounds with retention times similar to perchloroethylene will cause a high background resulting in decreased sensitivity, possibly to the point where the LOQ approaches 1 ppm. Common human metabolites found in exhaled breath, as well as chemicals normally found in dry cleaning plants, do not interfere with the analysis of perchloroethylene. Specific compounds tested and shown not to interfere with this method include: acetone, isoprene, methanol, ethanol, acetaldehyde, carbon tetrachloride, chloroform, benzene, butane, styrene, toluene and xylenes.

OTHER METHODS: NMAM method 1003 for halogenated hydrocarbons [2] calls for collection of sample on charcoal sorbent, followed by laboratory desorption with carbon disulfide, and subsequent analysis by gas chromatography with a flame ionization detector. NMAM method 2549, volatile organic compounds (screening) [3], uses a multi-bed sorbent tube for sample collection, thermal desorption, and laboratory analysis by gas chromatography / mass spectrometry. Estimated limits of detection for Methods 1003 and 2549 are 1.5 and 15 ppm, respectively, for 1-L samples, which are typical for exhaled breath analysis.

REAGENTS:

1. Perchloroethylene* in air, commercial mixed gas standards, or liquid perchloroethylene.
2. Air, ultra-pure, or Nitrogen, purified.
3. Dry-Rite™ desiccant, indicating or equivalent.

* See SPECIAL PRECAUTIONS

EQUIPMENT

1. Sampler: air bags, Tedlar™, 1-L, or other appropriate size.
2. Drying tube for exhaled breath sampling. Plastic tubing, ca. 1-cm ID, containing approximately 5 g indicating Dry-Rite, held in place with glasswool plugs.
3. Personal sampling pump, 0.02 to 5 L/min, or other rate suitable for filling sample bag, with flexible connecting tubing.
4. Tubing, PTFE, ca. 6 ft. length.
5. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop, column (p. 3704-1), and (if appropriate) strip chart recorder.
6. Syringes, gas tight, 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.

SPECIAL PRECAUTIONS: Perchloroethylene is a suspect carcinogen as well as an irritant to the eyes, nose, and skin. Wear appropriate protective clothing. 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 allow to warm up according to manufacturer's instructions. Select sampling mode.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. **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.

3. **Integrated Air Sample.**
   a. 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 twice with clean air, then fill with clean air and analyze for perchloroethylene (step 6).
   b. Attach sample bag to 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 PTFE tubing sufficient to reach the desired site. When sample size is small, a rubber squeeze bulb may be used in place of a personal sampling pump. In either case, flush tubing and pump/bulb 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.

c. Pump air sample into bag at a rate calculated to fill ≤80% of the bag capacity over the sampling period.

NOTE: The flow rate must be constant throughout the sampling period.

d. As soon as practical, but within 8 h after completion of sampling, introduce an aliquot of the sample into the GC (step 2).

4. **Exhaled Breath Sample** (adapted from Toutonghi [4])
   a. Move subject to an area where ambient analyte concentrations are insignificant.
   b. Instruct subject to take 4 normal breaths followed by 1 deep inhalation.
   c. Hold the deep breath for 10 seconds.
   d. After 10 seconds, exhale the first half of the breath into the room and the last half through a tube filled with Dry-Rite into a sampling bag.
   f. Close the bag valve and queue the sample for analysis.
5. Obtain the perchloroethylene peak height or area of the injected sample (see Figure 1).

CALIBRATION AND QUALITY CONTROL:

6. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph with at least three replicate determinations of six or more working standards. Plot peak height or area vs. mass or concentration of perchloroethylene.
   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 perchloroethylene peak from other substances known or predicted to be present in the field samples.
7. Establish a daily field calibration graph (peak height vs. mass or concentration of perchloroethylene).
   a. Fill Tedlar bags with standards, preferably commercially prepared and certified, or inject known amounts of pure perchloroethylene into Tedlar bags containing a metered volume of pure air or nitrogen. (See APPENDIX)
   b. Analyze working standards in triplicate under the same conditions as samples.
   c. Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

8. Determine mass, W (ppm), of perchloroethylene by comparison of sample peak height with daily calibration graph (step 7). Calculate concentration, C, of perchloroethylene in the sample volume injected, V (mL), applying the factor 6.8 to convert ppm to mg/m^3 at NTP.

$$C = \frac{6.8\ W}{V},\ mg/m^3$$

NOTE 1: $\mu g/mL \equiv mg/m^3$

NOTE 2: Some GCs will perform this calculation electronically if programmed appropriately during the calibration phase.

EVALUATION OF METHOD:

This method was evaluated over the range 0.1 to 100 ppm perchloroethylene in air using a Photovac 10S portable gas chromatograph (Photovac International, Deer Park, NY). Certified standard gas mixtures of 1.0 ppm perchloroethylene in air were obtained from Scott Specialty Gases, Inc., (Troy, MI) These were verified

by comparison with standards prepared from liquid and were then used to establish the calibration graphs. Analytical precision was determined by calculating the variation of replicate analyses of calibration standards and samples. Once calibration graphs were 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 tubes samples taken from the same bag. Additionally, a field evaluation was subsequently conducted in which results obtained using this method averaged 6% higher than results obtained using conventional laboratory GC analysis by NMAM 1003 [2]. Sample bags should be analyzed as soon after collection as practical. Perchloroethylene (at concentrations of 5, 25, and 100 ppm) was found to be stable in Tedlar bags for more than 8 hours (loss of analyte <8%); storage for 24 hours resulted in a greater loss of analyte with increased concentration (20% loss of analyte at 100 ppm after 24 hours). Evaluation of this method, which uses a capillary column, indicated that perchloroethylene can be separated from acetone, isoprene, methanol, ethanol, acetaldehyde, carbon tetrachloride, chloroform, benzene, butane, styrene, toluene and xylenes. These compounds were selected for testing because they are either common human metabolites or substances which are frequently used in dry cleaning facilities with perchloroethylene.

Most permanent gases, including water vapor, carbon monoxide, and carbon dioxide, are not detected using a photoionization detector, and therefore, do not interfere with the analysis. However, water vapor at very high concentrations in exhaled breath was considered likely to condense in the bags subsequent to collection. To prevent condensation, exhaled breath was dried by passing it through a desiccant before entering the sample bag. The use of desiccant during the collection of exhaled breath samples was shown to decrease the perchloroethylene concentration by 7.0% at 1 ppm and 9.6% at 10 ppm, for an average 8.3% loss of analyte as a result of drying. Correction can be made for this loss either mathematically by increasing the measurement proportionally or by passing the calibration gas through the drying tube prior to calibration of the instrument.

REFERENCES:

[1] Sweet ND [1996]. A field method for near real-time analysis of perchloroethylene in end-exhaled breath [Dissertation]. Cincinnati, OH: University of Cincinnati, College of Medicine, Department of Environmental Health.

[2] NIOSH [1994]. Hydrocarbons, halogenated: Method 1003. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1996]. Volatile organic compounds (screening): Method 2549. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed., 1st Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No.96-135.

[4] Toutonghi G, Echeverria D, Morgan M, et al [1994]. Characterization of exposure to perchloroethylene, with biological monitoring, in commercial dry cleaning workers, submitted for publication in Scandinavian Journal of Work and Industrial Health.

METHOD WRITTEN BY:

G. E. Burroughs, NIOSH, DPSE, and Nathan Sweet, University of Cincinnati

APPENDIX

The volume of liquid perchloroethylene needed to create a calibration standard, if a commercial standard is not utilized, can be calculated as follows:

$$V_l = \frac{ppm \cdot MW \cdot L}{SpGr \cdot MV \cdot 10^6}$$

In the above equations:

ppm	=	parts per million, by volume, of perchloroethylene
MW	=	molecular weight of perchloroethylene
MV	=	molar volume (this value if 24.45 L at 25°C and 760mm Hg, but should be corrected if temperature or pressure vary significantly from these values.
V_l	=	volume of liquid perchloroethylene, in mL
L	=	volume of air in bag, in liters
SpGr	=	specific gravity of perchloroethylene, in g/mL

Concentrations in ppm can be converted to mg/m^3 as follows:

$$mg/m^3 = \frac{(ppm)\ (MW)}{(MV)} = \frac{(ppm)\ (166)}{(24.45)} = (ppm) \times 6.8$$

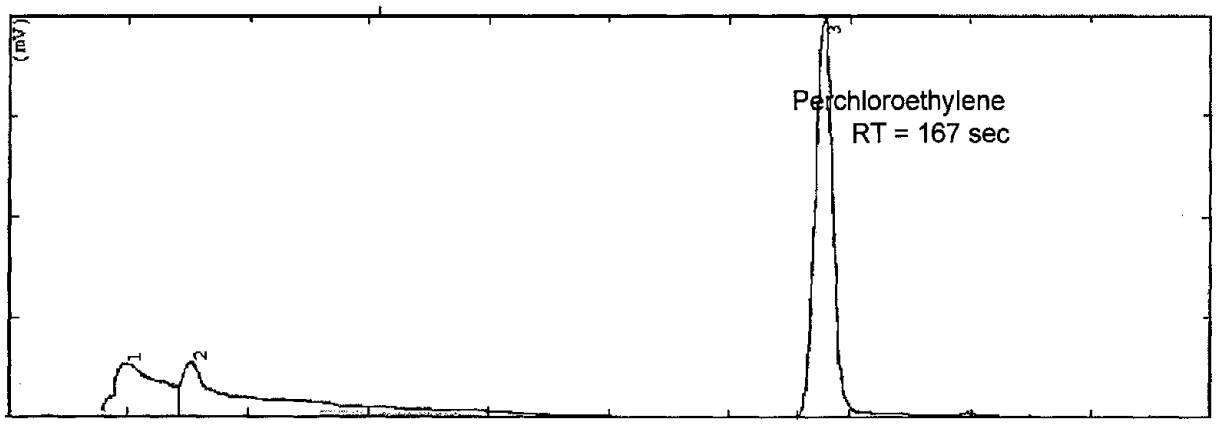


FIGURE 1 - Typical chromatogram obtained from the analysis of exhaled breath containing approximately 1.3 ppm perchloroethylene. Peak number 3 shows area of 598.1 mVs at a retention time of 167.4 sec. This is compared with a calibration curve in which a 1 ppm perchloroethylene standard produced a mean peak area of 452 mVs at a retention time of 167 sec.

PHOSPHINE 6002

PH_3 MW: 34.00 CAS: 7803-51-2 RTECS: SY7525000

METHOD: 6002, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1994**
Issue 2: 15 January 1998

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 permanganatereagent 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 to 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. 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. (step 10)
    d. Pipet 10 mL of the nonaqueous layer into a 25-mL volumetric flask containing 10 mL of the alcoholic sulfuric acid solution. (step 11)
    e. Analyze with samples and blanks (steps 15 through 18).
    f. 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.

POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs) 5800

MW: Variable CAS: None RTECS: None

METHOD: 5800, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: PACs are multi-numbered benzenoid-ring compounds. PACs contain polycyclic aromatic hydrocarbons (PAHs), substituted PAHs, and PAH heterocyclic derivatives.

NAMES & SYNONYMS: Total PACs as a class.

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (2-µm, 37-mm, PTFE filter + washed XAD-2 resin, 100/50 mg)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 5 L @ 0.01 mg/m^3
-MAX: 1000 L

SHIPMENT: Ship at @ 0 °C

SAMPLE STABILITY: at least 30 days @ 5 °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: FLOW INJECTION, FLUORESCENCE DETECTOR

ANALYTE: Polycyclic aromatic compounds as a chemical class

EXTRACTION: 4 mL hexane, rotated for at least 12 hours.

INJECTION VOLUME: 25 µL

MOBILE PHASE: 100% acetonitrile at 1.5 mL/min.

CALIBRATION: standard solutions of PACs based on Supelco QTM test mixture.

DETECTOR 1: fluorescence excitation 254 nm; emission 370 nm
RANGE: 0.04 to 250 µg/sample
ESTIMATED LOD: 0.012 µg/sample
PRECISION ($\hat{S}_r$): 0.042 @ 0.13 to 17 µg/sample [1]

DETECTOR 2: fluorescence excitation 254 nm; emission 400 nm
RANGE: 0.15 to 250 µg/sample
ESTIMATED LOD: 0.05 µg/sample
PRECISION ($\hat{S}_r$): 0.065 @ 0.13 to 17 µg/sample [1]

APPLICABILITY: This method is applicable for comparison of environments using the same fume source. The speciation of the PACs as a chemical class is accomplished by solid phase extraction followed by liquid-liquid extraction.

INTERFERENCES: All compounds producing detectable fluorescence at the chosen wavelengths and contained in the DMSO fraction after the sample preparation are identified as PACs.

OTHER METHODS: None identified for PACs as a class. Related methods are 2550, Benzothiazole in Asphalt Fume, by GC/sulfur chemiluminescence [2], and a gravimetric method 5042, Benzene Solubles and Total Particulate (Asphalt Fume) [3].

REAGENTS:

1. Hexane, HPLC grade.
2. Methanol, HPLC grade.
3. Methylene chloride, HPLC grade.
4. Dimethyl sulfoxide (DMSO), HPLC grade.
5. Calbration stock: Supelco QTM PAH mixture*

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Filter: PTFE-laminate membrane filter, 2-µm pore size, 37-mm, (Zefluor, Gelman Sciences, Ann Arbor, MI, 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: If sampling in bright sunlight, use opaque or foil-wrapped cassettes to prevent photodegradation.
   b. Solid sorbent: glass tube, 100 mm, 10-mm OD, sealed ends with plastic caps, containing two sections of washed XAD-2 resin (front = 100 mg; back = 50 mg), separated and retained with glass wool plugs (Supelco ORBO-42 Large or equivalent), connected to filter with minimum length PVC tubing.
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Robotics unit or apparatus for solid phase extraction (SPE). (Zymark Benchmate 2 or equivalent).
4. A solvent delivery system capable of delivering 1.5 mL/min of acetonitrile.
5. Autosampler or injection valve.
6. Two fluorescence detectors in series. One set at 254 nm excitation (ex) and 370 nm emission (em). The second set at 254 nm ex and 400 nm em.
7. Cyano solid phase extraction column (Supelco CN-SPE or equivalent).
8. 360° Rotator.
9. Aluminum foil
10. Volumetric flasks, various sizes.
11. Pipettes, various sizes.
12. Syringe or micropipet, various sizes.
13. Test tubes, 16 x 100 mm thin-walled and 16 x 100 mm test tubes with PTFE-lined caps.
14. Vials, autosampler, with PFTE-lined caps.
15. Refrigerant packs.

SPECIAL PRECAUTIONS: Total polycyclic aromatic compounds include the polycyclic aromatic hydrocarbons (PAHs). Some PAHs are irritants while others are carcinogenic. The standard also consists of PAHs. 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.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.

2. Sample 5 to 1000 L of air at 1.0 to 2.0 L/min.
3. Cap the filter and tube and pack securely for shipment with bagged refrigerant.
4. Refrigerate samples upon receipt at the laboratory at 4 °C.

SAMPLE PREPARATION:

NOTE: Some applications of the data need only total PACs per sample rather than total PACs per individual medium. In these cases, the filters and sorbent section may be combined into the same screw-capped test tube as a single sample.

5. Remove the samples from the refrigerator and allow to equilibrate to ambient temperature.
6. Extract filters.
   a. Transfer the filter using forceps to a 16 x 100 mm screw capped test tube.
   b. Add 4 mL of hexane.
   c. Rotate the sample for at least 12 hours using a 360° rotator.

   NOTE: Minimize exposure to light during extraction step.
7. Extract solid sorbent tubes.
   a. Transfer front glass wool plug and front sorbent section to a 16 x 100 screw-capped test tube.
   b. Transfer the back sorbent section and remaining glass wool plugs to a separate screw-capped test tube.
   c. Add 4 mL of hexane to each sample.
   d. Rotate the sample for at least 12 hours using a 360° rotator.

   NOTE: Minimize exposure to light during extraction step.
8. Solid phase extraction:
   a. Condition a cyano solid phase extraction column by washing in sequence with 3-mL aliquots of methanol, methylene chloride, and hexane at a flowrate of approximately 0.25 mL/sec.
   b. Transfer 2 mL of the extracted sample in hexane to the head of the cyano-SPE column.
   c. Elute at approximately 0.15 mL/sec and collect in a separate 16 x 100 mm screw capped test tube.
   d. Add 2 mL of hexane and elute through the column at approximately 0.15 mL/sec and combine with the first hexane eluate.
   e. Add 4 mL of DMSO to the hexane eluates, cap, and rotate for at least 12 hours.
   f. Using a Pasteur pipette, transfer an aliquot of the DMSO layer (bottom) to an autosampler vial.

CALIBRATION AND QUALITY CONTROL:

NOTE: This method uses a mixture of 16 PACs as the standard calibration solution to mimic the field samples. The commercial standard chosen was Supelco QTM Test Mixture that contains 2000 µg/mL for each of 16 PACs or 32000 µg/mL total PAC.

9. Calibrate daily with at least six working standards over the range of interest.
   a. Dilute aliquots of calibration stock solution (QTM Test Mixture) with DMSO.
   b. Analyze working standards and blanks (Steps 12 through 15). Intersperse standards among the samples.
   c. Prepare 2 calibration graphs (one for each detector) in terms of mass of total PACs. (Fluorescent peak area vs. µg of total PAC per sample).
10. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes (Steps 5 through 8) in the range of interest (Step 9) at least once for each lot of filters and sorbent tubes used for sampling.
    a. Prepare spiking solutions by making dilutions of the Supelco QTM Test Mixture with hexane.
    b. Using a microliter syringe, spike three filters and three solid sorbent tubes at five concentration levels with the QTM Test mixture. Allow the media to dry in the dark overnight.
    c. Analyze the filters and sorbent tubes (Steps 12 through 15). Prepare graphs of R or DE vs. µg recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration, recovery (R), and desorption efficiency (DE) graphs are in control.

MEASUREMENT:

12. Set solvent delivery system to pump 1.5 mL/min of acetonitrile through the system.
    NOTE: A guard column placed between the solvent delivery system and autosampler provides backpressure that aids the pumps in maintaining their prime.
13. Place two fluorescence detectors in series. Set the wavelengths of first detector at 254 nm ex and 370 nm em. Set the wavelengths of the second detector at 254 ex and 400 nm em.
14. Inject 25 µL of the sample into the solvent stream.
15. Measure peak areas.

CALCULATIONS:

NOTE: The mass of total PACs measured at each set of wavelengths is considered a separate analysis. Therefore, the establishment of calibration curves and data analysis are independent for each detector.

16. From the calibration graphs, read the mass (µg corrected for R or DE) of total PACs measured at each wavelength setting found on the filter (W_{fil}), front sorbent section (W_{sf}), and back sorbent section (W_{sb}) and on the average media blank filter (B_{fil}) and sorbent tube sections (B_{sf} and B_{sb}).
17. Calculate concentration of PACs at each wavelength setting (C 254ex/370em or C 254ex/400em) in the air volume sampled V(L) as the sum of the particulate concentration (filter) and the vapor concentration (sorbent tube). A dilution factor of 2 is applied since 2 mL of the original 4 mL of sample is processed through the SPE and liquid/liquid extraction.

$$\mathbf{C\ (ex/em)} = \frac{\mathbf{2\ (W_{fil} + W_{sf} + W_{sb} - B_{fil} - B_{sf} - B_{sb})}}{\mathbf{V}}\ \mathbf{,\ mg/m^3}$$

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

The method gives an indication of exposure to PACs as measured by two separate sets of spectrofluorometric wavelengths. The 254 nm ex/370 nm em response is used as an indication of the lower (2 to 4) ringed PACs that are usually considered irritants. The 254 nm ex/400 nm em response is used as an indication of the higher ringed (4 to 6) PACs that may be mutagenic or carcinogenic. As these measurements are only indications, the data are only applicable to exposures using the same asphalt fume source. No direct correlation of the data to adverse health effects can be made.

Recovery studies for the filter and tube were determined using sampling media spiked with known amounts of the Supelco QTM standard. A set of six filters and sorbent tubes were fortified with known amounts of the QTM Test mixture at four different concentrations per set. The efficiency for recovery from the sampling media, fractionation, and flow-injection analysis was shown to be about 90% for the 254 nm ex/370 nm em analysis and about 95% for the 254 nm ex/400 nm em analysis.

A 30-day storage study, consisting of sets of six filters and sorbent tubes spiked at four concentration levels with Supelco QTM standard, showed no loss when stored under refrigeration. This is reflected by approximately 90% recovery for the 254 nm ex/370 nm em analysis and about 95% for the 254 nm ex/400 nm em analysis. No collection studies were performed, but the sampling train was adopted from NMAM Method 5506 [4].

REFERENCES:

[1] Neumeister CE [1997]. Polycyclic aromatic compounds backup data report (unpublished), NIOSH, DPSE.

[2] NIOSH [1998]. Benzothiazole in asphalt fume: Method 2550. In: Eller PM, Cassinelli ME, Eds, NIOSH Manual of Analytical Methods, 4th Ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) 98- .

[3] NIOSH [1998]. Benzene solubles and total particulate (asphalt fume): Method 5042. In: Eller PM, Cassinelli ME, Eds, NIOSH Manual of Analytical Methods, 4th Ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) 98- .

[4] NIOSH [1994]. Polynuclear aromatic hydrocarbons: Method 5506. In: Eller PM, Cassinelli ME, Eds, NIOSH Manual of Analytical Methods, 4th Ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) 94-113.

METHOD WRITTEN BY:

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POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC 5506

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

METHOD: 5506, Issue 3	EVALUATION: PARTIAL	Issue 1: 15 May 1985 Issue 3: 15 January 1998

OSHA : Table 3
NIOSH: Table 3
ACGIH: Table 3

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	

NAMES & SYNONYMS: Polycyclic aromatic hydrocarbons, PAHs; also see Table 2.

SAMPLING

SAMPLER:	FILTER + SORBENT TUBE (37-mm, 2-µm, 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 light
FIELD BLANKS:	3 to 10 field blanks per set
MEDIA BLANKS:	6 to 10 media blanks per set

ACCURACY

RANGE STUDIED:	not determined
BIAS:	not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE:	HPLC, FLUORESCENCE/UV DETECTION
ANALYTE:	compounds listed above
EXTRACTION:	5 mL acetonitrile; ultrasonic bath, 30 to 60 minutes
INJECTION VOLUME:	10 to 50 µL
MOBILE PHASE:	acetonitrile/water gradient @ ambient temperature, 1 mL/min
COLUMN:	250 x 4.6-mm, reversed-phase, 5-µm C_{18}
DETECTOR:	UV @ 254 nm; fluorescence @ 340 nm (excitation), 425 nm (emission)
CALIBRATION:	standards in acetonitrile
RANGE:	see EVALUATION OF METHOD
ESTIMATED LOD:	see EVALUATION OF METHOD
PRECISION ($\hat{S}_r$):	see EVALUATION OF METHOD

APPLICABILITY: This method is applicable to samples that can be extracted with acetonitrile. This method is not applicable to samples that require a different extraction solvent or contain large amounts of highly adsorptive particulate matter, e.g., fly ash or diesel soot; also, this method is not applicable to asphalt fume samples.

INTERFERENCES: Any compound that elutes at the same HPLC 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]. Method 5515 uses the same sampling technique, with gas chromatographic measurement [2]. Method 5800 uses the same sampling technique, and a flow-injection method to determine total polycyclic aromatic compounds at two different sets of fluorescent wavelengths [3].

REAGENTS:

1. Water, distilled, deionized, degassed.
2. Acetonitrile, HPLC grade, degassed.
3. PAH test mixture,* a liquid standard containing the PAHs except benzo[e]pyrene (EPA 610 Polynuclear Aromatic Hydrocarbons, Supelco, Cat. No. 4-8743; or equivalent).
4. Benzo[e]pyrene,* solid (Supelco, Cat. No. 44-2475; or equivalent).

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Filter. 37-mm, 2-µm pore size, PTFE membrane filter laminated to PTFE, (Zefluor, Pall Gelman Sciences, Cat. No. P5PJ037; SKC Inc., Cat. No. 225-17-07; or equivalent filter), cellulose spacer ring, 37-mm OD, 32-mm ID, (SKC Inc., Cat. No. 225-23; or equivalent) in a 37-mm cassette filter holder.
      NOTE: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
   b. Sorbent tube, washed XAD-2 resin (front = 100 mg; back = 50 mg) (ORBO 43, Supelco, Cat. No. 2-0258; or equivalent), connected to filter with minimum length of PVC tubing. Plastic caps are required after sampling.
      NOTE: If pressure drop is excessive or pump fails, use a larger diameter sorbent tube with XAD-2 resin (ORBO 42 Large, Supelco, Cat. No. 2-0264U; or equivalent).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Refrigerant, bagged.
5. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
6. Forceps.
7. Syringe filters, 0.45-µm, 25-mm, PTFE (Acrodisc-CR, Pall Gelman Sciences, Cat. No. 4219; or equivalent).
8. Pipet, 5-mL.
9. Syringe or micropipets, 1- to 100-µL.
10. Ultrasonic bath.
11. HPLC, with gradient capability, fluorescence (excitation @ 340 nm, emission @ 425 nm) and UV (254 nm) detectors in series, electronic integrator, and a 250 x 4.6-mm C_{18} column (Vydac 201TP, The Separations Group, Hesperia, CA, Cat. No. 201TP54; or equivalent).
12. Volumetric flasks, 10- and 100-mL.
13. Recommendation: lighting in laboratory should be incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat all polynuclear aromatic hydrocarbons as carcinogens. Samples and unused standards are considered toxic waste. Dispose 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 PAHs.

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.
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 in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes by sublimation.
4. Cap the sorbent tube and wrap in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAHs; therefore, recommend using yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Extract PAH from filters.
   a. Add 5.0 mL of acetonitrile to each culture tube containing a filter. Similarly, add 5.0 mL of acetonitrile to each culture tube containing the media and reagent blanks. Cap the tubes.
   b. Place capped tubes in an ultrasonic bath for 30 to 60 min.
8. 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 tubes.
   d. Place capped tubes in an ultrasonic bath for 30 to 60 min.
9. Filter all sample extracts through an 0.45-µm syringe filter.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    NOTE: If a benzo[e]pyrene standard is needed, weigh desired amount and add to a known volume of the PAH test mixture.
    a. Dilute aliquots of the PAH test mixture (containing benzo[e]pyrene if needed) with acetonitrile in 10-mL volumetric flasks. The concentration range should cover most of the PAH concentrations in the samples.
    b. During analysis, intersperse working standards with samples and blanks.
    c. Prepare calibration graphs (peak area vs. µg of each PAH per sample).
11. 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 7, 9, and 13 through 15). Prepare graphs of R vs. amounts found.
       (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. Desorb and analyze (steps 8, 9, and 13 through 15). 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 or DE graphs if checks do not agree to within ±5% of R or DE graph.

12. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

13. Set HPLC according to manufacturer's instructions, conditions on page 5506-1, and steps 14 and 15.
14. Inject sample aliquot (10 to 50 µL). Start mobile phase gradient:
    a. Linear gradient from 60% acetonitrile/40% deionized water to 100% acetonitrile at 1 mL/min over 20 min.
    b. Hold at 100% acetonitrile for 20 min.
    c. Linear gradient to initial condition, 5 min.
15. Measure peak areas for each analyte using the appropriate detector as specified in Table 1.
    NOTE 1: The order of elution for the PAHs appears in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with acetonitrile, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary.

CALCULATIONS:

16. 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.
17. Calculate concentration, C (mg/m^3), as the sum of the particulate concentration and the vapor concentration in the actual air volume sampled, V (L).

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

NOTE 1: $\mu g/mL \equiv mg/m^3$

NOTE 2: 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., anthracene, fluoranthene, fluorene, naphthalene, phenanthrene).

EVALUATION OF METHOD:

The UV detector is used to analyze for some PAHs (see Table 1), and the remaining PAHs are analyzed by a fluorescent detector, which gave better sensitivity for some PAHs. The ranges of the limit of detection (LOD) and the limit of quantitation (LOQ) values for the 17 PAHs are reported in Table 4 [4]. The LOD and LOQ values varied because of differences in the detectors used and the concentrations of the standards. Therefore, it is important that the LOD and LOQ values be determined for each set of samples. The LOQs are the lower end of the analytical ranges. The upper end of the analytical ranges were not determined.

This method was evaluated by means of a user check [5]. An independent laboratory prepared spiked filters and sorbent tubes for a recovery and desorption efficiency study (see Table 4). For the filters, except naphthalene, the recovery results were greater than or equal to 75%. Since naphthalene is fairly volatile

under ambient conditions, this may account for the poor recovery results. For the sorbent tubes, only four of the 17 analytes had desorption efficiencies that were greater than or equal to 75%. During the user check, the sorbent tubes were extracted by adding 5 mL acetonitrile and were allowed to stand for 30 minutes with occasional swirling. In more recent quality control experiments, the desorption efficiencies were often better for some analytes (see Table 4) [4]. These results were achieved using an ultrasonic bath for 30 to 60 minutes. The results indicated the importance of preparing media spikes for recovery and desorption efficiency studies for each set of samples; moreover, the results reenforce this need when using new lots of media.

REFERENCES:

[1] NIOSH [1977]. Total particulate aromatic hydrocarbons: Method P&CAM 206. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A.

[2] NIOSH [1994]. Polynuclear aromatic hydrocarbons by GC: Method 5515. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1998]. Polycyclic aromatic compounds: Method 5800. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.

[4] NIOSH unpublished data.

[5] User Check Report for Method 5506, Analytical Report for NIOSH Sequence 4170 (NIOSH, DPSE, MRSB, unpublished, March 16, 1984).

[6] Handbook of Chemistry and Physics, 78th ed. [1997], Boca Raton, FL: CRC Press.

[7] IARC [1983]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: polynuclear aromatic compounds, Part 1, chemical, environmental and experimental data. Vol. 32. Lyon, France: World Health Organization, International Agency for Research on Cancer.

[8] Lenga RE, Votoupal KL, eds. [1993]. The Sigma-Aldrich library of regulatory and safety data, Volume 1. Sigma-Aldrich Company.

[9] NIOSH [1998]. Registry of toxic effects of chemical substances data base. Cincinnati, OH: National Institute for Occupational Safety and Health. Unpublished data base.

[10] NIOSH [1997]. NIOSH pocket guide to chemical hazards. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 97-140.

[11] ACGIH [1997]. 1997 TLVs® and BEIs®, Threshold limit values for chemical substances and physical agents, Biological exposure Indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists (ACGIH).

[12] NIOSH [1992]. NIOSH recommendations for occupational safety and health, compendium of policy documents and statements. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

METHOD REVISED BY:

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TABLE 1. FORMULAS AND PHYSICAL PROPERTIES.

COMPOUND (by M.W.)	FORMULA	WEIGHT	DETECTOR	MELTING POINT (°C)	BOILING POINT (°C)	REFERENCE
1. NAPHTHALENE	$C_{10}H_8$	128.17	UV	80.2	218	[6]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	UV	92.5	280	[6]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	UV	93.4	279	[6]
4. FLUORENE	$C_{13}H_{10}$	166.22	UV	115	295	[6]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	UV	215	340	[6]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	UV	99.2	340	[6
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	FL	108	384	[6]
8. PYRENE	$C_{16}H_{10}$	202.26	FL	151	404	[6]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	FL	167	435	[7]
10. CHRYSENE	$C_{18}H_{12}$	228.29	UV	258	448	[6]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	168	--	[7]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	217	480	[6]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	FL	177	495	[6, 8]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	FL	178	311	[6]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	FL	278	--	[7]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	FL	164	--	[7]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	FL	270	524	[7, 8]

TABLE 2. SYNONYMS, CAS AND RTECS NUMBERS.

COMPOUND (alphabetically)	SYNONYMS, CAS and RTECS Numbers*
1. ACENAPHTHENE	CAS # 83-32-9; RTECS # AB1000000
2. ACENAPHTHYLENE	acenaphthalene; 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

* Data from [6, 8, and 9].

TABLE 3. EXPOSURE LIMITS.*

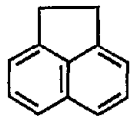
COMPOUND	OSHA†	NIOSH†	ACGIH‡
1. ANTHRACENE	0.2 mg/m^3	--	
2. BENZ[a]ANTHRACENE	--	--	suspect human carcinogen
3. BENZO[b]FLUORANTHENE	--	--	suspect human carcinogen
4. BENZO[a]PYRENE	0.2 mg/m^3	--	suspect human carcinogen
5. CHRYSENE	0.2 mg/m^3	potential occupational carcinogen§	animal carcinogen
6. NAPHTHALENE	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
7. PHENANTHRENE	0.2 mg/m^3	--	--
8. PYRENE	0.2 mg/m^3	--	--

* This table only includes the compounds with established exposure limit values.
† Information from [10].
‡ Information from [11].
§ Information from [12].

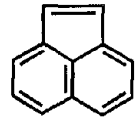
TABLE 4. LOD AND LOQ VALUES, AND RECOVERY DATA.

COMPOUND (by elution order)	Range of values*		Recoveries (%)†	
	LOD (µg per sample)	LOQ (µg per sample)	Filters	Sorbent tubes
1. NAPHTHALENE	0.20 - 0.80	0.39 - 2.6	49.6	68.5
2. ACENAPHTHYLENE	0.090 - 2.0	0.28 - 6.6	98.2	98.2
3. ACENAPHTHENE	0.20 - 5.0	0.58 - 16.	--	--
4. FLUORENE	0.030 - 0.30	0.099 - 0.26	95.0	95.0
5. PHENANTHRENE	0.0070 - 0.060	0.023 - 0.19	99.0, 90.4*	84.0, 92.5*, 82.6*
6. ANTHRACENE	0.0010 - 0.090	0.023 - 0.30	81.8, 94.4*	72.8, 96.2*, 72.9*
7. FLUORANTHENE	0.0020 - 0.090	0.0066 - 0.30	94.9, 90.4*	73.0, 93.5*, 81.7*
8. PYRENE	0.0010 - 0.30	0.0036 - 0.99	94.4, 76.1*	84.9, 77.0*, 75.9*
9. BENZ[a]ANTHRACENE	0.0010 - 0.090	0.0042 - 0.30	86.6, 92.7*	62.4, 95.0*, 72.3*
10. CHRYSENE	0.0070 - 0.20	0.023 - 0.37	94.6, 89.9*	62.7, 89.8*, 74.0*
11. BENZO[e]PYRENE	0.0060 - 0.80	0.020 - 2.6	110	48.3
12. BENZO[b]FLUORANTHENE	0.0030 - 0.20	0.011 - 0.66	94.8	64.2
13. BENZO[k]FLUORANTHENE	0.0020 - 0.040	0.0054 - 0.13	103	53.2
14. BENZO[a]PYRENE	0.0020 - 0.10	0.0051 - 0.33	101, 88.1*	50.4, 91.6*, 68.4*
15. DIBENZ[a,h]ANTHRACENE	0.0040 - 0.60	0.014 - 2.0	76.5	61.0
16. BENZO[ghi]PERYLENE	0.0030 - 0.50	0.011 - 1.7	76.5	61.0
17. INDENO[1,2,3-cd]PYRENE	0.0090 - 0.20	0.027 - 0.66	91.6	36.5

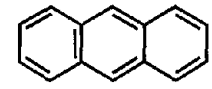
* Data from [4].
† Data from [5]



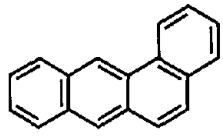
ACENAPHTHENE



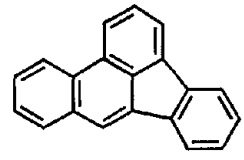
ACENAPHTHYLENE



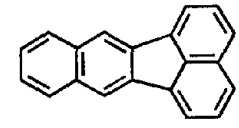
ANTHRACENE



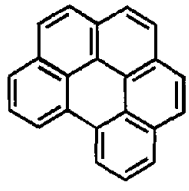
BENZ[a]ANTHRACENE



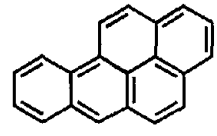
BENZO[b]FLUORANTHENE



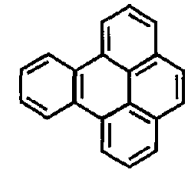
BENZO[k]FLUORANTHENE



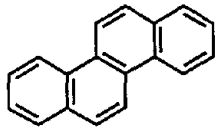
BENZO[g h i]PERYLENE



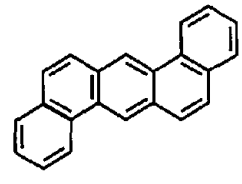
BENZO[a]PYRENE



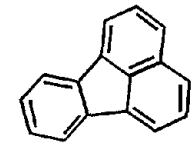
BENZO[e]PYRENE



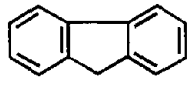
CHRYSENE



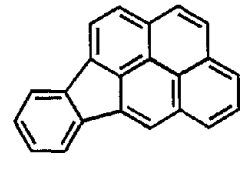
DIBENZ[a,h]ANTHRACENE



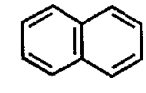
FLUORANTHENE



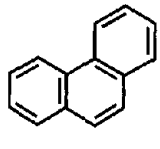
FLUORENE



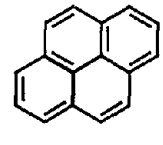
INDENO[1,2,3-c d]PYRENE



NAPHTHALENE



PHENANTHRENE



PYRENE

Figure 1. Structure of the PAHs.

RESORCINOL 5701

$C_6H_4(OH)_2$ MW: 110.1 CAS: 108-46-3 RTECS: VG9625000

METHOD: 5701, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PEL
NIOSH: 10 ppm
ACGIH: 10 ppm
(1 ppm = 4.49 mg/m³ @ NTP)

PROPERTIES: white crystals, hygroscopic; d 1.272 g/mL @ 20 °C; BP 280°C; MP 111°C; VP 2.66 x 10^{-5} kPa (2 x 10^{-4} mm Hg) @ 25 °C, vapor density 3.79 (air=1)

SYNONYMS: 1,3-benzenediol, m-benzenediol, 1,3-dihydroxybenzene, m-dihydroxybenzene, 3-hydroxyphenol, m-hydroxyphenol

SAMPLING

SAMPLER: FILTER / SOLID SORBENT TUBE
OVS tube: glass fiber filter, XAD-7

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 5 L
-MAX: 160 L

SHIPMENT: routine; protect from exposure to light

SAMPLE STABILITY: 30 days at 5 °C (protect from light)

BLANKS: 2 to 10 field blanks per 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: resorcinol

DESORPTION: 2 mL methanol

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 80° -230°C (12°C/min)

CARRIER GAS: Helium, 2.4 mL/min

COLUMN: capillary, 30 m x 0.28-mm ID; 0.25-µm film 100% dimethyl polysiloxane Mtx-1™ or equivalent [1]

CALIBRATION: solutions of resorcinol in methanol

RANGE: 12 to 5960 µg/sample [LOQ determined from XAD-7 solid sorbent DE recovery]

ESTIMATED LOD: 2 µg/sample

PRECISION ($\bar{S}_r$): 0.032 [1]

APPLICABILITY: The working range is 0.04 to 22.12 ppm (0.2 mg/m³ to 99.3 mg/m³) for a 60-L air sample. Under the GC parameters given in the method, resorcinol can be identified based upon retention time and quantified.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time may interfere.

OTHER METHODS: This method is based on the OSHA stopgap method for resorcinol [2].

REAGENTS:

1. Resorcinol, reagent grade.*
2. Methanol, chromatographic grade. *
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Calibration stock: Dissolve mg amount of resorcinol in 10 mL of solvent. Prepare additional standards by serial dilution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: XAD-7 OVS tube, 13-mm OD, containing two sections of XAD-7 (200 mg front section/100 mg back section) separated by polyurethane foam plug. A glass fiber filter precedes the front section and is held in place with a Teflon® ring. A polyurethane foam plug follows the back section. Tubes are commercially available (SKC # 226-57).
2. Personal sampling pump, 0.2 to 1.0 mL/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detection, integrator, and Mtx-1 capillary column (page 5701-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Vials, 4-mL, with screw caps.
7. Microliter syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.

SPECIAL PRECAUTIONS: Resorcinol is a toxic irritant and is also air and light sensitive. Methanol is flammable and a dangerous fire risk. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove front and rear caps from each tube immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1.0 L/min for a total sample size of 5 to 160 L.
4. Cap the samplers and pack securely for shipment. Protect samplers from exposure to light.

SAMPLE PREPARATION:

5. Place front sorbent section and glass fiber filter in a 4-mL screw cap vial. Place backup sorbent section in a separate vial. Discard foam plugs.
6. Add 2 mL of methanol to each vial and cap.
7. Place vials in an ultrasonic bath for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.

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 (peak area or height vs. µg resorcinol).

9. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 8).
   a. Prepare three samplers at each of six levels plus three media blanks.
   b. Raise the Teflon holding ring to prevent wicking, and inject a known amount of calibration stock solution directly onto the front sorbent bed of each OVS tube.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
   d. Desorb the samples (steps 5 through 7) and analyze together with standards and blanks (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 ensure that the calibration and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5701-1. Inject a 1-µL 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 with methanol, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for resorcinol 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 resorcinol in the air volume sampled, V (L):

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

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

This work extended the range of the OSHA stopgap method for recorcinol [2] to lower concentration levels. The method was evaluated for resorcinol over the range of 0.040 to 5.96 mg per sample. Table 1 shows the desorption efficiencies for each of the sampler components, glass fiber filter (alone) and XAD-7 sorbent, as well as the complete OVS tube. The 40 µg, 80 µg, 120 µg, and 200 µg levels were evaluated by NIOSH [1]. Higher concentration levels (298 to 5860 µg) were evaluated by OSHA [2]. The OSHA study tested retention

efficiency by spiking filters with 5.96 mg resorcinol and pulling humidified air through the tubes. The mean recovery from these samples was 99.7%, with no resorcinol found on the back up section. When stored at ambient temperature, resorcinol samples spiked at 120 µg were stable on the XAD-7 sorbent for 28 days, having a mean recovery of 97.5%. However, refrigerated storage is recommended.

REFERENCES:

[1] Pendergrass SM [1997]. Backup data report for Resorcinol Method Development. Cincinnati, OH: National Institute for Occupational Safety and Health, MRSB (NIOSH) (unpublished May).
[2] Eide, ME [1994]. OSHA Stopgap Method for Resorcinol, Salt Lake City, UT: OSHA Technical Center, Organic Service Branch I (March, 1994).

METHOD WRITTEN BY:

Stephanie M. Pendergrass, DPSE/NIOSH

TABLE 1. RECORCINOL RECOVERY DATA

Spike Level (µg)	Glass Fiber Filter 13-mm			XAD-7 Sorbent			OVS-7 Tube		
	n	% Rec	S_r	n	% Rec	S_r	n	% Rec	S_r
40	6	48.4	0.035	6	100.4	0.041	6	82.9	0.023
80	--	--	--	--	--	--	6	83.9	0.030
120	6	72.9	0.067	6	92.2	0.027	6	93.4	0.028
200	6	85.6	0.029	6	96.3	0.036	6	96.3	0.042
$\bar{S}_r$			0.047			0.035			0.032

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, Issue 3 **EVALUATION: FULL** **Issue 1: 15 August 1990**
Issue 3: 15 January 1998

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

SAMPLER:	CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell (HD) cyclone, or aluminum cyclone + 5-µm PVC membrane
FLOW RATE:	nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min; aluminum cyclone: 2.5 L/min
VOL-MIN:	400 L
-MAX:	1000 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 per set (See step 12.g.)
BULK SAMPLE:	high-volume or settled dust; to identify interferences

ACCURACY

RANGE STUDIED:	25 to 2500 µg/m³ [1] (800-L sample)
BIAS:	none known
OVERALL PRECISION ($\hat{S}_{rT}$):	0.09 (50 to 200 µg) [1]
ACCURACY:	± 18%

MEASUREMENT

TECHNIQUE:	X-RAY POWDER DIFFRACTION
ANALYTE:	crystalline SiO_2
ASH:	muffle furnace or RF plasma asher or dissolve in tetrahydrofuran
REDEPOSIT:	on 0.45-µm Ag membrane filter
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
CALIBRATION:	suspensions of silica in 2-propanol
RANGE:	0.02 to 2 mg SiO_2 per sample [2]
ESTIMATED LOD:	0.005 mg SiO_2 per sample [2]
PRECISION ($\bar{S}_r$):	0.08 @ 0.05 to 0.2 mg per sample [1]

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, ARDB, 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: Check each new lot of PVC filters by analyzing one or more by this method. For example, Gelman VM-1 filters (all lots) were found to be 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 through 8.
   b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), Aluminum (Al), or equivalent.
2. Area air sampler: PVC membrane filter, 37-mm diameter, 5-µm pore size; three-piece filter cassette.
3. Sampling pumps with flexible connecting tubing, capable of the following flow rates: nylon cyclone, 1.7 L/min; HD cyclone, 2.2 L/min; Al cyclone, 2.5 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size.
5. X-ray powder diffractometer (XRD) 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 (LTA) or muffle furnace, or ultrasonic bath (≥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, 2.2 ± 5% L/min with HD cyclone, ro 2.5 ± 5% Al 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, if dust in the work environment has not been previously characterized.

SAMPLE PREPARATION:

4. Samples may be characterized by one of the following methods, as appropriate.
   a. **Interference check.** Prepare area dust sample or settled dust bulk sample for XRD analysis by mounting the collection sample directly on an XRD sample holder, or by depositing or redepositing the dust on another filter for mounting, or by packing an XRD powder holder. Proceed to step 11.
   b. **Qualitative Analysis.** Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust particle size. 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 of 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 ± 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. NOTE: The following procedure for absorption correction is not necessary in situations that have been previously documented as requiring no corrections.

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

NOTE: There is an alternative to scanning an area air sample, settled dust sample, or ground bulk sample to prove lack of contamination. A slow scan of the three main peaks of quartz (also cristobalite and tridymite if their absence has not been previously confirmed) on a personal air sample, and verification that their intensity ratios are within 15% of pure quartz, is sufficient evidence that other materials are not interfering in the silica determination.

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. Field blanks may be analyzed by scanning the 2-theta 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 blank. Each laboratory should determine the specifics of field blank use for its application. When contamination does occur, the reason should be investigated and appropriate action taken. In practice, contamination of field blanks is extremely rare and usually is not consistent across filters. The analysis of blanks may be abbreviated if experience indicates that contamination is not likely with current field and laboratory operations; however, occasional confirmation of non-contamination is prudent.

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 ($\hat{I}^o_x$ 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 = $\hat{i}_{Ag}$/(average $\hat{I}^o_{Ag}$) = transmittance of sample
$\hat{i}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}^o_{Ag}$ = 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 ultrasonication 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 (S_r) 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, $\hat{S}_{rT}$:

Total (intra- and interlaboratory):	50 to 200 µg -- 0.29 [1]

REFERENCES:

[1] Anderson CC [9183]. Collaborative tests of two methods for determining free silica in airborne dust. U.S. Department of Health and Human Services, Publ. (NIOSH) 83-124.
[2] NIOSH [1983]. User check, UBTL, NIOSH Sequence #4121-M (unpublished)
[3] NIOSH [1974]. Criteria for a Recommended Standard: Occupational Exposure to Crystalline Silica. U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120.
[4] NIOSH [1979]. Silica, crystalline: Method P&CAM 259. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5., Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141.
[5] Ibid, Vol. 3, S315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] NIOSH [1977]. Documentation of the NIOSH Validation Tests. S315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.
[7] NIOSH [1977]. Silica (XRD): Method P&CAM 109. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A.
[8] Bumsted HE [1973]. Determination of alpha-quartz in the respirable portion of airborne particles by X-ray diffraction. Am Ind Hyg Assoc. J *34*:150.

[9] Peters ET [1976]. Evaluation Of the NIOSH X-ray diffraction method for the determination of free silica in respirable dust. Final Report, NIOSH Contract CDC-99-74-51.
[10] Talvitie NA [1964]. Determination of free silica: gravimetric and spectrophotometric procedures applicable to airborne and settled dust. Am Ind Hyg Assoc J *25*:169-178.
[11] Kupel RE, Kinser RE, Mauer PA [1968]. Separation and analysis of the less than 10-micron fractions of industrial dusts. Am Ind Hyg Assoc J *29*:364.
[12] Talvitie NA [1951]. Determination of quartz in presence of silicates using phosphoric acid. Anal Chem *23* (4).
[13] Williams DD [1959]. Direct quantitative diffractometric analysis. Anal Chem *31*:1841.
[14] Abell MT, Dollberg DD, Crable JV [1981]. Quantitative analysis of dust samples from occupational environments using computer automated X-ray diffraction. Advances in X-Ray Analysis *24*:37.
[15] Abell MT, Dollberg DD, Lange BA, Hornung RW, Haartz JC [1981]. Absorption corrections in X-ray diffraction dust analyses: procedures employing silver filters. Electron Microscopy and X-Ray Applications, V. 2, p. 115, Ann Arbor Science Publishers, Inc.
[16] Dollberg DD, Abell MT, Lange BA [1980]. Occupational health analytical chemistry: quantitation using x-ray powder diffraction. ACS Symposium Series, No. 120, 43.
[17] Altree-Williams S, Lee J, Mezin NV. Qualitative X-ray diffractometry on respirable dust collected on nuclepore filters. Ann Occup Health Hyg *20*:109.
[18] Leroux J, Powers C [1970]. Direct X-ray diffraction quantitative analysis of quartz in industrial dust films deposited on silver membrane filters. Occup Health Rev *21*:26.

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

TOLUENE (diffusive sampler) 4000

$C_6H_5CH_3$ 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)
(1 ppm = 3.77 mg/m³)

PROPERTIES: liquid; d 0.866 g/mL @ 20 °C; BP 110.6 °C; MP -95 °C; VP 3.8 kPa (28 mmHg; 3.7% v/v) @ 25 °C; explosive range 1.3 to 7.1% v/v in air

SYNONYMS: methylbenzene; phenyl methane; toluol

SAMPLING

SAMPLER: DIFFUSIVE SAMPLER (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/m³ [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/m³) 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: diffusive 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/mL 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. From the calibration graph and desorption volume, 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:

$$C = \frac{(W - B) \cdot 10^6}{t \cdot K}, \ mg/m^3$$

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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p-TOLUENESULFONIC ACID 5043

$C_7H_8O_3S$ MW: 172.20 CAS: 104-15-4 RTECS: XT6300000

METHOD: 5043, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA : no PELs
NIOSH: no RELs
ACGIH: no TLVs
(1 ppm = 7.03 mg/m^3 @ NTP)

PROPERTIES: solid; MP 106 to 107 °C when anhydrous; d 1.20 g/mL @ 20 °C; BP 140 °C @ 20 mm Hg; VP not significant @ 25 °C

NAMES & SYNONYMS: 4-methylbenzenesulfonic acid; *p*-methylphenylsulfonic acid; tosic acid

SAMPLING

SAMPLER: FILTER (13-mm glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 29 days @ 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: HPLC, UV DETECTOR

ANALYTE: *p*-toluenesulfonic acid

EXTRACTION: 2 mL 2% isopropanol in water v/v; ultrasonic bath, 10 min

INJECTION VOLUME: 100 µL

MOBILE PHASE: 21% acetonitrile/79% water containing 0.005 M Pic® A v/v; 1 mL/min

COLUMN: 3.9-mm ID x 15 cm stainless steel packed with 10-µm µ-Bondapak C_{18}

DETECTOR: UV @ 222 nm

CALIBRATION: standard solutions of p-toluenesulfonic acid in isopropanol: water

RANGE: 0.27 to 120 µg/sample [1]

ESTIMATED LOD: 0.08 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.046 @ 3 to 15 µg/sample [1]

APPLICABILITY: *p*-Toluenesulfonic acid at 0.0027 to 1.2 mg/m^3 can be determined in a 100-L air sample by this method. This method has been used to analyze samples collected at a foundry & machining company where *p*-toluenesulfonic acid was a catalyst in a process to produce a resin from resorcinol and furfuryl alcohol [2].

INTERFERENCES: None identified.

OTHER METHODS: Chromatographic methods for determination of *p*-toluenesulfonic acid in solution have been published [3-7]. None has been published for air analysis. An alternative air sampler for the present method is a midget impinger containing isopropanol [1,2].

REAGENTS:

1. *p*-Toluenesulfonic acid,* >98% pure.
2. Water, distilled.
3. Acetonitrile,* chromatographic quality.
4. Isopropanol, chromatographic quality.
5. PIC®A, "paired-ion chromatography," low UV reagent (Waters Corp., or equivalent). PIC®A contains water, tetrabutylammonium hydrogen sulfate, and phosphoric acid. Add entire vial of PIC®A to 1 L of distilled water to make 0.005 *M* solution.
6. Extraction solution: 2% Isopropanol/98% water (v/v). Add 20 mL of isopropanol to distilled water to make 1 L of solution.
7. *p*-Toluenesulfonic acid calibration stock solution, 4.0 mg/mL. Dissolve 200 mg *p*-toluenesulfonic acid in extraction solution to make 50 mL of solution.

*** See SPECIAL PRECAUTIONS**

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter in 2-piece filter holder (Swinnex, Millipore Corp., or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. HPLC, UV detector, 222 nm, integrator, and column (page 5043-1).
4. Vials, 4-mL, with PTFE-lined caps.
5. Graduated cylinder, 1-L, readable to 10 mL.
6. Volumetric flasks, 25- and 10-mL.
7. Syringes, 10-mL, 500-µL, and 100-µL.
8. Ultrasonic water bath.
9. Film, plastic, water resistant.
10. Syringe filters, 3-mm PTFE membranes, 0.45-µm pore size, in polypropylene housing.
11. Forceps.

SPECIAL PRECAUTIONS: *p*-Toluenesulfonic acid is highly irritating to the skin and mucous membranes; also, it can cause a potentially explosive reaction of acetic anhydride with water. Acetonitrile is toxic and is a fire hazard (flash point = 12.8 °C). Wear protective clothing and work in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach the sampler to the 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.
   NOTE: Limit the maximum loading of particulate matter on the filter to approximately 0.5 mg.
4. Seal ends of sampler with plastic film. Ship to laboratory at room temperature.

SAMPLE PREPARATION:

5. Using the forceps, transfer the 13-mm glass fiber filter to a 4-mL vial.
6. Add 2 mL of the extraction solution to the vial and cap securely.
7. Place the sample vial into an ultrasonic bath and agitate for 10 min.
8. Filter the sample solution through a PTFE membrane syringe filter.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range of interest: 0.04 to 60 µg/mL.
   a. Prepare working standards over the range of interest. Add a known amount of the calibration stock solution to an aliquot of the extraction solution.
   b. Analyze together with samples and blanks (steps 12 and 13).

c. Prepare calibration graph (peak area or height vs. µg of analyte).

10. Determine recovery (R) at least once for each lot of glass fiber filters in the calibration range (step 9). Prepare three filters at each of five concentration levels plus three media blanks.
    a. Place 13-mm glass fiber filters into 4-mL vials.
    b. With a microliter syringe, fortify each filter with a known amount of the calibration stock solution.
    c. Allow the uncapped vials to stand overnight at room temperature.
    d. Prepare and analyze with working standards (steps 5 through 8, and steps 12 and 13).
    e. Prepare graph of R vs. µg of analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and recovery graphs are in control.

MEASUREMENT:

12. Set high performance liquid chromatograph to manufacturer's recommendations and to conditions given on page 5043-1. Inject 100-µL aliquot manually or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with desorbing solution, reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area or height for *p*-toluenesulfonic acid.

CALCULATIONS:

14. Determine the mass, µg (corrected for R), of analyte found on the filter (W) and the average media blank (B).
15. Calculate the concentration, C, of *p*-toluenesulfonic acid in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Average recoveries of *p*-toluenesulfonic acid after fortification of 13-mm glass fiber filters with 3-, 6-, 10-, and 15-µg quantities of the compound were 1.02, 0.96, 1.04 and 0.96, respectively; precision ($\bar{S}_r$) was 0.046 (23 samples, pooled). After 29 days of storage at room temperature, the average recovery of 3-µg quantities of *p*-toluenesulfonic acid from glass fiber filters was 1.03; S_r was 0.023 (5 samples).

The purpose of the 2% isopropanol in samples and standards was to prevent possible deterioration of *p*-toluenesulfonic acid by bacteria during storage.

ALTERNATIVE METHOD:

As an alternative to the glass fiber filters, air samples of *p*-toluenesulfonic acid can be collected in midget impingers containing isopropanol at 1 L/min. After sampling, the impinger solution is transferred to a 20-mL glass vial and transported to the laboratory. The vial is placed onto a heating plate maintained at 80 °C, and the isopropanol is evaporated to dryness with a gentle stream of nitrogen (total evaporation time is about 1.5 hours). A 2-mL aliquot of 2% isopropanol in water is added to the vial, and the vial is placed into an ultrasonic bath for 30 seconds. Then the vial is tilted in order to wet the inside wall of the vial. Solution is filtered through a PTFE membrane syringe filter and is ready for analysis according to the method described above.

EVALUATION OF ALTERNATIVE METHOD:

Isopropanol was found to evaporate from the midget impinger during air sampling. Air at room temperature was drawn at 1 L/min through an impinger containing 20 mL of isopropanol. After 1 hour of pump operation, 6 mL of the isopropanol had evaporated, and the remaining 14 mL was cold because of evaporation. Separate recovery experiments were performed. The average recovery of 3-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of fortified isopropanol was 1.04 (Sr = 0.054 for 6 samples); the average recovery of 6-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of fortified isopropanol was 1.01 (S_r = 0.028 for 6 samples). After 29 days of storage at room temperature, the average recovery of 3-µg quantities of *p*-toluenesulfonic acid from 20-mL volumes of isopropanol was 0.95 (S_r = 0.050 for 6 samples). This alternative method and the method with glass fiber filters both have the same LOD and LOQ, because final sample solution volumes in the two methods are the same.

REFERENCES:

[1] Tucker SP [1997]. Backup data report for method 5043, *p*-Toluenesulfonic Acid. National Institute for Occupational Safety and Health, DPSE/NIOSH, (Unpublished report).
[2] Tucker SP [1996]. Analytical report for Sequence #8567, DPSE/MRSB. Cincinnati, OH: National Institute for Occupational Safety and Health. (Unpublished report).
[3] Lange FT, Wenz M, Brauch H [1995]. Trace-level determination of aromatic sulfonates in water by on-line ion-pair extraction/ion-pair chromatography and their behavior in the aquatic environment. J High Resolut Chromatogr *18*:243-252.
[4] Altenbach B, Giger W [1995]. Determination of benzene- and naphthalene sulfonates in wastewater by solid-phase extraction with graphitized carbon black and ion-pair liquid chromatography with UV detection. Anal Chem *67*:2325-2333.
[5] Bastian B, Knepper TP, Hoffmann P, Ortner HM [1994]. Fresenius' J Anal Chem *348*: 674-679.
[6] Brouwer ER, Slobodnik J, Lingeman H, Brinkman UAT [1992]. Analusis *20*: 121-126.
[7] Schullerer S, Brauch HJ, Frimmel FH [1990]. Vom Wasser *75*:83-97.

METHOD WRITTEN BY:

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$CH_3CO_2CHCH_2$ MW: 86.09 CAS: 108-05-4 RTECS: AK0875000

METHOD: 1453, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 August 1994**
Issue 2: 15 January 1998

OSHA : no PEL
NIOSH: C 4 ppm/15 min
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 3.52 mg/m³ @ 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; ethylene ethanoate; 1-acetoxyethylene; ethenyl acetate; vinyl acetate monomer; vinyl ethanoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (carbon molecular sieve; 160 mg/80 mg; ORBO-92 or equivalent)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 0.085 L @ 10 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: at least 30 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7.8 to 29.6 mg/m³ [2]

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl acetate

DESORPTION: 1.0 mL 95:5 methylene chloride: methanol

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 210 °C
-DETECTOR: 260 °C
-COLUMN: 35 °C, 5 min; 5 °C/min to 50 °C; hold 1 min

COLUMN: capillary, fused silica, 30 m x 0.32-mm, coated internally with 1.00-µm film 5% -(phenyl)-methylpolysiloxane, or equivalent

CALIBRATION: standard solutions of vinyl acetate in 95:5 methylene chloride: methanol

RANGE: 3 to 8700 µg per sample [1]

ESTIMATED LOD: 1 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.018 [1]

APPLICABILITY: The working range is 0.085 to 247 ppm (0.3 to 870 mg/m³) for a 10-L air sample. The method is sensitive enough for ceiling measurements. [1,2]

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 [2] and replaces NIOSH method P&CAM 278 [3].

REAGENTS:

1. Vinyl acetate, practical grade, inhibited with 275 to 325 ppm diphenylamine.
2. Methanol, distilled in glass.
3. Methylene chloride*, distilled in glass.
4. Eluent, 95:5 (v/v) methylene chloride:methanol.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.
8. Calibration stock solution, 74.7 mg/mL. Add 160 µL vinyl acetate into 2-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 (Supelco ORBO-92, or equivalent).
2. Personal sampling pump, 0.1 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with an 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.
6. Volumetric flasks, 2-mL.

SPECIAL PRECAUTIONS: Vinyl acetate can irritate the eyes, nose, and throat. Methylene chloride is an irritant, can be absorbed through the skin, and is a suspect carcinogen [4]. Wear protective clothing. 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 0.1 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 95:5 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 in the range of interest.
   a. Add known amounts of calibration stock to eluent in 2-mL volumetric flasks. 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. µg 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, µg (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):

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

NOTE: µg/L ≡ 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 to 710 µg per sample. The recovery from samples stored 14 days at 5 °C remained above 90% for the same levels. The pooled relative standard deviation ($\bar{S}_r$) obtained from replicate determinations of analytical standards in this range was 0.0073 [2]. 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 [2]. In a recent study to update this method, the average desorption efficiency for samples from 2.8 µg to 1120 µg per sample was 98.5% with a $\bar{S}_r = 0.018$ [1]. Recoveries ranged from 96.8% to 102%. Samples stored from 7 to 30 days at 5 °C had a recoveries above 93% [1].

REFERENCES:

[1] Yoon YH, Perkins JB [1998]. Vinyl acetate by GC-FID back-up data report (unpublished). DataChem Laboratories, Salt Lake City, UT.
[2] OSHA [1988]. 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).
[3] NIOSH [1978]. Vinyl acetate: Method P&CAM 278. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Vol 4. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175.
[4] NIOSH [1997]. NIOSH Pocket Guide to Chemical Hazards. Cincinnati, OH: U.S. Department of Health and Human Services, Publ. (NIOSH) 97-140, available as GPO Stock No. 017-033-00483-8 from Superintendent of Documents, Washington, DC 20402.

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