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THIS FOURTH SUPPLEMENT CONTAINS 51 METHODS INVOLVING 27 COMPOUNDS IS ENCLOSED AS AN ADDITION TO THE NIOSH MANUAL OF ANALYTICAL METHODS, 3RD EDITION (1984). THE METHODS FOR THE SUPPLEMENT HAVE BEEN SELECTED ON THE BASIS OF THEIR USE IN WORKPLACES, INPUT FROM THE USERS OF THE MANUAL AND NIOSH RESEARCH CHEMISTS, AND THE HEALTH IMPLICATIONS OF THE COMPOUNDS. MANY OF THESE METHODS HAVE BEEN INCLUDED "AS-IS" FROM THE SECOND EDITION OF THE MANUAL WITH A ONE-PAGE UPDATE INFORMATION ATTACHED TO EACH OF THEM. OTHER METHODS IN THIS SUPPLEMENT INCLUDE 8 THIRD- EDITION METHODS EITHER REVISED FROM THE MANUAL'S EARLIER INCLUSION OR NEWLY DEVELOPED ONES.

A NEW FOURTH EDITION OF THE NIOSH MANUAL OF ANALYTICAL METHODS (NMA) ALONG WITH ITS ELECTRONIC VERSION IS PLANNED FOR 1992.

ANY COMMENTS REGARDING THE SUPPLEMENT OR THE NMA IN GENERAL WOULD BE GREATLY APPRECIATED BY NIOSH AND SHOULD BE DIRECTED TO:

MANUAL COORDINATOR
NIOSH MANUAL OF ANALYTICAL METHODS
DIVISION OF PHYSICAL SCIENCE AND
ENGINEERING (R-2)
4676 COLUMBIA PARKWAY
CINCINNATI, OH 45226

TRANSMITTAL NOTICE

This is the fourth supplement to the NIOSH Manual of Analytical Methods (NMAM), 3rd edition (printed February 15, 1984, first supplement dated May 15, 1985, second supplement dated August 15, 1987, third supplement dated May 15, 1989). The contents of this supplement are dated August 15, 1990 and include the 51 methods on the reverse side of this page.

ACTION: To bring your NMAM up to date, please do the following:

- REMOVE the following pages: v through xiii (contents), HYDROGEN CYANIDE⁽¹⁾ (Method 6010), 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE⁽¹⁾ (Method 1020), pp. v through xiv (contents) and pp. A-11 through A-54 (indexes).
- ADD enclosed methods alphabetically⁽²⁾ to your Manual. Add the enclosed Table of Contents⁽³⁾ (pp. v through xiv) and Indexes⁽⁴⁾ (pp. A-11 through A-28 and yellow pages, A-29 through A-56).
- CHECK your methods against the enclosed Table of Contents to make sure you have all current methods. If methods are missing, contact GPO or NIOSH for replacements.
- NOTE: For many methods in the Manual, new OSHA PELs⁽⁵⁾, NIOSH RELs⁽⁶⁾, and ACGIH TLVs⁽⁷⁾, are in effect..
- NOTE: New guidelines⁽⁸⁾ in addition to those cited previously for protecting safety and health of health care workers.
- ERRATA: Change sampler in Acetaldehyde, method 2538 to Supelco ORB0-25, Cat. No. 2-0357

NOTES: (1) This method has been revised.

- (2) The alphabetical arrangement is most useful; however, the methods may be arranged numerically. As detailed on pp. 2-3 of the Introduction. Methods are numbered as follows: Organic Gases, 1000-4999; Organic Aerosols, 5000-5999; Inorganic Gases, 6000-6999; Inorganic Aerosols, 7000-7999; Biologicals, 8000-8999; Bulks, 9000-9999.
- (3) Current Issue dates have been added for each method. Discard previous versions.
- (4) The Index of Second Edition Method Numbers has been made more useful by a cross-reference to 3rd ed. method names.
- (5) OSHA PELs. TABLES Z-1-A, Z-2, and Z-3, Fed. Reg. Vol. 54, No. 12, January 19, 1989;
- (6) NIOSH RELs. Recommendations for Occupational Safety and Health Standard. MMWR 37 (S-7):1-29, Centers for Disease Control, Atlanta, Georgia, HHS Publ. (CDC) 88-8017 (August 26, 1988), or more recent issuance.
- (7) ACGIH TLVs. American Conference of Governmental Industrial Hygienists. TLVs and Biological Exposure Indices for 1989-90, ACGIH, Cincinnati, Ohio.
- (8) "Guidelines for Prevention of Transmission of Viruses to Health Care and Safety Workers", MMWR, Centers for Disease Control, Atlanta, Georgia, June 23, 1989.

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Methods included with the August 15, 1990, Supplement to the NMAM, 3rd ed. Method numbers with S or P&CAM prefix indicate second edition methods with one-page update attached and those with four digits indicate third edition methods:

<u>Method No.</u>	<u>Method</u>	<u>Method No.</u>	<u>Method</u>
S346	ALLYL GLYCIDYL ETHER	S42	METHYL ACETATE
S158	2-AMINOPYRIDINE	S38	METHYL ACRYLATE
5031	ASPARTAME	1615	METHYL tert-BUTYL ETHER (MTBE)
6011	BROMINE AND CHLORINE	S39	METHYL CELLOSOLVE ACETATE
S138	n-BUTYLAMINE	S374	METHYLCYCLOHEXANOL
S81	n-BUTYL GLYCIDYL ETHER	5029	4,4'-METHYLENEDIANILINE (MDA)
S249	CARBON DIOXIDE	S153	MONOMETHYLANILINE
S340	CARBON MONOXIDE	S149	MONOMETHYLHYDRAZINE
S67	CHLORINATED CAMPHENE	S321	NITRIC OXIDE
S11	CHLOROACETALDEHYDE	S7	p-NITROANILINE
P&CAM 337	p-CHLOROPHENOL	S72	PHENYL ETHER
P&CAM 285	CROTONALDEHYDE	S73	PHENYL ETHER-BIPHENYL MIXTURE
S143	1,1-DIMETHYLHYDRAZINE	S74	PHENYL GLYCIDYL ETHER
S166	DINITRO-o-CRESOL	S160	PHENYLHYDRAZINE
S49	ETHYL ACETATE	S332	PHOSPHINE
S36	ETHYL FORMATE	S299	RONNEL
P&CAM 300	ETHYLENIMINE	S245	SULFURYL FLUORIDE
7902	*FLUORIDES, aerosol and gas	P&CAM 355	TALC, RESPIRABLE
S173	FORMIC ACID	S208	TRIBUTYL PHOSPHATE
P&CAM 307	HEXACHLOROBUTADIENE	*1020	1,1,2-TRICHLORO- 1,2,2-TRIFLUOROETHANE
6010	*HYDROGEN CYANIDE	P&CAM 322	TRIMELLITIC ANHYDRIDE
P&CAM 296	HYDROGEN SULFIDE	S209	TRIORTHOCRESYL PHOSPHATE
S50	ISOPROPYL ACETATE	S210	TRIPHENYL PHOSPHATE
S368	ISOPROPYL ETHER	P&CAM 278	VINYL ACETATE
S77	ISOPROPYL GLYCIDYL ETHER		
7105	LEAD		
P&CAM 302	MALEIC ANHYDRIDE		

* Revision of a previously-issued 3rd Ed. method

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II. Methods

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
A. Air Samples (A through G in Vol. 1, H through Z in Vol. 2)		
ACETALDEHYDE (GC).....	5/89	2538
ACETALDEHYDE (HPLC).....	8/87	3507
ACETIC ACID	5/89	1603
ACETIC ANHYDRIDE	5/85	3506
ACETONE CYANOHYDRIN	5/85	2506
ACETONITRILE	2/84	1606
ACIDS, INORGANIC	2/84	7903
Hydrobromic acid Hydrofluoric acid Phosphoric acid		
Hydrochloric acid Nitric acid Sulfuric acid		
ACROLEIN	2/84	2501
ACRYLONITRILE	5/89	1604
ALCOHOLS I (desorption in 99:1 CS ₂ :2-butanol)	2/84	1400
tert-Butyl alcohol Isopropyl alcohol Ethanol		
ALCOHOLS II (desorption in 99:1 CS ₂ :2-propanol)	2/84	1401
n-Butyl alcohol Isobutyl alcohol		
sec-Butyl alcohol n-Propyl alcohol		
ALCOHOLS III (desorption in 95:5 CS ₂ :2-propanol)	2/84	1402
Allyl alcohol Isoamyl alcohol Methyl isobutyl carbinol		
Cyclohexanol Diacetone alcohol		
ALCOHOLS IV (desorption in 95:5 CH ₂ Cl ₂ :methanol)	2/84	1403
2-Butoxyethanol 2-Ethoxyethanol 2-Methoxyethanol		
ALDEHYDES, SCREENING	5/89	2539
ALDRIN and LINDANE	2/84	5502
ALKALINE DUSTS	8/87	7401
ALLYL CHLORIDE	2/84	1000
ALLYL GLYCIDYL ETHER.....	8/90	5346
ALUMINUM	2/84	7013
AMINES, ALIPHATIC	5/89	2010
Diethylamine Dimethylamine		

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
AMINES, AROMATIC	5/85	2002
Aniline N,N-Dimethyl-p-toluidine 2,4-Xylidine		
N,N-Dimethylaniline p-Toluidine		
AMINOETHANOL COMPOUNDS	8/87	2007
2-Aminoethanol 2-Diethylaminoethanol		
2-Dibutylaminoethanol		
AMINOETHANOL COMPOUNDS II	5/89	3509
Monoethanolamine (MEA) Diethanolamine (DEA)		
Triethanolamine (TEA)		
2-AMINOPYRIDINE.....	8/90	5158
AMMONIA	5/85	6701
ANISIDINE	5/85	2514
ARSENIC (hydride AAS)	8/87	7900
ARSENIC, ORGANO-	5/85	5022
p-Aminophenylarsonic acid Methylarsonic acid		
Dimethylarsenic acid		
ARSENIC TRIOXIDE (graphite AAS)	2/84	7901
ARSINE	5/85	6001
ASBESTOS (bulk)	5/89	9002
ASBESTOS FIBERS	5/89	7402
ASPARTAME.....	8/90	5031
AZELAIC ACID	5/85	5019
 BARIUM, soluble compounds	8/87	7056
BENZENE by portable GC	8/87	3700
BENZIDINE and 3,3'-DICHLOROBENZIDINE	5/85	5509
BENZOYL PEROXIDE	2/84	5009
BERYLLIUM	8/87	7102
BIPHENYL	8/87	2530
BORON CARBIDE	5/85	7506
BROMINE AND CHLORINE.....	8/90	6011
BROMOTRIFLUOROMETHANE	8/87	1017
BROMOXYNIL and BROMOXYNIL OCTANOATE	2/84	5010
1,3-BUTADIENE	8/87	1024
1-BUTANETHIOL	5/89	2525
2-BUTANONE	2/84	2500
n-BUTYLAMINE.....	8/90	5138
n-BUTYL GLYCIDYL ETHER.....	8/90	581
 CADMIUM	8/87	7048
CALCIUM	2/84	7020
CARBARYL	5/85	5006
CARBON BLACK	2/84	5000
CARBON DIOXIDE.....	8/90	5249
CARBON DISULFIDE	5/85	1600
CARBON MONOXIDE.....	8/90	5340
CHLORDANE	5/89	5510
CHLORINATED CAMPHENE.....	8/90	567
CHLORINATED DIPHENYL ETHER	8/87	5025
CHLORINATED TERPHENYL	2/84	5014
CHLOROACETALDEHYDE.....	8/90	511
CHLOROACETIC ACID	8/87	2008

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
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CHLOROPRENE	2/84	1002
CHROMIUM	2/84	7024
CHROMIUM, HEXAVALENT	5/89	7600
CHROMIUM, HEXAVALENT	5/89	7604
COAL TAR PITCH VOLATILES	5/85	5023
COBALT	2/84	7027
COPPER (dust and fume)	2/84	7029
CRESOLS	2/84	2001
CROTONALDEHYDE	8/90	P&CAM 285
CYANIDES (aerosol and gas)	2/84	7904
CYANURIC ACID	5/89	5030
1,3-CYCLOPENTADIENE	5/85	2523
2,4-D and 2,4,5-T	2/84	5001
DEMETON	5/85	5514
DIAZOMETHANE	5/85	2515
DIBORANE	8/87	6006
DIBROMODIFLUOROMETHANE	5/85	1012
DIBUTYL PHOSPHATE	5/85	5017
DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE	5/85	5020
DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUOROETHANE	8/87	1018
sym-DICHLOROETHYL ETHER	2/84	1004
DICHLOROFLUOROMETHANE	5/85	2516
1,1-DICHLORO-1-NITROETHANE	2/84	1601
1,2-DICHLOROPROPANE	5/85	1013
DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE	5/89	2540
DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	5/85	2004
1,1-DIMETHYLHYDRAZINE	8/90	S143
DIMETHYL SULFATE	5/85	2524
DINITRO-O-CRESOL	8/90	S166
DIOXANE	5/85	1602
DYES, BENZIDINE, o-ANISIDINE, and o-TOLIDINE	5/85	5013
ELEMENTS (ICP)	2/84	7300
Aluminum Iron Platinum Tungsten		
Arsenic Lead Selenium Vanadium		
Beryllium Lithium Sodium Yttrium		
Calcium Magnesium Silver Zinc		
Cadmium Manganese Tellurium Zirconium		
Chromium Molybdenum Tin		
Cobalt Nickel Titanium		
Copper Phosphorus Thallium		
ENDRIN	5/89	5519
EPICHLOROHYDRIN	2/84	1010
EPN, MALATHION, and PARATHION	2/84	5012
ESTERS I	2/84	1450
n-Amyl acetate Ethyl acrylate		
sec-Amyl acetate Isoamyl acetate		
n-Butyl acetate Isobutyl acetate		

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
sec-Butyl acetate	Methyl isoamyl acetate	
t-Butyl acetate	n-Propyl acetate	
2-Ethoxyethyl acetate		
ETHYL ACETATE.....	8/90	S49
ETHYL BROMIDE	5/85	1011
ETHYL CHLORIDE	5/85	2519
ETHYL ETHER	5/85	1610
ETHYL FORMATE.....	8/90	S36
ETHYLENE CHLOROHYDRIN	5/85	2513
ETHYLENE DIBROMIDE	8/87	1008
ETHYLENE GLYCOL	2/84	5500
ETHYLENE OXIDE	8/87	1614
ETHYLENE OXIDE (portable GC)	8/87	3702
ETHYLENE THIOUREA	2/84	5011
ETHYLENIMINE	8/90	P&CAM 300
FIBERS	5/89	7400
FLUORIDES.....	8/90	7902
FORMALDEHYDE [2-(hydroxymethyl)piperidine].....	5/89	2541
FORMALDEHYDE (chromotropic acid)	5/89	3500
FORMALDEHYDE (Girard T)	5/89	3501
FORMIC ACID.....	8/90	S173
FURFURAL	8/87	2529
FURFURYL ALCOHOL	5/89	2505
GLUTARALDEHYDE	5/89	2531
GLYCIDOL	5/85	1608
HEXACHLOROBUTADIENE.....	8/90	P&CAM 307
HEXACHLORO-1,3-CYCLOPENTADIENE	5/85	2518
HYDRAZINE	2/84	3503
HYDROCARBONS, BP 36 - 126 °C	2/84	1500
Benzene	n-Heptane	n-Octane
Cyclohexane	n-Hexane	n-Pentane
Cyclohexene	Methylcyclohexane	Toluene
HYDROCARBONS, AROMATIC	2/84	1501
Benzene	α-Methylstyrene	Vinyltoluene
p-tert-Butyltoluene	Naphthalene	Xylene
Cumene	Styrene	
Ethylbenzene	Toluene	
HYDROCARBONS, HALOGENATED	8/87	1003
Benzyl chloride	1,1-Dichloroethane	
Bromoform	1,2-Dichloroethylene	
Carbon tetrachloride	Ethylene dichloride	
Chlorobenzene	Hexachloroethane	
Chlorobromomethane	Methylchloroform	
Chloroform	Tetrachloroethylene	
o-Dichlorobenzene	1,1,2-Trichloroethane	
p-Dichlorobenzene	1,2,3-Trichloropropane	

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
HYDROGEN CYANIDE	8/90	6010
HYDROGEN SULFIDE	8/90	P&CAM 296
HYDROQUINONE	2/84	5004
IODINE	8/87	6005
ISOCYANATES	5/89	5521
ISOPHORONE	2/84	2508
ISOPROPYL ACETATE	8/90	S50
ISOPROPYL ETHER	8/90	S368
ISOPROPYL GLYCIDYL ETHER	8/90	S77
KEPONE	2/84	5508
KETONES I (desorption in CS ₂)	5/89	1300
Acetone 2-Hexanone		
Cyclohexanone Methyl isobutyl ketone		
Diisobutyl ketone 2-Pentanone		
KETONES II (desorption in 99:1 CS ₂ :methanol)	2/84	1301
Camphor 5-Methyl-3-heptanone		
Ethyl butyl ketone Methyl-(n-amy)-ketone		
Mesityl oxide		
LEAD (AA - FLAME).....	2/84	7082
LEAD (AA - FLAMELESS)	8/90	7105
LEAD SULFIDE	2/84	7505
MALEIC ANHYDRIDE	8/90	P&CAM 302
MERCURY	5/89	6009
METHANOL	2/84	2000
METHYLAL	5/85	1611
METHYL ACETATE	8/90	S42
METHYL ACRYLATE	8/90	S38
METHYL BROMIDE	5/85	2520
METHYL tert-BUTYL ETHER (MTBE)	8/90	1615
METHYL CELLOSOLVE ACETATE	8/90	S39
METHYL CHLORIDE	8/87	1001
METHYLCYCLOHEXANOL	8/90	S374
METHYLCYCLOHEXANONE	5/85	2521
METHYLENE CHLORIDE	8/87	1005
4,4'-METHYLENEDIANILINE (MDA)	8/90	5029
METHYL ETHYL KETONE PEROXIDE	8/87	3508
METHYL IODIDE	5/85	1014
METHYL METHACRYLATE	5/89	2537
MEVINPHOS (Phosdrin)	2/84	2503
MINERAL OIL MIST	8/87	5026
MONOMETHYLANILINE	8/90	S153
MONOMETHYLHYDRAZINE	8/90	S149
NAPHTHAS	2/84	1550
Coal tar naphtha Petroleum ether Stoddard solvent		
Kerosene Petroleum naphtha		
Mineral spirits Rubber solvent		

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
NAPHTHYLAMINES	8/87	5518
NICKEL CARBONYL	8/87	6007
NITRIC OXIDE	8/90	S321
p-NITROANILINE	8/90	S7
NITROBENZENES	5/85	2005
4-Chloronitrobenzene Nitrobenzene Nitrotoluene		
NITROETHANE	8/87	2526
NITROGEN DIOXIDE	2/84	6700
NITROGLYCERIN/EGDN	2/84	2507
NITROMETHANE	8/87	2527
2-NITROPROPANE	8/87	2528
NITROSAMINES	5/89	2522
N-nitrosodimethylamine N-nitrosomorpholine		
N-nitrosodiethylamine N-nitrosopiperidine		
N-nitrosodipropylamine N-nitrosopyrrolidine		
N-nitrosodibutylamine		
NITROUS OXIDE (field-readable)	2/84	6600
NUISANCE DUST, RESPIRABLE	2/84	0600
NUISANCE DUST, TOTAL	2/84	0500
1-OCTANETHIOL	2/84	2510
ORGANOTIN COMPOUNDS	8/87	5504
OXYGEN (field-readable)	5/85	6601
PARAQUAT	5/85	5003
PENTACHLOROETHANE	5/85	2517
PENTACHLOROPHENOL	5/89	5512
PHENOL	2/84	3502
PHENYL ETHER	8/90	S72
PHENYL ETHER-BIPHENYL MIXTURE	8/90	S73
PHENYL GLYCIDYL ETHER	8/90	S74
PHENYLHYDRAZINE	8/90	S160
PHOSPHINE	8/90	S332
PHOSPHORUS	8/87	7905
PHOSPHORUS TRICHLORIDE	5/85	6402
POLYCHLOROBENZENES	8/87	5517
POLYCHLOROBIPHENYLS	8/87	5503
POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)	5/85	5506
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		
POLYNUCLEAR AROMATIC HYDROCARBONS (GC)	5/85	5515
Acenaphthene Benzo[ghi]perylene Fluorene		
Acenaphthylene Benzo[a]pyrene Indeno[1,2,3-cd]pyrene		
Anthracene Benzo[e]pyrene Naphthalene		
Benz[a]anthracene Chrysene Phenanthrene		
Benzo[b]fluoranthene Dibenz[a,h]anthracene Pyrene		
Benzo[k]fluoranthene Fluoranthene		

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
PROPYLENE OXIDE	5/85	1612
PYRETHRUM	5/85	5008
PYRIDINE	8/87	1613
QUARTZ in coal mine dust	5/89	7603
RIBAVIRIN	5/89	5027
RONNEL	8/90	5299
ROTENONE	2/84	5007
SILICA, AMORPHOUS	5/85	7501
SILICA, CRYSTALLINE (XRD)	5/89	7500
SILICA, CRYSTALLINE (color)	2/84	7601
SILICA, CRYSTALLINE (IR)	2/84	7602
STIBINE	8/87	6008
STRYCHNINE	5/85	5016
SULFUR DIOXIDE	5/89	6004
SULFURYL FLUORIDE	8/90	5245
TALC, RESPIRABLE	8/90	P&CAM 355
p-TERPHENYL	5/85	5021
1,1,2,2-TETRABROMOETHANE	5/85	2003
1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	8/87	1016
1,1,2,2-TETRACHLOROETHANE	8/87	1019
TETRAETHYL LEAD	8/87	2533
TETRAETHYL PYROPHOSPHATE (TEPP)	2/84	2504
TETRAHYDROFURAN	5/85	1609
TETRAMETHYL LEAD	8/87	2534
TETRAMETHYL THIOUREA	5/85	3505
THIRAM	2/84	5005
TOLUENE (passive)	8/87	4000
2,4- & 2,6-TOLUENEDIAMINE (TDA).....	5/89	5516
TOLUENE-2,4-DIISOCYANATE (TDI).....	8/87	2535
TRIBUTYL PHOSPHATE	8/90	5208
TRICHLOROETHYLENE	8/87	1022
TRICHLOROETHYLENE (portable GC)	8/87	3701
TRICHLOROFLUOROMETHANE	8/87	1006
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	8/90	1020
TRIMELLITIC ANHYDRIDE	8/90	P&CAM 322
TRIORTHOCRESYL PHOSPHATE	8/90	5209
TRIPHENYL PHOSPHATE	8/90	5210
2,4,7-TRINITROFLUOREN-9-ONE	5/85	5018
TUNGSTEN (soluble and insoluble)	5/85	7074
TURPENTINE	2/84	1551
VALERALDEHYDE	5/89	2536
VANADIUM OXIDES	8/87	7504
VINYL ACETATE	8/90	P&CAM 278

<u>METHOD NAME</u>	<u>LATEST ISSUE</u>	<u>METHOD NUMBER</u>
VINYL BROMIDE	2/84	1009
VINYL CHLORIDE	2/84	1007
VINYLDENE CHLORIDE	8/87	1015
WARFARIN	2/84	5002
WELDING AND BRAZING FUME	2/84	7200
Cadmium Copper Manganese Silver		
Chromium Iron Nickel Zinc		
ZINC	2/84	7030
ZINC OXIDE	2/84	7502
8. Biological Samples (Vol. 1)		
ALAD in blood	2/84	8000
BENZIDINE in urine (TLC)	2/84	8304
BENZIDINE in urine (GC)	2/84	8306
2-BUTANONE, ETHANOL and TOLUENE in blood	2/84	8002
ELEMENTS in blood or tissue	5/85	8005
Antimony Lanthanum Silver		
Cadmium Lead Strontium		
Chromium Manganese Tin		
Cobalt Molybdenum Titanium		
Copper Nickel Zinc		
Iron Platinum		
FLUORIDE in urine	2/84	8308
HIPURIC ACID in urine (color)	2/84	8300
HIPURIC and METHYL HIPURIC ACIDS in urine (HPLC)	2/84	8301
LEAD in blood and urine	2/84	8003
MBOCA in urine	5/85	8302
METALS in urine (ICP)	2/84	8310
Aluminum Lead Silver		
Barium Manganese Strontium		
Cadmium Molybdenum Tin		
Chromium Nickel Titanium		
Copper Platinum Zinc		
Iron		
PENTACHLOROPHENOL in blood	2/84	8001
PENTACHLOROPHENOL in urine	2/84	8303
PHENOL and p-CRESOL in urine	5/85	8305
POLYCHLOROBIPHENYLS in serum	2/84	8004
C. Bulk Samples (Vol. 1)		
CHRYSTILE ASBESTOS	2/84	9000
ASBESTOS (bulk by PLM)	5/89	9002

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I. A. INDEX OF THIRD EDITION METHOD NUMBERS

3rd ed. Method Number	Substance	3rd ed. Method Number	Substance
0500	NUISANCE DUST, TOTAL		Methyl isobutyl ketone
0600	NUISANCE DUST, RESPIRABLE		2-Pentanone
1000	ALLYL CHLORIDE	1301	KETONES II:
1001	METHYL CHLORIDE		Camphor
1002	CHLOROPRENE		Ethyl butyl ketone
1003	HYDROCARBONS, HALOGENATED:		Mesityl oxide
	Benzyl chloride		Methyl (n-amyl) ketone
	Bromoform		5-Methyl-3-heptanone
	Carbon tetrachloride	1400	ALCOHOL I:
	Chlorobenzene		tert-Butyl alcohol
	Chlorobromomethane		Ethanol
	Chloroform		Isopropyl alcohol
	o-Dichlorobenzene	1401	ALCOHOL II:
	p-Dichlorobenzene		n-Butyl alcohol
	1,1-Dichloroethane		sec-Butyl alcohol
	1,2-Dichloroethylene		Isobutyl alcohol
	Ethylene dichloride		n-Propyl alcohol
	Hexachloroethane	1402	ALCOHOLS III:
	Methylchloroform		Allyl alcohol
	Tetrachloroethylene		Cyclohexanol
	1,1,2-Trichloroethane		Diacetone alcohol
	1,2,3-Trichloropropane		Isoamyl alcohol
1004	sym-DICHLOROETHYL ETHER		Methyl isobutyl carbinol
1005	METHYLENE CHLORIDE	1403	ALCOHOLS IV:
1006	TRICHLOROFLUOROMETHANE		2-Butoxyethanol
1007	VINYL CHLORIDE		2-Ethoxyethanol
1008	ETHYLENE DIBROMIDE		Methyl cellosolve
1009	VINYL BROMIDE	1450	ESTERS I:
1010	EPICHLOROHYDRIN		n-Amyl acetate
1011	ETHYL BROMIDE		sec-Amyl acetate
1012	DIBROMODIFLUOROMETHANE		n-Butyl acetate
1013	1,2-DICHLOROPROPANE		sec-Butyl acetate
1014	METHYL IODIDE		tert-Butyl acetate
1015	VINYLDENE CHLORIDE		2-Ethoxyethyl acetate
1016	1,1,1,2-TETRACHLORO- 2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO- 1,2-DIFLUOROETHANE		Ethyl acrylate
1017	BROMOTRIFLUOROMETHANE		Isoamyl acetate
1018	DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUROETHANE		Isobutyl acetate
1019	1,1,2,2-TETRACHLOROETHANE		Methyl isoamyl acetate
1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE		n-Propyl acetate
1022	TRICHLOROETHYLENE	1500	HYDROCARBONS, BP 36 - 126 °C:
1024	1,3-BUTADIENE		Benzene
1300	KETONES I:		Cyclohexane
	Acetone		Cyclohexene
	Cyclohexanone		n-Heptane
	Diisobutyl ketone		n-Hexane
	2-Hexanone		Methylcyclohexane
			n-Octane
			n-Pentane
			Toluene

3rd Ed. Method Number	Substance	3rd Ed. Method Number	Substance
1501	HYDROCARBONS, AROMATIC:	2008	CHLOROACETIC ACID
	Benzene	2010	AMINES, ALIPHATIC
	p-tert-Butyl toluene		Diethylamine
	Cumene		Dimethylamine
	Ethylbenzene	2500	2-BUTANONE
	α-Methylstyrene	2501	ACROLEIN
	Napthalene	2503	MEVINPHOS (Phosdrin)
	Styrene	2504	TETRAETHYL PYROPHOSPHATE (TEPP)
	Toluene	2505	FURFURYL ALCOHOL
	Vinyl toluene	2506	ACETONE CYANOHYDRIN
	Xylene	2507	NITROGLYCERIN/EGDN
1550	NAPHTHAS	2508	ISOPHORONE
	Coal tar naphthas	2510	1-OCTANETHIOL
	Kerosene	2513	ETHYLENE CHLOROHYDRIN
	Mineral spirits	2514	ANISIDINE
	Petroleum ether	2515	DIAZOMETHANE
	Petroleum naphtha	2516	DICHLOROFLUOROMETHANE
	Rubber solvent	2517	PENTACHLOROETHANE
	Stoddard solvent	2518	HEXACHLORO-1,3-CYCLOPENTADIENE
1551	TURPENTINE	2519	ETHYL CHLORIDE
1600	CARBON DISULFIDE	2520	METHYL BROMIDE
1601	1,1-DICHLORO-1-NITROETHANE	2521	METHYL CYCLOHEXANONE
1602	DIOXANE	2522	NITROSAMINES
1603	ACETIC ACID		N-Nitrosodimethylamine
1604	ACRYLONITRILE		N-Nitrosodiethylamine
1606	ACETONITRILE		N-Nitrosodipropylamine
1608	GLYCIDOL		N-Nitrosodibutylamine
1609	TETRAHYDROFURAN		N-Nitrosomorpholine
1610	ETHYL ETHER		N-Nitrosopiperidine
1611	METHYLAL		N-Nitrosopyrrolidine
1612	PROPYLENE OXIDE	2523	1,3-CYCLOPENTADIENE
1613	PYRIDINE	2524	DIMETHYL SULFATE
1614	ETHYLENE OXIDE	2525	1-BUTANETHIOL
1615	METHYL tert-BUTYL ETHER (MTBE)	2526	NITROETHANE
2000	METHANOL	2527	NITROMETHANE
2001	CRESOLS	2528	2-NITROPROPANE
2002	AMINES, AROMATIC:	2529	FURFURAL
	Aniline	2530	BIPHENYL
	N,N-Dimethylaniline	2531	GLUTARALDEHYDE
	N,N-Dimethyl-p-toluidine	2533	TETRAETHYL LEAD (as Pb)
	p-Toluidine	2534	TETRAMETHYL LEAD (as Pb)
	2,4-Xylidine	2535	TOLUENE-2,4-DIISOCYANATE
2003	1,1,2,2-TETRABROMOETHANE	2536	VALERALDEHYDE
2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	2537	METHYL METHACRYLATE
2005	NITROBENZENES:	2538	ACETALDEHYDE (GC)
	4-Chloronitrobenzene	2539	ALDEHYDES, SCREENING
	Nitrobenzene	2540	DIETHYLENETRIAMINE,
	Nitrotoluene		ETHYLENEDIAMINE, &
2007	AMINOETHANOL COMPOUNDS:		TRIETHYLENETETRAMINE
	2-Aminoethanol		
	2-Dibutylaminoethanol		
	2-Diethylaminoethanol		

3rd Ed. Method Number	Substance
2541	FORMALDEHYDE (2-HMP)
3500	FORMALDEHYDE (chromotropic acid)
3501	FORMALDEHYDE (Girard T)
3502	PHENOL
3503	HYDRAZINE
3505	TETRAMETHYL THIOUREA
3506	ACETIC ANHYDRIDE
3507	ACETALDEHYDE (HPLC)
3508	METHYL ETHYL KETONE PEROXIDE
3509	AMINOETHANOL COMPOUNDS II
3700	BENZENE by portable GC
3701	TRICHLOROETHYLENE by portable GC
3702	ETHYLENE OXIDE by portable GC
4000	TOLUENE
5000	CARBON BLACK
5001	2,4-D and 2,4,5-T
5002	WARFARIN
5003	PARAQUAT
5004	HYDROQUINONE
5005	THIRAM
5006	CARBARYL (Sevin)
5007	ROTENONE
5008	PYRETHRUM
5009	BENZOYL PEROXIDE
5010	BROMOXYNIL AND BROMOXYNIL OCTANOATE
5011	ETHYLENE THIOUREA
5012	EPN, MALATHION, and PARATHION
5013	DYES, BENZIDINE, <i>o</i> -ANISIDINE, and <i>o</i> -TOLIDINE
5014	CHLORINATED TERPHENYL
5016	STRYCHNINE
5017	DIBUTYL PHOSPHATE
5018	2,4,7-TRINITROFLUOREN-9-ONE
5019	AZELAIC ACID
5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE
5021	<i>o</i> -TERPHENYL
5022	ARSENIC, ORGANO-: <i>p</i> -Aminophenylarsonic acid Dimethylarsenic acid Methylarsonic acid
5023	COAL TAR PITCH VOLATILES
5025	CHLORINATED DIPHENYL ETHER
5026	MINERAL OIL MIST
5027	RIBAVIRIN
5029	4,4'-METHYLENEDIANILINE (MDA)
5030	CYANURIC ACID
5031	ASPARTAME
5500	ETHYLENE GLYCOL
5502	ALDRIN and LINDANE
5503	POLYCHLOROBIPHENYLS
5504	ORGANOTIN COMPOUNDS (as Sn) Bibutyltin bis(isooctyl

3rd Ed. Method Number	Substance
	mercaptoacetate)
	Tetrabutyltin
	Tributyltin chloride
	Tricyclohexyltin hydroxide
5506	POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)
5508	KEPONE
5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE
5510	CHLORDANE
5512	PENTACHLOROPHENOL
5514	DEMETON
5515	POLYNUCLEAR AROMATIC HYDROCARBONS (GC)
5516	2,4- & 2,6-TOLUENEDIAMINE
5517	POLYCHLOROBENZENES Pentachlorobenzene 1,2,4,5-Tetrachlorobenzene 1,2,4-Trichlorobenzene
5518	NAPHTHYLAMINES 1-Naphthylamine 2-Naphthylamine
5519	ENDRIN
5521	ISOCYANATES
6001	ARSINE
6004	SULFUR DIOXIDE
6005	IODINE
6006	DIBORANE
6007	NICKEL CARBONYL
6008	STIBINE
6009	MERCURY
6010	HYDROGEN CYANIDE
6011	BROMINE AND CHLORINE
6402	PHOSPHORUS TRICHLORIDE
6600	NITROUS OXIDE
6601	OXYGEN
6700	NITROGEN DIOXIDE
6701	AMMONIA
7013	ALUMINUM
7020	CALCIUM
7024	CHROMIUM
7027	COBALT
7029	COPPER (fume and dust)
7030	ZINC
7048	CADMIUM
7056	BARIUM, soluble compounds
7074	TUNGSTEN (soluble and insoluble)
7082	LEAD (FLAME AAS)
7102	BERYLLIUM
7105	LEAD (FLAMELESS AAS)

3rd Ed. Method Number	Substance
7200	WELDING AND BRAZING FUME: Cadmium Chromium Copper Iron Manganese Nickel Silver Zinc
7300	ELEMENTS (ICP): Aluminum Phosphorus Arsenic Platinum Beryllium Selenium Cadmium Silver Calcium Sodium Chromium Tellurium Cobalt Thallium Copper Tin Iron Titanium Lead Tungsten Lithium Vanadium Magnesium Yttrium Manganese Zinc Molybdenum Zirconium Nickel
7400	FIBERS
7401	ALKALINE DUSTS
7402	ASBESTOS FIBERS
7500	SILICA, crystalline, respirable
7501	SILICA, AMORPHOUS
7502	ZINC OXIDE
7504	VANADIUM OXIDES
7505	LEAD SULFIDE
7506	BORON CARBIDE
7600	CHROMIUM HEXAVALENT (UV-VIS)
7601	SILICA, CRYSTALLINE (color)
7602	SILICA, CRYSTALLINE (IR)
7603	QUARTZ in coal mine dust
7604	CHROMIUM, HEXAVALENT (IC)
7900	ARSENIC (hydride AAS)
7901	ARSENIC TRIOXIDE (graphite AAS)
7902	FLUORIDES
7903	ACIDS, INORGANIC (IC): Hydrogen bromide Hydrogen chloride Hydrogen fluoride Nitric acid Phosphoric acid Sulfuric acid
7904	CYANIDES (aerosol and gas)
7905	PHOSPHORUS
8000	ALAD in blood

3rd Ed. Method Number	Substance
8001	PENTACHLOROPHENOL in blood
8002	2-BUTANONE, ETHANOL, and TOLUENE in blood
8003	LEAD in blood and urine
8004	POLYCHLORINATED BIPHENYLS in serum
8005	ELEMENTS in blood or tissue Antimony Molybdenum Cadmium Nickel Chromium Platinum Copper Silver Iron Strontium Lanthanum Thallium Lead Vanadium Lithium Zinc Magnesium Zirconium Manganese
8300	HIPPURIC ACID in urine (color)
8301	HIPPURIC and METHYL HIPURIC ACIDS in urine (HPLC)
8302	MBOCA in urine
8303	PENTACHLOROPHENOL in urine
8304	BENZIDINE in urine (TLC)
8305	PHENOL and p-CRESOL in urine
8306	BENZIDINE in urine (GC)
8308	FLUORIDE in urine
8310	METALS in urine Aluminum Molybdenum Barium Nickel Cadmium Platinum Chromium Silver Copper Strontium Iron Tin Lead Titanium Manganese Zinc
9000	CHRYSTILE ASBESTOS (bulk)
9002	ASBESTOS (bulk)

V. B. INDEX OF SECOND EDITION METHOD NUMBERS

(The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols. 1 through 7).

CRDT = Criteria Document

SDS = Sampling Data Sheet from NIOSH Publication 77-159

NRNR = Not revised and not recommended for use

NRIU = Not revised because of infrequent usage by NIOSH; the 2nd Ed. method is recommended for use at present.

<u>2nd Ed.</u>			<u>3rd Ed.</u>
Method	Vol.	<u>Substance</u>	<u>Method [Number]</u>
<u>Number</u>	<u>Number</u>		
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
			NITROGEN DIOXIDE [6700]
	109	1	Silica (XRD)
			SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)
			SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide
			see CARBON MONOXIDE [S340]
	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-ICP [7300]
	124	1	Selenium in urine
			NRIU
	125	1	Formaldehyde
			FORMALDEHYDE [2541, 3500, 3501]
	126	1	Hydrogen sulfide
			see HYDROGEN SULFIDE [P&CAM 296]
	127	1	Acetone
			KETONES I [1300]
	127	1	Benzene
			HYDROCARBONS, BP 36-126 °C [1500]; BENZENE [3700]; HYDROCARBONS, AROMATIC [1501]
	127	1	2-Butanone
			2-BUTANONE [2500]
	127	1	Carbon tetrachloride
			HYDROCARBONS, HALOGENATED [1003]
	127	1	Chloroform
			HYDROCARBONS, HALOGENATED [1003]
	127	1	p-Dioxane
			DIOXANE [1602]
	127	1	Ethylene dichloride
			HYDROCARBONS, HALOGENATED [1003]
	127	1	Methyl chloroform
			HYDROCARBONS, HALOGENATED [1003]
	127	1	Methylene chloride
			METHYLENE CHLORIDE [1005]
	127	1	Styrene
			HYDROCARBONS, AROMATIC [1501]
	127	1	Tetrachloroethylene
			HYDROCARBONS, HALOGENATED [1300]
	127	1	Toluene
			HYDROCARBONS, BP 35-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
	127	1	1,1,2-Trichloroethane
			HYDROCARBONS, HALOGENATED [1300]
	127	1	Trichloroethylene
			TRICHLOROETHYLENE [1022, 3701]
	127	1	Xylene
			HYDROCARBONS, AROMATIC [1501]
	139	1	Arsenic
			ARSENIC [7900] ARSENIC TRIOXIDE [7901]; ELEMENTS-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]

<u>2nd Ed.</u>			
Method	Vol.		
<u>Number</u>	<u>Number</u>	<u>Substance</u>	
P&CAM	145	1	Mercury in urine
	146	1	Sulfur dioxide
	152	1	Chromium
	153	1	Ozone
	154	1	Ozone
	158	1	Parathion
	159	1	Oil mist
	160	1	Sulfur dioxide
	163	1	Sulfur dioxide
	165	1	Mercury in urine
	167	1	Mercury in blood
	168	1	Aniline
	168	1	o-Toluidine
	168	1	2,4-Xylidine
	168	1	Dimethylaniline
	169	1	Chromic acid
	173	1,5	Aluminum
	173	1	Antimony
	173	1,5	Arsenic
	173	1,5	Barium
	173	1,5	Beryllium
	173	1,5	Bismuth
	173	1,5	Cadmium
	173	1,5	Calcium
	173	1,5	Chromium
	173	1,5	Cobalt
	173	1,5	Copper
	173	1,5	Indium
	173	1,5	Iron
	173	1,5	Lead
	173	1,5	Lithium
	173	1,5	Magnesium
	173	1,5	Manganese
	173	1,5	Molybdenum
	173	1,5	Nickel
	173	1,5	Palladium
	173	1,5	Potassium
	173	1,5	Rubidium
	173	1,5	Silicon
	173	1,5	Silver
	173	1,5	Sodium
	173	1,5	Strontium
	173	1,5	Tellurium
	173	1,5	Thallium
	173	1,5	Vanadium
	173	1,5	Zinc
	175	5	Mercury
	176	1	Tin
	177	1	Gallium
	178	1	Vinyl chloride
	179	1	Carbon disulfide

<u>3rd Ed.</u>	
<u>Method</u>	<u>[Number]</u>
MERCURY IN URINE	[8309]
SULFUR DIOXIDE	[6004]
CHROMIUM	[7024]; ELEMENTS-ICP [7300]
NRIU	
NRIU	
EPN, MALATHION and PARATHION	[5012]
MINERAL OIL MIST	[5026]
SULFUR DIOXIDE	[6004]
SULFUR DIOXIDE	[6004]
NRIU	
NRIU	
AMINES, AROMATIC	[2002]
AMINES, AROMATIC	[2002]
AMINES, AROMATIC	[2002]
AMINES, AROMATIC	[2002]
CHROMIUM, HEXAVALENT	[7600, 7604]
ALUMINUM	[7013]; ELEMENTS-ICP [7300]
NRIU	
ARSENIC	[7900]; ARSENIC TRIOXIDE [7901];
ELEMENTS-ICP	[7300]
NRIU	
BERYLLIUM	[7102]; ELEMENTS-ICP [7300]
NRIU	
CADMIUM	[7048]; ELEMENTS-ICP [7300]
CALCIUM	[7020]; ELEMENTS-ICP [7300]
CHROMIUM	[7024]; ELEMENTS-ICP [7300]
COBALT	[7027]; ELEMENTS-ICP [7300]
COPPER	[7029]; ELEMENTS-ICP [7300]
NRIU	
ELEMENTS-ICP	[7300]
LEAD	[7082]; ELEMENTS-ICP [7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
NRIU	
NRIU	
NRIU	
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ELEMENTS-ICP	[7300]
ZINC	[7030]; ELEMENTS-ICP [7300]
NRIU; see MERCURY	[6009]
ELEMENTS-ICP	[7300]
NRIU	
VINYL CHLORIDE	[1007]
CARBON DISULFIDE	[1600]

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Method	Vol.		
<u>Number</u>	<u>Number</u>	<u>Substance</u>	<u>Method [Number]</u>
P&CAM	180	1 Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	181	1 Selenium	ELEMENTS-ICP [7300]
	182	1 Chromium	CHROMIUM [7024]; CHROMIUM HEXAVALENT [7600, 7604]; ELEMENTS-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-ICP [7300]
	189	1 Antimony	NRIU
	190	1 Indium	NRIU
	191	1 Cadmium	CADMIUM [7048]; ELEMENTS-ICP [7300]
	191	1 Lead	LEAD [7082]; ELEMENTS-ICP [7300]
	192	1 Arsenic in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	193	1 Antimony in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	194	1 Indium in blood	NRIU
	195	1 Lead in blood	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	196	1 Arsenic in urine	NRIU
	197	1 Antimony in urine	NRIU
	198	1 Gallium in urine	NRIU
	199	1 Indium in urine	NRIU
	200	1 Lead in urine	LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	201	1 Methyl chloride	METHYL CHLORIDE [1001]
	202	1 Acrylonitrile	NRIU; see ACRYLONITRILE [1604]
	203	1 Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
	204	1 Sulfur dioxide	NRIU; see SULFUR DIOXIDE [6004]
	205	1 Ammonia	NRIU; see AMMONIA [6701]
	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
	211	1 Acrolein	ACROLEIN [2501]
	212	1 Fluorides	ACIDS, INORGANIC [7903]
	213	1 bis-(Chloromethyl)ether	NRIU
	214	1 Lead in air or blood	LEAD [7082]; ELEMENTS-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	COAL TAR PITCH VOLATILES [5023]
	219	1 Phosgene	NRIU
	220	1 Chloromethyl methyl ether	NRIU

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<u>Method</u>	<u>Vol.</u>	<u>Substance</u>	<u>Method [Number]</u>
<u>Number</u>	<u>Number</u>		
P&CAM	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 NITROGEN DIOXIDE [6700]
	232	1 Formic acid	NRIU
	234	1 Dyes, benzidine, o-tolidine	DYES [5013]
	235	1 Formaldehyde	NRIU; see FORMALDEHYDE [2541, 3500, 3501]
	236	1 MOCA	NRIU
	237	1 Tissue preparation	ELEMENTS IN BLOOD OR TISSUE [8005]
	239	1 Asbestos	FIBERS [7400]; ASBESTOS FIBERS [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)	CHRYSTOTILE ASBESTOS [9000]; ASBESTOS (bulk) [9002]
	246	1 3,3'-Dichlorobenzidine	BENZIDINE and 3,3'-DICHLOROBENZIDINE [5509]
	247	1 Methanol	METHANOL [2000]
	248	1 1,1-Dimethyl hydrazine	NRNR; see 1,1-DIMETHYL HYDRAZINE [S143]
	248	1 Hydrazine	HYDRAZINE [3503]
	248	1 Methyl hydrazine	NRNR; see MONOMETHYL HYDRAZINE [S149]
	248	1 Phenyl hydrazine	NRNR; see PHENYLHYDRAZINE [S160]
	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	VINYLDENE 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

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<u>Method</u>	<u>Vol.</u>	<u>Substance</u>	<u>Method [Number]</u>
<u>Number</u>	<u>Number</u>		
P&CAM	270	4	Aminoethanol compounds
	271	4	Tungsten
	272	4	2-Nitropropane
	273	4	4-Nitrobiphenyl
	276	4	Ethylenediamine
	277	4	Methylamine
	278	4	Vinyl acetate
	279	4	Beryllium in tissue
	280	4	N,N-Dimethyl-p-toluidine
	281	4	Ethylene thiourea
	282	4	Tetramethyl thiourea
	283	4	Oil mist
	284	4	4-Dimethylaminoazobenzene
	285	5	Crotonaldehyde
	286	5	Arsenic
	288	5	Beryllium
	290	5	Vanadium
	291	5	α -Chloroacetophenone
	294	5	Cyclopentadiene
	295	5	Dichlorovos
	296	6	Hydrogen sulfide
	297	5	Dibutyl phosphate
	298	5,7	Nickel
	299	5	Dimethylnitrosamine
	300	5	Ethylenimine (aziridine)
	301	5	Dimethyl sulfate
	302	5	Maleic anhydride
	303	5	Styrene oxide
	304	5	OCBM
	305	5	Phosphorus trichloride
	307	5	Hexachlorobutadiene
	308	5	Hexachlorocyclopentadiene
	309	5	Chrysotile asbestos (bulk)
	310	5	Hydrogen chloride
	313	6	Warfarin
	314	5	Trichloroisocyanuric acid
	315	5	Benzidine in urine
	316	6	Silica, amorphous
	317	6	Diethylcarbamoyl chloride
	318	6	Formaldehyde
	319	6	Chromium (VI)
	320	6	Arsenic, organo-
	321	6	1,2-Dichloropropane
	322	6	Trimellitic anhydride
	323	6	Titanium diboride
	324	6	Boron carbide
	325	6	Benzidine, o-anisidine, and o-tolidine dyes
			AMINOETHANOL COMPOUNDS [2007]; AMINOETHANOL COMPOUNDS II [3509] TUNGSTEN [7074]; ELEMENTS-ICP [7300] 2-NITROPROPANE [2528] NRIU DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE [2540] NRIU VINYL ACETATE [P&CAM 278] ELEMENTS IN BLOOD OR TISSUE [8005] AMINES, AROMATIC [2002] ETHYLENE THIOUREA [5011] TETRAMETHYL THIOUREA [3505] MINERAL OIL MIST [5026] NRIU CROTONALDEHYDE [P&CAM 285] ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300] BERYLLIUM [7102]; ELEMENTS-ICP [7300] ELEMENTS-ICP [7300] NRIU 1,3-CYCLOPENTADIENE [2523] NRIU HYDROGEN SULFIDE [P&CAM 296] DIBUTYL PHOSPHATE [5017] ELEMENTS-ICP [7300] NITROSAMINES [2522] ETHYLENIMINE [P&CAM 300] NRIU MALEIC ANHYDRIDE [P&CAM 302] NRIU NRIU PHOSPHORUS TRICHLORIDE [6402] HEXACHLOROBUTADIENE [P&CAM 307] HEXACHLORO-1,3-CYCLOPENTADIENE [2518] CHRYSOTILE ASBESTOS [9000] ACIDS, INORGANIC [7903] WARFARIN [5002] NRIU BENZIDINE IN URINE [8304, 8306] SILICA, AMORPHOUS [7501] NRIU FORMALDEHYDE [2541, 3500, 3501] CHROMIUM, HEXAVALENT [7600, 7604] ARSENIC, ORGANO- [5022] 1,2-DICHLOROPROPANE [1013] TRIMELLITIC ANHYDRIDE [P&CAM 322] NRIU BORON CARBIDE [7506] DYES [5013]

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Method	Vol.			
Number	Number	Substance	Method [Number]	
P&CAM	326	6	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]; ISOCYANATES [5521]
	327	6	Hippuric acid in urine	HIPPURIC ACID IN URINE [8300]
	328	6	ALAD in blood	ALAD IN BLOOD [8000]
	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	p-CHLOROPHENOL [P&CAM 337]
	338	7	Ethylene glycol	ETHYLENE GLYCOL [5500]
	339	7	Inorganic acids	ACIDS, INORGANIC [7903]
	340	7	Acetone cyanohydrin	ACETONE CYANOHYDRIN [2506]
	341	7	Diborane	DIBORANE [6006]
	342	7	MOCA in urine	MBOCA IN URINE [8302]
	343	7	Polychlorobenzenes	POLYCHLOROBENZENES [5517]
	344	7	Nickel carbonyl	NICKEL CARBONYL [6007]
	345	7	Welding and brazing fume	WELDING AND BRAZING FUME [7200]
	346	7	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	347	7	MDI	NRNR; see ISOCYANATES [5521]
	348	7	2,4,7-Trinitro-9-fluorenone	2,4,7-TRINITROFLUOREN-9-ONE [5018]
	349	7	Vinyl bromide	VINYL BROMIDE [1009]
	350	7	Lead sulfide	LEAD SULFIDE [7505]
	351	7	Elements by ICP	ELEMENTS-ICP [7300]
	354	7	Formaldehyde	FORMALDEHYDE [2541, 3500, 3501]
	355	--	Talc, respirable	TALC, RESPIRABLE [P&CAM 355]
	357	--	n-Octanethiol	1-OCTANETHIOL [2510]
	358	--	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	359	--	Benzidine in urine	BENZIDINE IN URINE [8304, 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	2-BUTANONE, 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	2-BUTANONE [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	2-BUTANONE [2500]
	S4	2	Hydrogen sulfide	NRIU
	S5	2	Manganese	ELEMENTS-ICP [7300]
	S7	5	p-Nitroaniline	p-NITROANILINE [S7]
	S8	2	Ozone	NRIU

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Method Number	Vol. Number	Substance	Method [Number]
S10	2	Camphor	KETONES II [1301]
S11	5	Chloroacetaldehyde	CHLOROACETALDEHYDE [S11]
S12	2	Mesityl oxide	KETONES II [1301]
S13	2	5-Methyl-3-heptanone	KETONES II [1301]
S15	2	Methyl (n-amyl) ketone	KETONES II [1301]
S16	2	Ethyl butyl ketone	KETONES II [1301]
S17	5	Furfural	FURFURAL [2529]
S18	2	Hexone (MIBK)	KETONES I [1300]
S19	2	Cyclohexanone	KETONES I [1300]
S20	2	2-Pentanone	KETONES I [1300]
S22	2	p-tert-Butyltoluene	HYDROCARBONS, AROMATIC [1501]
S23	2	Cumene	HYDROCARBONS, AROMATIC [1501]
S24	4	Diphenyl	BIPHENYL [2530]
S25	2	Vinyl toluene	HYDROCARBONS, AROMATIC [1501]
S26	2	α -Methyl styrene	HYDROCARBONS, AROMATIC [1501]
S27	2	Terphenyl	p-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 [S36]
S37	2	Methyl isoamyl acetate	ESTERS I [1450]
S38	2	Methyl acrylate	METHYL ACRYLATE [S38]
S39	2	Methyl cellosolve acetate	METHYL CELLOSOLVE ACETATE [S39]
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 [S42]
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 [S49]
S50	2	Isopropyl acetate	ISOPROPYL ACETATE [S50]
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]

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<u>Method</u>	<u>Vol.</u>	<u>Substance</u>	<u>Method [Number]</u>
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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 [S67]
S69	2	Dipropylene glycol methyl ether	NRIU
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	PHENYL ETHER [S72]
S73	2	Phenyl ether-biphenyl mixture	PHENYL ETHER-BIPHENYL MIXTURE [S73]
S74	2	Phenyl glycidyl ether	PHENYL GLYCIDYL ETHER [S74]
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	ISOPROPYL GLYCIDYL ETHER [S77]
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 [S81]
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	TRICHLOROFLUOROMETHANE [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	DIBROMODIFLUOROMETHANE [1012]
S108	2	Dichlorotetrafluoroethane	DICHLORODIFLUOROMETHANE and 1,2-DICHLORO- TETRAFLUOROETHANE [1018]
S109	2	Dichlorofluoromethane	DICHLOROFLUOROMETHANE [2516]
S110	2	1,2-Dichloroethylene	HALOGENATED HYDROCARBONS [1003]
S111	2	Dichlorodifluoromethane	DICHLORODIFLUOROMETHANE and 1,2-DICHLORO- TETRAFLUOROETHANE [1018]
S112	2	Chloroprene	CHLOROPRENE [1002]
S113	2	Chlorobromomethane	HYDROCARBONS, HALOGENATED [1003]

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<u>Method</u>	<u>Vol.</u>		<u>Method</u>	<u>[Number]</u>
<u>Number</u>	<u>Number</u>	<u>Substance</u>		
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	BROMOTRIFLUOROMETHANE	[1017]
S126	2	1,2,3-Trichloropropane	HYDROCARBONS, HALOGENATED	[1003]
S128	2	Trichloronaphthalene	NRU	
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	[1020]
S130	2	Tetrachloronaphthalene	NRU	
S131	2	1,1,1,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE	
S132	2	1,1,2,2-Tetrachlorodifluoroethane	and 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 [S138]; AMINES, ALIPHATIC	[2010]
S139	3	Diethylamine	AMINES, ALIPHATIC	[2010]
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS [2007];	
			AMINOETHANOL COMPOUNDS II [3509]	
S141	4	Diisopropylamine	see AMINES, ALIPHATIC	[2010]
S142	3	Dimethylamine	AMINES, ALIPHATIC	[2010]
S143	3	1,1-Dimethyl hydrazine	1,1-DIMETHYL HYDRAZINE	[S143]
S144	3	Ethylamine	NRU	
S146	3	N-Ethyl morpholine	NRU	
S147	3	Isopropylamine	NRU	
S148	6	Methylamine	NRU	
S149	3	Methyl hydrazine	MONOMETHYL HYDRAZINE	[S149]
S150	3	Morpholine	NRU	
S152	3	Triethylamine	NRU	
S153	3	Monomethylaniline	MONOMETHYLANILINE	[S153]
S155	3	Tetramethylsuccinonitrile	NRU	
S156	3	Acrylonitrile	ACRYLONITRILE	[1604]
S158	4	2-Aminopyridine	NRU	
S160	3	Phenyl hydrazine	PHENYLHYDRAZINE	[S160]
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	NRU	
S167	3	Cresol	CRESOLS	[2001]
S168	3	o-Toluidine	AMINES, AROMATIC	[2002]

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Method	Vol.		Method	Number
Number	Number	Substance	Method	Number
S169	4	Acetic acid	ACETIC ACID	[1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE	[3506]
S173	5	Formic acid	FORMIC ACID	[S173]
S174	3	Sulfuric acid	ACIDS, INORGANIC	[7903]
S175	3	Hydrogen bromide	ACIDS, INORGANIC	[7903]
S176	3	Hydrogen fluoride	FLUORIDES [7902]; ACIDS, INORGANIC	[7903]
S178	3	2-Hexanone	KETONES I	[1300]
S179	3	Phthalic anhydride	NRIU	
S181	4	Quinone	NRIU	
S182	5	Silver	ELEMENTS-ICP	[7300]
S183	3	Tin	ELEMENTS-ICP	[7300]
S185	3	Zirconium	ELEMENTS-ICP	[7300]
S186	3	Copper	COPPER [7029]; ELEMENTS-ICP	[7300]
S187	3	Tellurium hexafluoride	NRIU	
S188	3	Rhodium, fume and dust	NRIU	
S189	3	Rhodium, soluble	NRIU	
S190	3,7	Selenium	ELEMENTS-ICP	[7300]
S191	3,7	Platinum	ELEMENTS-ICP	[7300]
S193	3	Molybdenum	ELEMENTS-ICP	[7300]
S194	5	Hafnium	NRIU	
S198	3	Barium	BARIUM [7056]	
S199	4	Mercury	NRIU; see MERCURY	[6009]
S200	3	Yttrium	ELEMENTS-ICP	[7300]
S201	5	Tantalum	ELEMENTS-ICP	[7300]
S203	4	Cobalt	COBALT [7027]; ELEMENTS-ICP	[7300]
S204	3,7	Tellurium	ELEMENTS-ICP	[7300]
S205	3	Calcium	CALCIUM [7020]; ELEMENTS-ICP	[7300]
S206	3	Nickel	ELEMENTS-ICP	[7300]
S208	3	Tributyl phosphate	TRIBUTYL PHOSPHATE	[S208]
S209	3	Triorthocresyl phosphate	TRIORTHOCRESYL PHOSPHATE	[S209]
S210	3	Triphenyl phosphate	TRIPHENYL PHOSPHATE	[S210]
S211	5	1-Chloro-1-nitropropane	NRIU	
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE	[1601]
S214	4	Dinitrobenzene	NRIU	
S215	4	Dinitrotoluene	NRIU	
S216	3	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN	[2507]
S217	3	Nitrobenzene	NITROBENZENES	[2005]
S218	3	p-Nitrochlorobenzene	NITROBENZENES	[2005]
S219	4,6	Nitroethane	NITROETHANE	[2526]
S220	6	Nitromethane	NITROMETHANE	[2527]
S223	3	Nitrotoluene	NITROBENZENES	[2005]
S224	3	Tetranitromethane	NRIU	
S225	3	Tetryl	NRIU	
S227	3	n-Propyl nitrate	NRIU	
S228	4	Picric acid	NRIU	
S229	3	Arsine	ARSINE [6001]	
S237	3	Hydrazine	HYDRAZINE [3503]	
S243	4	Stibine	STIBINE [6008]	
S244	5	Sulfur hexafluoride	NRIU	
S245	6	Sulfuryl fluoride	SULFURYL FLUORIDE	[S245]
S246	3	Hydrogen chloride	ACIDS, INORGANIC	[7903]
S248	3	Carbon disulfide	CARBON DISULFIDE	[1600]
S249	3	Carbon dioxide	CARBON DIOXIDE	[S249]

<u>2nd Ed.</u>			<u>3rd Ed.</u>	
<u>Method</u>	<u>Vol.</u>	<u>Substance</u>	<u>Method</u>	<u>[Number]</u>
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	MINERAL OIL MIST	[5026]
S273	3	Carbaryl (Sevin)	CARBARYL	[5006]
S274	3	DDT	NRIU	
S275	3	Aldrin	ALDRIN and LINDANE	[5502]
S276	5	ANTU	NRIU	
S278	6	Chlordane	CHLORDANE	[5510]
S279	5	2,4-D	2,4-D and 2,4,5-T	[5001]
S280	6	Demeton	DEMETON	[5514]
S281	3	p-Dichlorobenzene	HYDROCARBONS, HALOGENATED	[1003]
S283	3	Dieldrin	NRIU	
S284	6	Endrin	ENDRIN	[5519]
S285	3	EPN	EPN, MALATHION, and PARATHION	[5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE	[1607, 3702]
S287	5	Heptachlor	NRIU	
S288	4	Hydrogen cyanide	CYANIDES	[7904]; HYDROGEN CYANIDE [6010]
S290	3	Lindane	ALDRIN and LINDANE	[5502]
S291	5	Methyl formate	NRIU	
S292	3	Naphthalene	HYDROCARBONS, AROMATIC	[1501]
S293	3	Nicotine	NRIU	
S294	5	Paraquat	PARAQUAT	[5003]
S295	3	Parathion	EPN, MALATHION, and PARATHION	[5012]
S296	6	Mevinphos (Phosdrin)	MEVINPHOS	[2503]
S297	4	Pentachlorophenol	PENTACHLOROPHENOL	[5512]
S298	6	Pyrethrum	PYRETHRUM	[5008]
S299	6	Ronnel	RONNEL	[S299]
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-ICP	[7300]
S308	4	Sulfur dioxide	SULFUR DIOXIDE	[6004]
S309	3	Arsenic	ARSENIC	[7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-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-ICP [7300]
S313	3	Cadmium fume	CADMIUM	[7048]; ELEMENTS-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]

<u>2nd Ed.</u>			<u>3rd Ed.</u>	
Method	Vol.		Method	[Number]
<u>Number</u>	<u>Number</u>	<u>Substance</u>		
S317	3	Chromium, hexavalent	CHROMIUM, HEXAVALENT [7600]; CHROMIUM	
			HEXAVALENT [7604]	
S318	3	Xylene	HYDROCARBONS, AROMATIC [1501]	
S319	4	Nitric acid	ACIDS, INORGANIC [7903]	
S320	4	Nitrogen dioxide	NITROGEN DIOXIDE [6700]	
S321	4	Nitric oxide	NITRIC OXIDE [5321]	
S323	3	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]	
S327	4	Formaldehyde (Girard T)	FORMALDEHYDE [2542, 3501, 3500]	
S328	3	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]	
S329	3	Methylene chloride	METHYLENE CHLORIDE [1005]	
S330	3	Phenol	PHENOL [3502]	
S332	5	Phosphine	PHOSPHINE [5332]	
S333	3	Phosphoric acid	ACIDS, INORGANIC [7903]	
S334	4	Phosphorus	PHOSPHORUS [7905]	
S335	3	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]	
S336	3	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]	
S339	3	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]	
S340	4	Carbon monoxide	CARBON MONOXIDE [5340]	
S341	3,7	Lead	LEAD [7082]; ELEMENTS-ICP [7300]	
S342	6	Mercury, organo	NRIU	
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500];	
			HYDROCARBONS, AROMATIC [1501]; TOLUENE	
			[4000]	
S345	5	Acetaldehyde	ACETALDEHYDE [3507]	
S346	4	Allyl glycidyl ether	ALLYL GLYCIDYL ETHER [5346]	
S347	5	Ammonia	AMMONIA [6701]	
S348	5	Ammonium sulfamate	NRIU	
S349	3	Boron oxide	NUISANCE DUST TOTAL [0500]	
S350	4	n-Butyl mercaptan	1-BUTANETHIOL [2525]	
S351	3	Chloroform	HYDROCARBONS, HALOGENATED [1003]	
S352	3	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]	
S354	4	Copper fume	COPPER [7029]; ELEMENTS-ICP [7300]	
S356	5	Crag herbicide I	NRIU	
S357	3	sym-Dichloroethyl ether	sym-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-ICP [7300]	
S367	3	Isophorone	ISOPHORONE [2508]	
S368	3	Isopropyl ether	ISOPROPYL ETHER [5368]	
S369	3	Magnesium oxide fume	ELEMENTS-ICP [7300]	
S370	3	Malathion	EPN, MALATHION, and PARATHION [5012]	
S371	4	Methoxychlor	NRIU	
S372	3	Methyl bromide	METHYL BROMIDE [2520]	
S374	4	Methylcyclohexanol	METHYL CYCLOHEXANOL [5374]	
S375	4	Methylcyclohexanone	METHYL CYCLOHEXANONE [2521]	
S376	3	Molybdenum	ELEMENTS-ICP [7300]	
S378	3	Octane	HYDROCARBONS, BP 36-126 °C [1500]	
S379	3	Pentane	HYDROCARBONS, BP 36-126 °C [1500]	

<u>2nd Ed.</u>		
Method	Vol.	
<u>Number</u>	<u>Number</u>	<u>Substance</u>
S380	3	Naphtha, petroleum
S381	4	Sodium hydroxide
S382	3	Stoddard solvent
S383	4	Tetraethyl lead
S384	4	Tetramethyl lead
S385	3	Titanium dioxide
S388	4	Vanadium
S391	3	Vanadium
CRDT	--	Fibrous glass
CRDT	--	Nitrous oxide
CRDT	--	Organotins
SDS29	--	Nuisance dust, respirable

<u>3rd Ed.</u>	
<u>Method [Number]</u>	
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NAPHTHAS [1550]	
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TETRAMETHYL LEAD [2534]	
NRIU	
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ELEMENTS-ICP [7300]	
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V. C. INDEX OF NAMES AND SYNONYMS

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*   Example: The references to method title and number are listed in the following manner:
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*   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)
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 Acetic acid 1,1-dimethylethyl ester, see ESTERS I, 1450
 Acetic acid ethenyl ester, see VINYL ACETATE, P&CAM 278
 Acetic acid ethylene glycol monoethyl ether ester, see ESTERS I, 1450
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 ACETONE CYANOHYDRIN, 2506
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 CAS #141-43-5, see AMINOETHANOL COMPOUNDS, 2007; AMINOETHANOL COMPOUNDS II, 3509
 CAS #141-78-6, see ETHYL ACETATE, S49
 CAS #141-79-7, see KETONES II, 1301
 CAS #142-82-5, see HYDROCARBONS, BP 36-126 °C, 1500
 CAS #142-92-7, see ESTERS I, 1450
 CAS #143-33-9, see CYANIDES, 7904
 CAS #143-50-0, see KEPONE, 5508
 CAS #151-50-4, see ETHYLENIMINE, P&CAM 300
 CAS #151-50-8, see CYANIDES, 7904
 CAS #191-24-2, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #192-97-2, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #193-39-5, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #205-99-2, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #206-44-0, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #207-08-9, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #208-96-8, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #218-01-9, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
 CAS #280-57-9, see TRIETHYLENETETRAMINE, 2540
 CAS #298-03-3, see DEMETON, 5514
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 CAS #302-01-2, see HYDRAZINE, 3503
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 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; (HPLC, ELECTROCHEMICAL AND UV), 5521
 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
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 CAS #621-64-7, see NITROSAMINES, 2522

CAS #626-38-0, see ESTERS I, 1450
 CAS #628-63-7, see ESTERS I, 1450
 CAS #628-96-6, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
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 CAS #823-40-5, see 2,6-TOLUENEDIAMINE, 5516
 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 NUISANCE DUST, TOTAL 0500; NUISANCE DUST, RESPIRABLE, 0600
 CAS #1305-62-0, see CALCIUM, 7020; ELEMENTS, 7300
 CAS #1305-78-8, see CALCIUM, 7020; ELEMENTS, 7300
 CAS #1306-19-0, see CADMIUM, 7048; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
 CAS #1307-96-6, see COBALT, 7027; ELEMENTS, 7300
 CAS #1308-38-9, see CHROMIUM, 7024; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
 CAS #1310-58-3, see ALKALINE DUSTS, 7401
 CAS #1310-65-2, see ALKALINE DUSTS, 7401
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 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; ELEMENTS, 7300
 CAS #1317-38-0, see COPPER, 7029
 CAS #1317-39-1, see COPPER, 7029; ELEMENTS, 7300
 CAS #1317-65-3, see NUISANCE DUST, TOTAL, 0500; NUISANCE DUST, RESPIRABLE, 0600;
 CALCIUM, 7020; ELEMENTS, 7300
 CAS #1327-53-3, see ARSENIC TRIOXIDE, 7901
 CAS #1330-20-7, see HYDROCARBONS, AROMATIC, 1501
 CAS #1331-22-2, see METHYLCYCLOHEXANONE, 2521
 CAS #1332-21-4, see FIBERS, 7400
 CAS #1333-82-0, see CHROMIUM, HEXAVALENT, 7600, 7609
 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 NUISANCE DUST, TOTAL, 0500; NUISANCE DUST, RESPIRABLE, 0600;
 ALUMINUM, 7013
 CAS #1461-22-9, see ORGANOTIN COMPOUNDS, 5504
 CAS #1461-25-2, see ORGANOTIN COMPOUNDS, 5504
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 CAS #1634-04-4, see METHYL tert-BUTYL ETHER, 1615
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 CAS #1689-99-2, see BROMOXYNIL and BROMOXYNIL OCTANOATE, 5010
 CAS #1910-42-5, see PARAQUAT, 5003
 CAS #1937-37-7, see DYES, 5013
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 CAS #2104-64-5, see EPN, MALATHION, and PARATHION, 5012
 CAS #2426-08-6, see n-BUTYL GLYCIDYL ETHER, 581
 CAS #2429-71-2, see DYES, 5013
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 CAS #2699-79-8, see SULFURYL FLUORIDE, 5245
 CAS #2782-91-4, see TETRAMETHYL THIOUREA, 3505
 CAS #4016-14-2, see ISOPROPYL GLYCIDYL ETHER, 577
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 CAS #7439-92-1, see LEAD, 7082, 7105; ELEMENTS, 7300; LEAD in blood and urine, 8003

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 CAS #7440-33-7, see TUNGSTEN, 7074; ELEMENTS, 7300
 CAS #7440-38-2, see ARSENIC, 7900
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 CAS #7440-41-7, see BERYLLIUM, 7102; ELEMENTS, 7300
 CAS #7440-43-9, see CADMIUM, 7048; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
 CAS #7440-47-3, see CHROMIUM, 7024; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
 CAS #7440-48-4, see COBALT, 7027; ELEMENTS, 7300
 CAS #7440-50-8, see COPPER, 7029; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
 CAS #7440-66-6, see ZINC, 7030; WELDING and BRAZING FUME, 7200; ELEMENTS, 7300
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 CAS #7647-01-0, see ACIDS, INORGANIC, 7903
 CAS #7664-38-2, see ACIDS, INORGANIC, 7903
 CAS #7664-39-3, see FLUORIDES, 7902; ACIDS, INORGANIC, 7903
 CAS #7664-41-7, see AMMONIA, 3505
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 CAS #7681-49-4, see FLUORIDES, 7902
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 CAS #7719-12-2, see PHOSPHORUS TRICHLORIDE, 6402
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 CAS #7783-06-4, see HYDROGEN SULFIDE P&CAM, 296
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 CAS #8030-30-6, see NAPHTHAS, 1550
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 CAS #8065-48-3, see DEMETON, 5514
 CAS #9004-34-6, see NUISANCE DUST, TOTAL, 0500; NUISANCE DUST, 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, S321
 CAS #10102-44-0, see NITROGEN DIOXIDE, 6700
 CAS #11097-69-1, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
 CAS #11126-42-4, see CHLORINATED TERPHENYL, 5014
 CAS #12001-28-4, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
 CAS #12001-29-5, see FIBERS, 7400; ASBESTOS FIBERS, 7402; CHRYSOTILE ASBESTOS (bulk), 9000;
 ASBESTOS (bulk), 9002
 CAS #12069-32-8, see BORON CARBIDE, 7506
 CAS #12172-73-5, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
 CAS #13121-70-5, see ORGANOTIN COMPOUNDS, 5504
 CAS #13463-39-3, see NICKEL CARBONYL, 6007
 CAS #13768-00-8, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
 CAS #13775-53-6, see FLUORIDES, 7902
 CAS #14464-46-1, see SILICA, CRYSTALLINE (XRD), 7500; (color), 7601; (IR), 7602
 CAS #14567-73-8, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
 CAS #14807-96-6, see TALC, RESPIRABLE, P&CAM 355
 CAS #14808-60-7, see SILICA, CRYSTALLINE (XRD), 7500; (color), 7601; (IR), 7602
 CAS #15468-32-3, see SILICA, CRYSTALLINE (XRD), 7500; (color), 7601; (IR), 7602

CAS #16071-86-6, see DYES, 5013
CAS #17068-78-9, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
CAS #19287-45-7, see DIBORANE, 6006
CAS #22839-47-0, see ASPARTAME, 5031
CAS #25013-15-4, see HYDROCARBONS, AROMATIC, 1501
CAS #25168-24-5, see ORGANOTIN COMPOUNDS, 5504
CAS #25639-42-3, see METHYLCYCLOHEXANOL, 5374
CAS #27323-18-8, see POLYCHLOROBIPHENYLS, 5503
CAS #29191-52-4, see ANISIDINE, 2514
CAS #36791-04-5, see RIBAVIRIN, 5027
CAS #53469-21-9, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
CAS #55720-99-5, see CHLORINATED DIPHENYL ETHER, 5025

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}(\text{O})\text{CH}_2$ ALLYL GLYCIDYL ETHER
2ND EDITION METHOD #: S346 DATE ISSUED: 01/21/77
M.W.: 114.16 CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS: PROPERTIES: liquid; d 0.962 g/mL;
BP 154 °C;
OSHA: TWA 5 ppm; STEL 10 ppm (skin) VP 0.267 kPa (2 mm Hg) @ 20 °C;
NIOSH: TWA 5 ppm; STEL 10 ppm (skin) vapor density (air=1) 3.32
ACGIH: TWA 5 ppm; STEL 10 ppm (skin)
(1 ppm = 4.67 mg/m³ @ NTP)

SYNONYMS: AGE, 1-allyloxy-2,3-epoxypropane; CAS #106-92-3

SAMPLER: Tenax-GC tube, 100 mg/50 mg

FLOW RATE: ≤0.2 L/min

RECOMMENDED VOLUME: ≤8 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of allyl glycidyl ether in diethyl ether in the range 65 to 270 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: current standards/recommended levels are included in measurement range

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
- [2] Levin, J.-O. et al., Solid Sorbent Sampling and Chromatographic Determination of Glycidyl Ethers in Air, J. Chromatogr., 454, 121-128, (1988).

Allyl Glycidyl Ether

Analyte:	Allyl Glycidyl Ether	Method No.: S346
Matrix:	Air	Range: 19-87 mg/cu m
OSHA Standard:	10 ppm (45 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on Tenax-GC desorption with ether, GC/FID	Validation Date: 1/21/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a Tenax-GC tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.
- 1.2 The Tenax-GC in each tube is transferred to a vial and the allyl glycidyl ether is desorbed with diethyl ether and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 19-87 mg/cu m at an atmospheric temperature of 17°C and atmospheric pressure of 752 mm Hg using a 3-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at 90% relative humidity when sampling a test atmosphere at 2X OSHA standard. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the Tenax-GC resin tube. This capacity can vary with the concentrations of analyte and other substances in the air. (See Section 5.2)

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 19-87 mg/cu m was 0.057. This value corresponds to a 2.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The sorbent tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When an atmosphere at 90% relative humidity containing 92 mg/cu m of allyl glycidyl ether was sampled at 0.8 liter per minute, 5% breakthrough was observed after 15 minutes (capacity = 12 liters or 1.1 mg). The sample size recommended is two-thirds the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard to minimize the probability of overloading the sampling tube and allow sampling with the 0.2 lpm sampling pump.
- 5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate of 0.2 liters per minute (Reference 11.3).

- 6.2 Resin tubes. Glass tube with both ends flame-sealed, 10-cm long with 8-mm O.D. and 6-mm I.D., containing 2 sections of 35/60 mesh Tenax-GC resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.
- 6.3 Gas chromatograph with a flame ionization detector.
- 6.4 Column, (20-ft x 1/8 in. stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Sample containers with Teflon-lined caps, 5-ml.
- 6.7 Microliter syringes. 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots for dilution.
- 6.8 Pipettes. 2-ml, delivery type.
- 6.9 Volumetric flasks: 1- and 10-ml or convenient sizes for making standard solutions and dilution of samples.
7. Reagents
 - 7.1 Methyl ether, anhydrous.
 - 7.2 Allyl glycidyl ether, 99%.
 - 7.3 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in ether.
 - 7.4 Hexane. This solvent is used to prepare the allyl glycidyl ether solutions for the desorption efficiency determination.
 - 7.5 Nitrogen, purified.
 - 7.6 Hydrogen, prepurified.
 - 7.7 Air, filtered compressed.
8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory

analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling tube series in the line; the tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples:

- 8.3.1 Immediately before sampling, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (3 mm).
- 8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The resin tube series should be placed in a vertical direction during sampling to minimize channeling through the resin.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.
- 8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate of 0.2 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The resin tube should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.
- 8.3.8 With each batch of 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 100-mg section is transferred to a 5-ml screw-capped sample container. The separating section of glass wool is removed and discarded.

The second 50-mg section is transferred to another container. These two sections are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of ether is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 ml of internal standard solution in ether.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 200°C injector temperature
5. 280°C manifold temperature (detector)
6. 150°C column temperature

A retention time of approximately 10.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The internal standard elutes between ether and the allyl glycidyl ether.

8.4.4 A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax-GC to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the equivalent 1X OSHA standard level.

- 8.5.2 Preparation of analytical samples for desorption efficiency determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of allyl glycidyl ether found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of allyl glycidyl ether found in the sample.

The analytical samples are prepared as follows: Tenax-GC, equivalent to the amount in the front section (100 mg), is measured into a 5-ml screw capped vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of allyl glycidyl ether in hexane (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10- μ l aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5X, 1X and 2X of the OSHA standard) were prepared by adding an amount of allyl glycidyl ether equivalent to that present in a 3-liter sample at the selected level. A stock solution containing 67.34 milligrams of allyl glycidyl ether per milliliter of hexane was prepared. One, 2 and 4 microliter aliquots of the solution were added to the Tenax-GC resin tubes to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the resin. A parallel blank tube was treated in the same manner except that no sample was added to it.

The procedure described can be used to prepare the analytical samples which are analyzed to determine desorption efficiency over the concentration range of interest.

- 8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 ml of ether with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of ether containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in μg recovered from the tube divided by the weight in μg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependant on the amount of allyl glycidyl ether collected on the resin. Plot the desorption efficiency versus weight of allyl glycidyl ether found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

9.1 Solutions of allyl glycidyl ether should be prepared over the appropriate concentration range in diethyl ether. The solutions should be prepared by addition of allyl glycidyl ether to 2.0 ml of diethyl ether in 5-ml vials. The allyl glycidyl ether may either be added neat using a microliter syringe or one may use the hexane solution described in Section 8.5.2. The concentration of standards can be expressed in terms of μg of allyl glycidyl ether per 2 ml of ether.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in $\mu\text{g}/2.0 \text{ ml}$.

For the internal standard method, use ether containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g}/2.0 \text{ ml}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in μg , corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 2.0 ml ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (100-mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (100-mg) blank section}$$

A similar procedure is followed for the backup (50-mg) section.

- 10.3 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

- 10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.
- 10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air samples (mm Hg)

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to μg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Allyl Glycidyl Ether, No. S346, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_5H_4NNH_2$

2-AMINOPYRIDINE

2ND EDITION METHOD #: S158

DATE ISSUED: 09/30/77

M.W.: 94.12

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; MP 58.1 °C;
BP 210.6 °C; VP low @ 20 °C;
vapor density (air=1) 3.2

OSHA: TWA 0.5 ppm

NIOSH: TWA 0.5 ppm

ACGIH: TWA 0.5 ppm

(1ppm = 3.85 mg/m³ @ NTP)

SYNONYMS: 2-pyridinamine; CAS #504-29-0

SAMPLER: Tenax GC tube, two tubes in series, front=35 mg, back=17 mg

FLOW RATE: 0.01 to 0.2 L/min.

RECOMMENDED VOLUME: 12 L

MEASUREMENT TECHNIQUE: gas chromatography, FID, thermal desorption

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples; media blanks, 6

RECOMMENDED MEASUREMENT OPTIONS: Carbowax 20M/0.8% KOH packed column or equivalent;
sorbent tubes and thermal desorption systems are now commercially
available

MEASUREMENT CALIBRATION: standard solutions of 2-aminopyridine in water in the range
2 to 70 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

2-Aminopyridine

Analyte:	2-Aminopyridine	Method No.: S158
Matrix:	Air	Range: 0.91-3.60 mg/cu m
OSHA Standard:	0.5 ppm (2 mg/cu m)	Precision ($\overline{CV}_T$): 0.061
Procedure:	Adsorption on Tenax GC, thermal desorption, GC	Validation Date: 9/30/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through two glass tubes in series containing Tenax GC to trap 2-aminopyridine vapors.
- 1.2 2-Aminopyridine is thermally desorbed from the Tenax GC, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.913-3.59 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 758 mm Hg, using a 12-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Tenax GC. This capacity may vary with the concentrations of 2-aminopyridine and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of 0.134 liter/minute and relative humidity of 84% and temperature of 25°C. The breakthrough test was conducted at a concentration of 4.10 mg/cu m.

3. Interferences

- 3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

- 3.2 Any compound that has the same retention time as 2-aminopyridine at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.913-3.59 mg/cu m was 0.061. This value corresponds to a 0.12 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.4% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.56 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of 2-aminopyridine found on the backup Tenax GC tube exceeds 25% of that found on the front tube, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.
- 6.2 Tenax GC Tubes: Separate front and backup sampling tubes are used in this method. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 13 cm long with a 6-mm O.D. and a 4-mm I.D. The front tube contains 35 mg of 35/60 mesh Tenax GC*, and the

* Tenax GC is a solid adsorbent manufactured by Enka, N.V., The Netherlands. It is available through most gas chromatographic equipment suppliers.

backup tube contains 17 mg. Tenax GC is held in place in the tube with 3-mm plugs of glass wool. The Tenax GC is placed within 4 cm of one end of the tube. The sample tube length may need to be adjusted to accommodate the GC inlet. The pressure drop across the tubes must be less than 10 mm of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use, each tube must be thermally desorbed for 3 minutes at 240°C using a nitrogen flow through the tube to rid the Tenax GC of any interfering substances. The front and backup tubes are joined together with a short piece of flexible tubing, and the ends of the sampling train are capped with plastic caps.

- 6.3 Thermal Desorption Apparatus: This apparatus is designed to use the gas chromatograph inlet heater as the source of heat for thermal desorption. The inlet should have an opening of at least 6 mm in diameter and be deep enough to allow the sample tube to be inserted. The apparatus consists of three parts as illustrated in Figures S158-1 and S158-2.

6.3.1 Sample Tube Holder (Figure S158-1A): This assembly is composed of a Swagelok Quick-Connect** stem (stainless steel #QC6-S-600) with a 3/8-in tube fitting on the opposite end. The fitting is drilled out to allow the 6-mm O.D. sample tube to pass through it. A Teflon tube (4 cm long with a 3/8-in O.D. and 5.5 mm I.D.) connects the stem to a 3/8 in to 1/4 in tube fitting reducer. Teflon ferrules are used with the connecting nuts to hold the Teflon tube. The sample tube is inserted through the stem and into the Teflon tube. Tightening the connecting nut to finger tightness secures the sample tube in place. The Teflon tube may have to be replaced after excessive use.

6.3.2 Gas Chromatograph Inlet Fitting (Figure S158-1B): This assembly consists of a Swagelok Quick-Connect** body (stainless steel #QC6-B-4PF) which has been rethreaded to fit onto the gas chromatograph injection port. The ball and spring in the body must be removed to allow the sample tube to pass through. This fitting replaces the septum nut. Other injector parts that interfere with insertion of the sample tube must be removed.

The inlet fitting is sealed to the injection port with a Teflon gasket.

6.3.3 Valves and Carrier Gas Lines (Figure S158-2): The flow of carrier gas is regulated by a system incorporating two needle valves and two 3-way valves. The carrier gas is split into two lines regulated by needle valves. When a sample tube is being thermally desorbed, the majority of carrier gas flows

**Patented by Crawford Fitting Company.

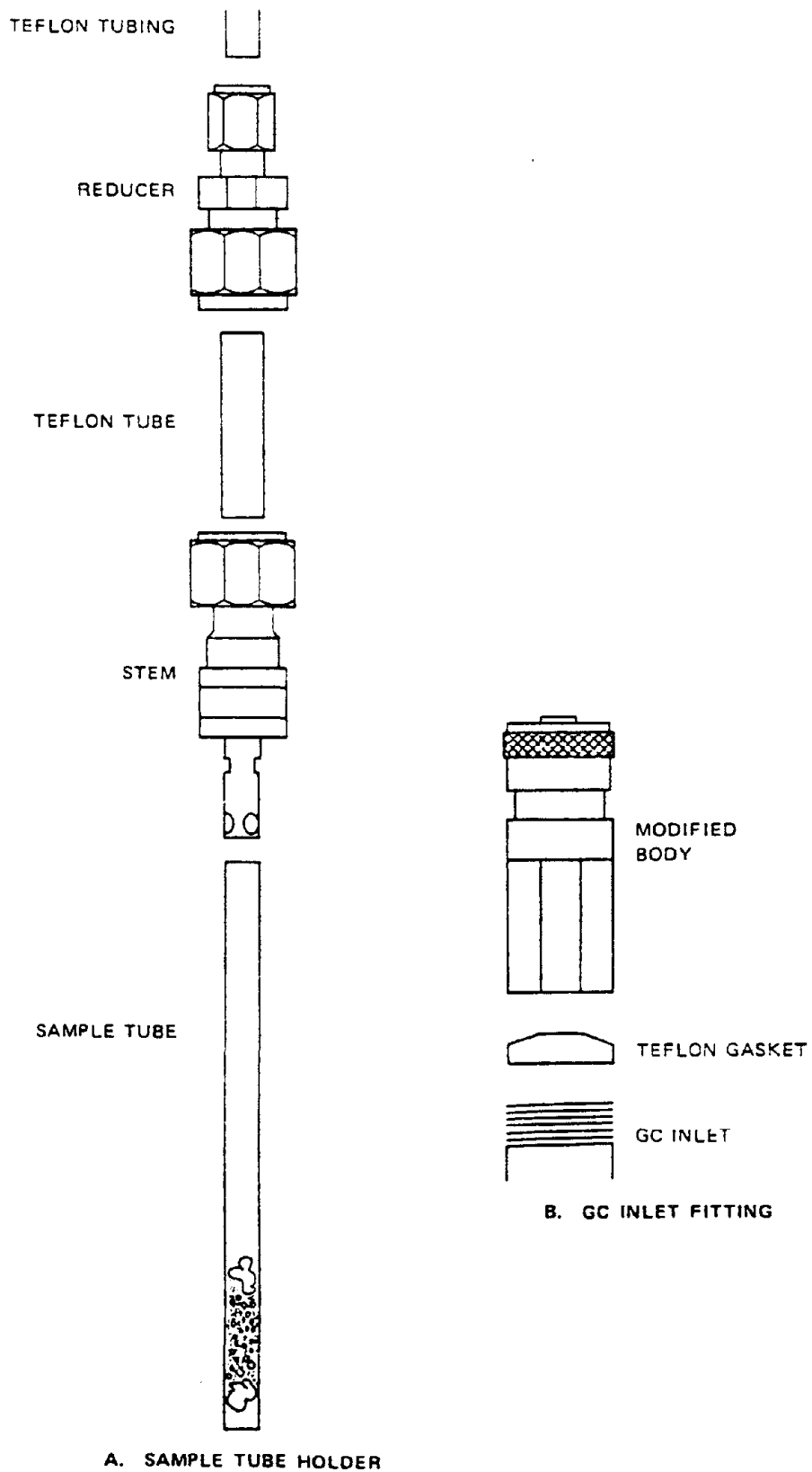


FIGURE S158-1

S158-4

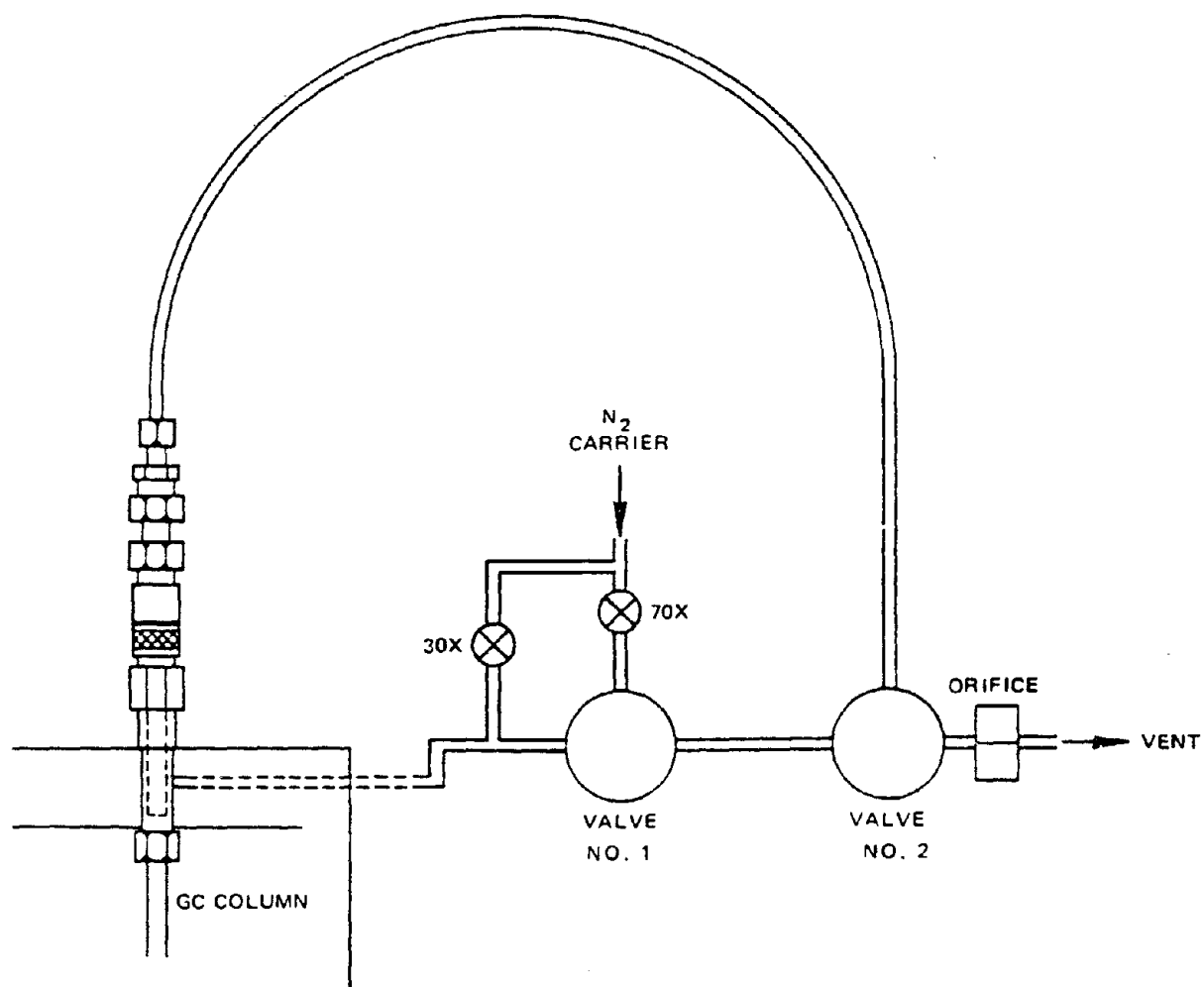


FIGURE S158-2 VALVES AND CARRIER GAS LINES

S158-5

through the sample tube. A minor flow enters at the normal GC inlet port to allow additional carrier gas to flow over the sample tube. Three-way valve #1 is used to split the carrier flow as described above or route the entire flow to the inlet port for normal use of the GC or injection of standards. Three-way valve #2 is used to vent the carrier flow when the sample tube holder is being loaded with a sample tube. It is also used to relieve pressure before disconnecting the desorber from the inlet after a sample is analyzed. A 0.02-in flc limiting orifice is placed at the valve #2 vent so that pressure is relieved slowly. Sudden changes in pressure may disrupt the gas chromatographic column packing or the sorbent in the sample tube. The thermal desorption assembly is connected to valve #2 with a 1/4-in O.D. Teflon tubing.

- 6.4 Gas Chromatograph equipped with a flame ionization detector.
- 6.5 Column (5-ft long x 1/4-in O.D. glass) packed with Carbopack B coated with 4% Carbowax 20M and 0.8% KOH.
- 6.6 An electronic integrator or some other suitable method of determining peak areas.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 2-Aminopyridine, reagent grade.
- 7.2 Nitrogen, purified.
- 7.3 Hydrogen, prepurified.
- 7.4 Air, filtered, compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

- 8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative Tenax GC tubes in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tubes. All tubes must be packed with Tenax GC from the same manufacturer's lot.
 - 8.3.2 The tube containing the smaller amount of Tenax GC is used as a backup tube and should be positioned nearer the sampling pump. Air should flow through the front tube before entering the backup tube.
 - 8.3.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tubes.
 - 8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.
 - 8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
 - 8.3.7 The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.
 - 8.3.8 With each batch of 10 samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.
 - 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
 - 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Tenax GC tubes. A minimum of 18 extra Tenax GC front and backup tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the caps from the ends of the sample tube. Wipe off the outside of the tube with clean lab wiper.

8.4.2 Thermal Desorption of Samples

1. Place auxiliary valves in position so that the carrier gas is split between the sample tube holder and the inlet (valve #1 dividing flow) and so that flow to sample tube holder is vented (valve #2 open to vent).
2. Load the sample tube holder by inserting the sample through the stem and just into the Teflon tube with connecting nut loose. Tighten the connecting nut to finger tightness to secure the sample tube in place. The sorbent material should be at the end opposite connecting nut.
3. Insert the sample tube into the gas chromatograph by joining the stem of the sample tube holder to the inlet of the gas chromatograph inlet fitting.
4. Turn the carrier gas valve #1 to allow the carrier to pass through the sample tube.
5. Allow the sample to thermally desorb for 3 minutes at inlet temperature of 240°C onto the head of the GC which is set at 125°C.
6. Program the column oven temperature from 125°C to 250°C at a rate of 25°C/minute.

8.4.3 GC Conditions. The typical operating conditions for the chromatograph are:

1. Thermal desorption mode - 60 ml/min nitrogen carrier gas flow through sample tube holder; 20 ml/min nitrogen carrier gas flow to inlet.
2. Standards injection mode - 80 ml/min nitrogen carrier gas flow to inlet.
3. Both modes - 50 ml/min hydrogen gas flow to detector; 500 ml/min (50 psig) air flow to detector.

- 8.4.4 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Tenax GC.
- 8.5.2 Tenax GC sample tubes containing 35 mg of Tenax GC from the same batch as that used in obtaining the samples are used to determine the desorption efficiency. A known amount of a water solution of 2-aminopyridine is injected directly onto the Tenax GC with a microliter syringe, and the tube is capped. The amount injected is equivalent to that present in a 12-liter air sample at the selected level. The solutions of 2-aminopyridine in water are prepared so that the amount injected is no more than 2.0 microliters. This is to minimize the effects of excess solvent on the GC column.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared and allowed to stand for at least overnight to assure complete adsorption of the 2-aminopyridine onto the Tenax GC. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are thermally desorbed and analyzed in exactly the same manner as the sampling tubes described in Section 8.4.

To inject standards into the GC, the normal septum injection port is installed and all of the carrier gas is allowed to flow through the normal inlet position (valve #1 combining flow). The same volume of 2-aminopyridine is injected directly into the GC injection port with the same syringe used in preparation of the samples.

To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. One microliter of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from

the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. No more than a 3% difference in area is to be expected between duplicate injections.

Standards are injected into the GC with column oven temperature set at 125°C.

Immediately after injection, the oven temperature is programmed to 225°C at a rate of 25°C/minute. Standards are analyzed before and after a set of samples is analyzed.

The desorption efficiency (D.E.) equals the average weight in μg recovered from the tube divided by the weight in μg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

The desorption efficiency is dependent on the amount of 2-aminopyridine collected on the Tenax GC. Plot the desorption efficiency versus weight of 2-aminopyridine found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms versus peak area. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

- 9.1 Prepare a stock standard solution containing 345 mg/ml of 2-aminopyridine in water.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in water. Prepare at least 5 working standards to cover the range of 2.3-70 micrograms/sample. This range is based on a 12-liter sample and 2-microliter injections.
- 9.3 Prepare a standard calibration curve by plotting micrograms 2-aminopyridine versus peak area.

10. Calculations

10.1 Read the weight, in μg , corresponding to each peak area from the standard curve.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample} = \mu\text{g found in front sample tube}$

$\mu\text{g blank} = \mu\text{g found in front blank tube}$

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

10.6 The concentration of 2-aminopyridine in the air sampled can be expressed in mg/cu m .

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of 2-aminopyridine = 94.1
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication # 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-03-00231-2.
- 11.2 Backup Data Report for 2-Aminopyridine, prepared under NIOSH Contract No. 210-76-0123.

FORMULA: C₁₄H₁₈N₂O₅ (see APPENDIX)

ASPARTAME

M.W.: 294.34

METHOD: 5031

ISSUED: 8/15/90

OSHA: no PEL

PROPERTIES: solid; MP 248-250 °C

NIOSH: no REL

ACGIH: no TLV

SYNONYMS: L-aspartyl-L-phenylalanine methyl ester; 3-amino-N-(alpha-carboxyphenethyl)-succinamic acid N-methyl ester; CAS #22839-47-0

SAMPLING	MEASUREMENT
SAMPLER: filter, 1- μ m, 37-mm PTFE	! TECHNIQUE: HPLC, UV DETECTION
FLOW RATE: 1.0 to 2.5 L/min.	! ANALYTE: Aspartame
VOL-MIN: 70 L @ 0.1 mg/m ³	! EXTRACTION: 2 mL of Eluent B. (See Reagents 8)
-MAX: 1200 L	! INJECTION: 25 μ L
SHIPMENT: Routine	! COLUMN: C ₁₈ , 10 μ m particle size
SAMPLE STABILITY: stable at least 30 days at 20 °C [1]	! DETECTOR: UV, 220 nm
FIELD BLANKS: 10% of samples	! MOBILE PHASE: 60% Eluent A/ 40% Eluent B, isocratic
MEDIA BLANKS: at least 3 per sample set	! CALIBRATION: standard solutions of Aspartame in Eluent B
ACCURACY	! RANGE: 7 to 800 μ g per sample [1]
RANGE STUDIED: not studied	! ESTIMATED LOD: 2 μ g per sample [1]
BIAS: not determined	! PRECISION (s _r): 0.026 @ 4.4 to 435 μ g per sample [1]
OVERALL PRECISION (s _r): not determined	!

APPLICABILITY: The working range is 0.07 to 8 mg/m³ for a 100-L air sample. The method has been used to analyze personal and area air samples during a health hazard evaluation at a commercial food packaging plant. [1]

INTERFERENCES: Food additives such as flavoring (artificial flavors), stabilizers (ascorbic acid) and food colors (FD&C yellow) collected along with Aspartame sampling, did not affect the analysis [1].

OTHER METHODS: An HPLC method for the analysis of aspartame in bulk has been reported. [2]

REAGENTS:

1. Aspartame™, 96% pure.
2. Water, deionized.
3. Acetonitrile, distilled in glass.
4. Methanol, distilled in glass.
5. 1-Heptanesulfonic acid sodium salt.
6. Monobasic sodium phosphate.
7. Phosphoric acid, reagent grade.
8. Eluent A: Add 2.062 g 1-heptanesulfonic acid sodium salt and 0.45 g monobasic potassium phosphate to 1.0 L deionized water and adjust pH to 2.5 with dilute phosphoric acid.*
9. Eluent B: Add 2.062 g 1-heptanesulfonic acid sodium salt to 1.0 L of 3:2 (v/v) acetonitrile-water, and adjust pH to 3.0 with dilute phosphoric acid.
10. Extraction solution: Same as eluent B.
11. Calibration stock solution: 5 mg/mL. Add 0.05 g Aspartame and dilute with 10 mL Eluent B.

EQUIPMENT:

1. Sampler: 1- μ m, 37-mm PTFE filter (Millipore FALP or equivalent) with a cellulose backup pad in a 37-mm polystyrene 2-piece cassette.
2. Personal sampling pump capable of 1 to 2.5 L/min, with flexible connecting tubing.
3. High-performance liquid chromatograph (HPLC) with UV detector, 220-nm, integrator and C₁₈ column (page 5031-1).
4. Sample filter apparatus: 0.45- μ m, PTFE.
5. Syringe, 10-mL, disposable.
6. Vials, glass, scintillation, 20-mL with PTFE-lined caps.
7. Syringes, microliter, readable to 0.1- μ L.
8. Pipets, various sizes.
9. Tweezers.
10. Ultrasonic water bath.
11. pH meter.

*see SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Phosphoric acid is extremely corrosive. Work with care in a hood using protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front and rear plugs immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately controlled flow rate between 1.0 and 2.5 L/min for a sample volume of 70 to 1200 L.
4. At the completion of sampling, replace both plugs and pack the sampler securely for shipment. Include appropriate number of blanks in the shipment.

SAMPLE PREPARATION:

5. Remove the PTFE filter with tweezers and transfer to a 20-mL scintillation vial. Discard the back-up pad. Add 2.0 mL extraction solution.
6. Agitate the samples for 1 hour in an ultrasonic water bath.
7. Filter the sample solution using a disposable syringe fitted with a 0.45- μ m PTFE filter into a clean vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
 - a. Add known amounts of calibration stock solutions to Eluent B, using serial dilutions as needed to obtain concentrations in the range of 1 to 400 μ g/mL.
 - b. Analyze with samples and blanks (steps 11 through 13).
 - c. Prepare a calibration graph (peak area vs. mass of Aspartame, μ g per sample).

9. Determine the recovery at least once for each lot of filters used for sampling in the range of interest. Prepare six filters at each of three levels plus three media blanks.
 - a. Add known amounts of Aspartame in methanol to the filters.
 - b. Cover filters. Allow to stand overnight for solvent evaporation.
 - c. Prepare samples (step 5 through 7), and analyze (step 11 through 13) together with standards.
 - d. Determine recovery (R). Construct a graph of R vs. μg Aspartame recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control

MEASUREMENT:

11. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 5031-1.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak areas.

CALCULATIONS:

14. Determine the mass, μg (corrected for recovery) of Aspartame found on the sample filter (W) and the average blank filter (B).
15. Calculate concentration (C) of Aspartame in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

A calibration curve constructed from nine standards over the range 0.5 to 463 $\mu\text{g/mL}$ Aspartame in solution was linear and indicated a limit of detection (LOD) of 2 μg per filter and a limit of quantitation (LOQ) of 7 μg per filter. Test samples were prepared by spiking filters with known amounts of Aspartame from a solution in methanol at levels between 4.4 μg per filter and 434 μg per filter. At each level, three filters were subjected to each of the following studies (Table 1):

- a. To evaluate extraction efficiency, the filters were analyzed immediately.
- b. To assess storage stability, spiked filters were stored for 1 month prior to analysis.
- c. To investigate the stability of the material on the filter during sampling, spiked filters were attached to a sampling pump and 1000 L of laboratory air was drawn through them at 2.5 L/min before analysis.

Table 1: Average Percent Recovery (n=3) of Aspartame

Spiked Amount (μg) (n=3)	Extraction Efficiency (%RSD)	Sampling Stability (%RSD)	Storage Stability @ 30 days (%RSD)
4.4	100 (2.3)	100 (1.3)	-
43.5	103 (4.8)	98 (3.1)	102 (2.7)
217	101 (1.8)	100 (2.4)	-
435	101 (1.3)	101 (1.3)	-

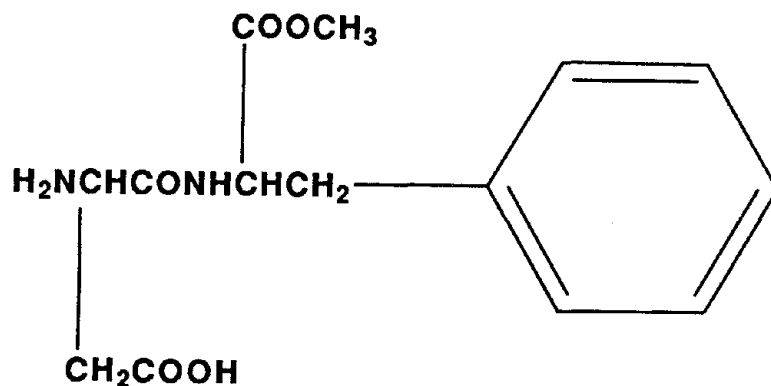
REFERENCES:

- [1] Albrecht, W., G. Burr, and C. Neumeister. Sampling and Analytical Method for Workplace Monitoring of Aspartame in Air., App. Ind. Hyg., 4:9 (1989).
- [2] Verzella, G., G. Bagnasco, and A. Mangia. Ion-Pair High-Performance Liquid Chromatographic Analysis of Aspartame and Related Products., J. Chromatogr., 349, 83 (1985).

METHOD WRITTEN BY: Charles Neumeister, NIOSH/DPSE

APPENDIX:

STRUCTURAL FORMULA FOR ASPARTAME



FORMULA: (1) Br₂; (2) Cl₂

BROMINE AND CHLORINE

M.W.: (1) 159.82; (2) 70.91

METHOD: 6011

ISSUED: 8/15/90

OSHA: (1) 0.1 ppm; STEL 0.3 ppm
(2) 0.5 ppm; STEL 1 ppm
NIOSH: (1) 0.1 ppm; STEL 0.3 ppm [1]
(2) 0.5 ppm; STEL 1 ppm
ACGIH: (1) 0.1 ppm; STEL 0.3 ppm
(2) 0.5 ppm; STEL 1 ppm
((1) 1 ppm = 6.53 mg/m³)
((2) 1 ppm = 2.90 mg/m³)

PROPERTIES: (1) liquid; d 3.119 g/mL @ 20 °C;
BP 58.78 °C; VP 23.3 kPa (175 mm Hg) @ 20 °C;
vapor density (air=1) 5.5

(2) gas; d 3.214 g/L at 0 °C;
BP -34.6 °C; vapor density (air=1) 2.5

SYNONYMS: (1) CAS #7726-95-6; (2) CAS #7782-50-5

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.45 µm, silver membrane)	! !TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION !
FLOW RATE: 0.3 to 1 L/min	!ANALYTE: bromide ion (Br ⁻), chloride ion (Cl ⁻) !
VOL-MIN: (1) 8 L @ 0.1 ppm (2) 2 L @ 0.5 ppm -MAX: (1) 360 L (2) 90 L	!EXTRACTION: 3 mL 6 mM Na ₂ S ₂ O ₃ , 10 min ! !INJECTION VOLUME: 50 µL !
SHIPMENT: routine	!COLUMNS: Dionex HPIC-AG4A guard, HPIC-AS4A separator, !MFC-1 precolumn, AMMS anion suppressor !
SAMPLE STABILITY: ≥30 days at 25 °C [2]	!DETECTOR SETTING: 10 µS full scale !
FIELD BLANKS: 10% of samples	!ELUENT: 0.25 mM NaHCO ₃ /4 mM Na ₂ CO ₃ / !0.78 mM p-cyanophenol, 2 mL/min !
	!CALIBRATION: standard solutions of Cl ⁻ and Br ⁻ !in deionized water !
RANGE STUDIED: (1) 0.07 to 1.42 mg/m ³ (72-L samples) (2) 0.35 to 6.77 mg/m ³ (15-L samples)	!RANGE: (1) 5 to 150 µg Br ⁻ per sample !(2) 2 to 50 µg Cl ⁻ per sample [2] !
BIAS: not significant [2]	!ESTIMATED LOD: (1) 1.6 µg Br ⁻ per sample !(2) 0.6 µg Cl ⁻ per sample [2] !
OVERALL PRECISION (s _p): (1) 0.069; (2) 0.075 [2]	!PRECISION (s _p): (1) 0.045 @ 5 to 100 µg per sample !(2) 0.067 @ 5.3 to 100 µg per !sample [2] !

APPLICABILITY: The working ranges for Br₂ and Cl₂ are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m³) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m³) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference up to a maximum of 15 µg per sample. HBr gives a positive interference as it is sampled continuously.

OTHER METHODS: P&CAM 209 (colorimetric) [3], OSHA Methods ID-101 [4] and ID-108 [5] are alternatives.

REAGENTS:

1. Sodium thiosulfate, reagent grade.
2. Water, deionized.
3. Extraction solution: 6 mM $\text{Na}_2\text{S}_2\text{O}_3$. Dissolve 0.474 g $\text{Na}_2\text{S}_2\text{O}_3$ in 500 mL deionized water.
4. Eluent: 0.25 M NaHCO_3 /4 M Na_2CO_3 0.78 M p-cyanophenol. Dissolve 0.041 g NaHCO_3 , 0.848 g Na_2CO_3 and 0.186 g p-cyanophenol in 2 L filtered deionized water.
5. Suppressor regenerant, 0.025 M H_2SO_4 . Dilute 2.8 mL conc. H_2SO_4 to 4 L with deionized water.*
6. Calibration stock solutions.
1 mg/mL (as anion).
(1) Dissolve 0.149 g KBr in 100 mL deionized water
(2) Dissolve 0.21 g KCl in 100 mL deionized water.

*see SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Assemble, in a 25-mm, carbon-filled polypropylene cassette with 50-mm extension (Nuclepore or Gelman):
 - a. Prefilter (Gelman 0.5 μm Zefluor or Nuclepore 0.4- μm Polyester) and porous plastic support pad (Nuclepore).
 - b. Silver membrane filter*, 0.45- μm (Nuclepore, Poretics, or equivalent) and porous plastic support pad (Nuclepore).
2. Personal sampling pump, 0.3 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph with Dionex MFC-1, HPIC-AG4A, HPIC-AS4A columns, AMMS anion micromembrane suppressor, conductivity detector and integrator (page 6011-1).
4. Bottles, 30-mL, wide mouth with screw caps, amber or opaque polyethylene.
5. Micropipettes, with disposable tips.
6. Volumetric flasks, 10- and 100-mL.
7. Repipet reagent dispensers, 0 to 10-mL.
8. Syringes, 10-mL, polyethylene, luer-tip.
9. Forceps.

*Silver membrane filters must be cleaned prior to use (see Appendix).

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive to skin, eyes, and mucous membranes. Wear protective clothing. Handle in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.3 and 1 L/min for a total sample size of 8 to 360 L for bromine or 2 to 90 L for chlorine.
4. Seal ends of sampler with plugs. Pack securely for shipping.

SAMPLE PREPARATION:

5. Under very dim or red light, open cassette and transfer the filter with forceps to amber bottle. Add 3 mL 6 M $\text{Na}_2\text{S}_2\text{O}_3$ and cap.
NOTE: Silver halides are photosensitive. Protect from light during transfer and desorption.
6. Allow samples to stand a minimum of 10 min with occasional swirling.
NOTE: Once desorbed, samples are no longer photosensitive.
7. Uncap the sample bottles and add 7 mL deionized water for a total solution volume of 10 mL.
8. Pour sample into 10-mL plastic syringe for manual injection or into autosampler vials.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards covering the range of 0.2 to 15 μg bromide and/or 0.05 to 5 μg chloride per mL of sample.
 - a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark with deionized water.
 - b. Prepare fresh working standards biweekly.
 - c. Analyze working standards together with samples and blanks (steps 11 through 13).
 - d. Prepare a calibration graph (peak height vs. concentration of anion)
10. Analyze three quality control spikes, three analyst spikes and media blanks to ensure that calibration graph is in control.

MEASUREMENT:

11. Set ion chromatograph according to manufacturer's instructions and to conditions given on page 6011-1.

NOTE: The use of an inline filter (5 μm) in the eluent stream prior to the chromatographic columns is recommended.

12. Inject 50- μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from syringe to ensure complete rinse of the sample loop.
13. Measure peak height. If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. From the calibration graph, determine the mass of Br^- or Cl^- in each sample, W (μg), and in the average blank, B (μg).
15. Calculate the concentration, C (mg/m^3), of Br_2 or Cl_2 in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{ mg}/\text{m}^3$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of Br_2 and Cl_2 at both high (80%) and low (20%) relative humidities [2]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m^3 for Br_2 and 0.354 to 6.77 mg/m^3 for Cl_2 . Overall recovery for Br_2 was 98.8% with total coefficient of variation, CV_T of 6.8%. Overall recovery for Cl_2 was 98.6% with total coefficient of variation, CV_T of 6.7%. Samples for Cl_2 were stable at least 30 days at 25 $^\circ\text{C}$ ($103 \pm 4\%$ Recovery) and up to 60 days at 5 $^\circ\text{C}$ ($101 \pm 3\%$ Recovery). The Br_2 samples were stable up to 60 days at 25 $^\circ\text{C}$ ($99.2 \pm 10.1\%$ Recovery).

REFERENCES:

- [1] NIOSH Testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H020, August 1, 1988.
- [2] Cassinelli, M.E. Development of a Solid Sorbent Monitoring Method for Chlorine and Bromine with Determination by Ion Chromatography, In review for submission to Appl. Occup. Environ. Hyg., June, 1990.
- [3] NIOSH Manual of Analytical Methods, 2nd ed.; Taylor, D.G., Ed.; U.S. Department of Health Education and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; DHEW (NIOSH) Publication No. 77-157, 1977.
- [4] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-101). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.
- [5] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-108). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

METHOD WRITTEN BY: Mary Ellen Cassinelli, NIOSH/DPSE

APPENDIX: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 mM $\text{Na}_2\text{S}_2\text{O}_3$.
2. Allow to stand for a minimum of 10 min with occasional swirling.
3. Discard solution and rinse thoroughly with deionized water. Allow the filters to stand in last rinse for a few minutes.
4. Remove filters from bottles and dry between layers of absorbent laboratory towels.
5. Store cleaned filters between paper disks in manufacturer's container. Filters are stable for at least 8 months.

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FORMULA: $C_4H_9NH_2$

n-BUTYLAMINE

2ND EDITION METHOD #: S138

DATE ISSUED: 07/08/77

M.W.: 73.14

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: C 5 ppm (skin)
NIOSH: C 5 ppm (skin)
ACGIH: C 5 ppm (skin)
(1ppm = 2.99 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.741 g/mL @ 20 °C;
BP 77.8 °C;
VP 11 kPa (82mm Hg) @ 20 °C;
vapor density (air=1) 2.5

SYNONYMS: 1-aminobutane; CAS #109-73-9

SAMPLER: solid sorbent tube, sulfuric acid-coated silica gel, 150 mg/75 mg

FLOW RATE: 1 L/min

RECOMMENDED VOLUME: 15 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: nitrogen-specific detector and a capillary column may be
used for improved sensitivity

MEASUREMENT CALIBRATION: standard solutions of n-butylamine in methanol/water in
the range 12 to 450 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 12 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH analytical sequence #4795 [1]

APPLICABILITY: the sulfuric acid can be added to the samples after they have arrived
in the laboratory for analysis. NIOSH Method 2010 for aliphatic amines
[2] may also be used for this amine

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/DPSE, Analytical Sequence #4975, Measurement Research Support Branch, Cincinnati, Ohio, NIOSH (unpublished, 1986).
- [2] NIOSH Manual of Analytical Methods, 3rd edition, Method No. 2010, 3rd Supplement, 1989.
- [3] LASL Progress Report, "Development of Air Monitoring Techniques Using Solid Sorbents," October 1 to March 31, 1976. NIOSH Contract 1A-75-31.
- [4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
- [5] Kuwata, K. et al. Determination of Trace Aliphatic Amines in Air, *Anal. Chem.*, 55 (13), 2199-2201 (1983).

n-Butylamine

Analyte:	n-Butylamine	Method No.:	S138
Matrix:	Air	Range:	8.1 - 35.5 mg/cu m
OSHA Standard:	5 ppm (15 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.092
Procedure:	Adsorption on sulfuric acid-treated silica gel, desorption with 50% methanol, GC/FID		
	Validation Date: 7/8/77		

1. Principle of the Method

- 1.1 A known volume of air is drawn through a sulfuric acid-treated silica gel tube to trap the organic vapors present. The sampling tube consists of front and backup adsorbing sections.
- 1.2 The treated silica gel in each section is transferred to a vial and the n-butylamine is desorbed with 50% methanol and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 8.09-35.5 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 769 mm Hg using a 15-liter sample volume. When an atmosphere at 90% relative humidity containing 34.4 mg/cu m of n-butylamine was sampled at 0.8 liter per minute, no breakthrough was observed after 240 minutes (190 liters); the capacity of the acid-treated silica gel is at least 6.5 mg under the conditions of these breakthrough studies.
- 2.2 This method is capable of measuring much smaller amounts of n-butylamine if the desorption efficiency is adequate. Desorption efficiency must be determined over the concentration range of interest.
- 2.3 The upper limit of the range of the method is dependent on the adsorptive capacity of the treated silica gel tube. This capacity can vary with the concentrations of analyte and other substances in the air.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

- 3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.09-35.5 mg/cu m was 0.0923. This value corresponds to a 1.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.6% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.
- 4.3 The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The sorbent tubes are analyzed by means of a quick, instrumental method.
- 5.2 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will effect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated with one tube only.
- 5.3 This method is limited to sampling atmospheres where the relative humidity is less than 60%.

6. Apparatus

6.1 Sampling Equipment

- 6.1.1 Sampling Pump. A calibrated personal sampling pump whose flow can be determined to within $\pm 5\%$ at the recommended flow rate of 1.0 liter per minute.

- 6.1.2 Sampling Tubes. The sampling tube consists of a glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D. and 4-mm I.D., containing two sections of 20/40 mesh sulfuric acid-treated silica gel. The front adsorbing section contains 150 mg of treated silica gel, the backup section, 75 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm Hg at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

The sulfuric acid-treated silica gel may be prepared as follows: A known amount of 20/40 mesh silica gel is placed in a drying oven at 125°C for one hour to activate the silica gel. The gel is then cooled to a constant weight, W. Reagent grade concentrated sulfuric acid is added dropwise by means of a disposable pipet to 1.25 W, or 25% by weight acid. A glass stirring rod is used to more evenly distribute the sulfuric acid. The treated silica gel is then returned to the drying oven for one hour with intermittent mixing. The treated silica gel should be stored in an airtight container.

- 6.1.3 Barometer.
- 6.1.4 Thermometer.
- 6.1.5 Stopwatch.
- 6.1.6 Hygrometer or other suitable device for measuring relative humidity.
- 6.2 Gas chromatograph with a flame ionization detector.
- 6.3 Column (6 ft x 1/4-in O.D. x 2-mm I.D. glass), packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Sample containers, 2-mL with Teflon-lined caps.
- 6.6 Microliter syringes, 10- and 500-microliter and other convenient sizes for making standards and for taking sample aliquots for dilution.
- 6.7 Pipets, 1-mL, delivery type.
- 6.8 Volumetric flasks, 1- and 10-mL, or convenient sizes for making standard solutions.

7. Reagents

- 7.1 50% methanol (50 parts methanol + 50 parts water).
- 7.2 1.0 N potassium hydroxide.
- 7.3 n-Butylamine, reagent grade.
- 7.4 n-Butyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 1.0 N potassium hydroxide.
- 7.5 Nitrogen, purified.
- 7.6 Hydrogen, prepurified.
- 7.7 Air, filtered, compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling tube in the line; the tube is described in Section 6.1.2. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples

Note: This method is limited to sampling atmospheres where relative humidity is less than 60%.

- 8.3.1 Immediately before sampling, break the two ends of the treated silica gel tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The section containing 75 mg of treated silica gel is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The treated silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the treated silica gel.
- 8.3.5 A sample size of 15 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The treated silica gel tube should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.
- 8.3.8 With each batch of ten samples, submit one treated silica gel tube which has been handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped, treated silica gel tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file in front of the first section of treated silica gel and broken open. The glass wool is removed and discarded. The treated silica gel in the front 150-mg section is transferred to a 2-mL screw-capped sample container. The separating section of glass wool is removed and discarded. The second 75-mg section is transferred to another container. These two sections are analyzed separately.
- 8.4.2 Desorption of Sample. Prior to analysis, 1 mL of 50% methanol is pipetted into each sample container. Desorption should be done for 2 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.
- 8.4.3 Neutralization of Sample. Withdraw a 500-microliter aliquot of the supernatant liquid and transfer to another 2-mL vial. Add 500 microliters of 1.0 N potassium hydroxide solution.

Note: If the internal standard method is used, add the internal standard solution made up in 1.0 N potassium hydroxide.

- 8.4.4 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 20 mL/min (60 psig) Nitrogen carrier gas flow

2. 30 mL/min (25 psig) Hydrogen gas flow to detector
3. 300 mL/min (60 psig) Air flow to detector
4. 175°C injector temperature
5. 195°C manifold temperature (detector)
6. 90°C column temperature

A retention time of approximately ten minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately 22 minutes.

8.4.5 A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.6 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as described in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of sulfuric acid-treated silica gel to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of treated silica gel used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the OSHA standard level.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of n-butylamine found in the samples.

The analytical samples are prepared as follows: 150 mg of acid-treated silica gel is measured into a 2-mL screw-capped vial. This treated silica gel must be from the same batch as that used in obtaining the samples. A known amount of a solution of n-butylamine in water (spiking solution) is injected directly into the treated silica gel by means of a microliter syringe. Adjust the

concentration of the spiking solution such that no more than a 10- μ L aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) were prepared by adding an amount of n-butylamine equivalent to that present in a 15-liter sample at the selected level. A stock solution containing 55.5 milligrams of n-butylamine per milliliter of water was prepared. Two, four and eight microliter aliquots of the solution were added to the treated silica gel tubes to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the treated silica gel. A parallel blank tube was treated in the same manner except that no sample was added to it.

- 8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 1 mL of 50% methanol. A 500-microliter aliquot is transferred and treated with 500 microliters 1.0 N potassium hydroxide. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare all sample solutions using 500 microliters of 1.0 N potassium hydroxide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in μ g recovered from the tube divided by the weight in μ g added to the tube, or

$$D.E. = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of n-butylamine collected on the treated silica gel. Plot the desorption efficiency versus weight of n-butylamine found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

- 9.1 Solutions of n-butylamine should be prepared over the appropriate concentration range. The spiking solution described in Section 8.5.2 should be used with the same syringe used in the preparation

of the samples. Two, four and eight microliter aliquots are added to 1 mL of 50% methanol in 2-mL vials. A 500-microliter aliquot of each standard solution is transferred to a second 2-mL vial and treated with 500 microliters 1.0 N potassium hydroxide.

- 9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area against sample concentration in $\mu\text{g/mL}$.

For the internal standard method, use 1.0 N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 65% of the concentration at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g/mL}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in μg , corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on μg per ml and the volume of sample injected is identical to the volume of the standards injected.

- 10.2 Corrections for the blank must be made for each sample:

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (150 mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (150 mg) blank section}$$

A similar procedure is followed for the backup (75 mg) section.

- 10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{DE}}$$

- 10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.
- 10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.3)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{73.14} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

73.14 = molecular weight of n-butylamine

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Back Data Report for n-Butylamine, No. S138, prepared under NIOSH Contract No. 210-76-0123.

S138-10

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_4H_9OCH_2CH(O)CH_2$	n-BUTYL GLYCIDYL ETHER
2ND EDITION METHOD #: S81	DATE ISSUED: 02/14/75
M.W.: 130.19	CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: liquid; d 0.910 g/mL @ 20 °C;
	BP 164-166 °C;
OSHA: TWA 25 ppm	VP 0.4 kPa (3 mm Hg) @ 20 °C;
NIOSH: C 5.6 ppm	vapor density (air=1) 4.5
ACGIH: TWA 25 ppm	
(1 ppm = 5.32 mg/m ³ @ NTP)	

SYNONYMS: 2,3-epoxypropyl butyl ether; CAS #2426-08-6

SAMPLER: charcoal tube, 100 mg/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: ≤10 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: fused silica capillary column, 300-m x 0.32-mm ID, 0.1-μm DB-5 [2] may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of n-butyl glycidyl ether in carbon disulfide in the range 0.01 to 5 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.01 mg per sample [2]

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: [3]

APPLICABILITY: method was not evaluated at current NIOSH REL

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402
 - [2] NIOSH Analytical Report, Analytical Sequence #5542, Measurement Research Support Branch (NIOSH, unpublished, 1985).
 - [3] NIOSH Health Hazard Evaluation report No. HETA 86-339-174 (NIOSH unpublished, 1986).
 - [4] Levin, J. O. et al., Solid Sorbent Sampling and Chromatographic Determination of Glycidyl Ethers in Air, J. Chromatogr., 454, 121-128, (1988).
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n-Butyl Glycidyl Ether

Analyte:	n-Butyl Glycidyl Ether	Method No.: S81
Matrix:	Air	Range: 133-542 mg/cu m
OSHA Standard:	50 ppm (270 mg/cu m)	Precision ($\overline{CV}_T$): 0.074
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 133-542 mg/cu m at an atmospheric temperature and pressure of 22°C and 767 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-810 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 8 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of n-butyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 23 mg of n-butyl glycidyl ether when

a test atmosphere containing 530 mg/cu m of n-butyl glycidyl ether in air was sampled at 0.183 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 133-542 mg/cu m was 0.074. This value corresponds to a 20 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 1.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 n-Butyl Glycidyl Ether, reagent grade.
- 7.3 Purified nitrogen.
- 7.4 Prepurified hydrogen.
- 7.5 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 180°C injector temperature
 5. 275°C manifold temperature (detector)
 6. 130°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: CO₂

CARBON DIOXIDE

2ND EDITION METHOD #: S249

DATE ISSUED: 10/29/76

M.W.: 44.01

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: gas; sp. gr. 1.02 (liquid);

BP -78.5 °C;

VP >101 kPa (>760 mm Hg) @ 20 °C

OSHA: TWA 10,000 ppm; STEL 30,000 ppm

NIOSH: TWA 5,000 ppm; STEL 30,000 ppm

ACGIH: TWA 5,000 ppm; STEL 30,000 ppm

(1 ppm = 1.8 mg/m³ @ NTP)

SYNONYMS: carbonic acid gas; carbonic anhydride; CAS #124-38-9

SAMPLER: gas sampling bags, five-layer

FLOW RATE: 0.05 L/min

RECOMMENDED VOLUME: 5 L

MEASUREMENT TECHNIQUE: gas chromatography, thermal conductivity detector

FIELD BLANKS OR MEDIA BLANKS: not required

RECOMMENDED MEASUREMENT OPTIONS: portable gas chromatograph with thermal conductivity detector may be used to monitor the workplace in near real-time.

MEASUREMENT CALIBRATION: bag standard made from a known volume of air and a known volume of a carbon dioxide standard in the range 1 to 11000 ppm

ESTIMATED LIMIT OF DETECTION (LOD): 1 ppm

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method is specific for carbon dioxide.

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] Kokkonen, P. Analysis of Coke Oven Gas by Gas Chromatography, *J. Chromatogr.* **391**(2), 435-441 (1987).

[3] Fuchs, P. Fast Analysis of Argon, Oxygen, Methane, Carbon Monoxide, Carbon Dioxide with Capillary Gas Chromatographs. *Anal. Chem.*, **333**(7), 738 (1989).

8/15/90

NIOSH Manual of Analytical Methods



Carbon Dioxide

Analyte:	Carbon Dioxide	Method No.:	S249
Matrix:	Air	Range:	2270-10000 ppm
OSHA Standard:	5000 ppm (9000 mg/cu m)	Precision ($\overline{CV}_T$):	0.014
Procedure:	Collection in gas sampling bag, GC with thermal conductivity detector	Validation Date:	10/29/76

1. Principle of the Method

- 1.1 A known volume of air is collected in a five-layer gas sampling bag by means of a low flow rate personal sampling pump capable of filling a bag.
- 1.2 The carbon dioxide content of the samples is determined by gas chromatography using a thermal conductivity detector.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 2270-9990 ppm at an atmospheric temperature of 20.5°C and atmospheric pressure of 757 mm Hg using a 3.5 liter sample volume. The working range of the method is estimated to be 500-15000 ppm, under the experimental conditions cited.
- 2.2 The upper limit of the range of the method and the absolute sensitivity have not been established.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2270-9990 ppm was 0.014. This value corresponds to a 69-ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples in bags are analyzed by means of a quick instrumental method.
- 5.2. One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.

6. Apparatus

- 6.1 Personal Sampling Pump. A personal sampling pump capable of filling a bag at approximately 0.05 liter per minute is required. This pump should be calibrated to within $\pm 5\%$.
- 6.2 Gas Sampling Bag. 5-liter capacity; only the five-layer sampling bags manufactured by Calibrated Instruments, Inc. (731 Saw Mill Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and storage for at least 7 days. The bag is fitted with a metal valve and hose bib. For the preparation of calibration standards in the laboratory, 5-liter Saran or Tedlar bags could be used.
- 6.3 Gas Chromatograph. The unit must be equipped with a thermal conductivity detector and a 5-milliliter gas sampling loop or equivalent. A portable unit with no column temperature control is adequate.
- 6.4 Column. (5-ft x 1/4-in stainless steel) packed with 80/100 mesh Porapak QS.
- 6.5 Area Integrator. An electronic integrator or some other suitable method for measuring peak areas.

6.6 Gas-tight syringes. 10-ml and other convenient sizes for making standards.

6.7 Calibrated Rotameters. convenient sizes for making standards.

7. Reagents

7.1 Carbon dioxide, 99% or higher purity.

7.2 Nitrogen, purified.

7.3 Helium, purified.

7.4 Air, filtered compressed.

8. Procedure

8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the closure mechanism and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with carbon dioxide-free air and evacuated. This procedure is repeated at least twice.

Bags may be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Observe for any discernable leaks and any volume changes or slackening of the bag, preferably over at least a one-hour period.

8.2 Calibration of Personal Pumps. Each personal pump should be calibrated to minimize errors associated with uncertainties in the sample volume collected. Although sample volume is not actually used in this determination, the pump should be calibrated to avoid over filling the bags; i.e., a maximum sampling time can be determined based on flow rate and sample volume which is approximately equal to 80% volume of bag.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, attach a small piece of Tygon or plastic tubing to the hose bib of the five-layer gas sampling bag.

8.3.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump.

8.3.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required.

8.3.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liters per minute or less, but not less than 0.01 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.6 The gas sampling bag should be labeled appropriately and sealed tightly.
- 8.3.7 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of getting punctured during shipping.

8.4 Analysis of Samples

- 8.4.1 GC Conditions. The typical operating conditions for the gas chromatograph are:

- 1. 100 ml/min (25 psig) helium carrier gas flow.
- 2. Ambient injector temperature.
- 3. 70°C manifold temperature (detector)
- 4. Ambient column temperature

A retention time of approximately 2 minutes is to be expected for the analyte under these conditions and at ambient temperatures of 20-25°C using the column recommended in Section 6.4. The carbon dioxide elutes after oxygen and nitrogen.

- 8.4.2 GC Analysis. The gas sampling bag is attached to the sample loop of the GC unit via a short piece of tubing. Open the closure valve of the gas sampling bag and fill the 5-ml sample loop by gently squeezing the sample bag. To allow the sample in the loop to attain atmospheric pressure, release the pressure applied to the sample bag just prior to turning the sample loop valve to inject the sample onto the column.

- 8.4.3 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve as discussed in Section 9.

9. Calibration and Standards

- 9.1 Completely evacuate a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Introduce 1.0 liter of filtered air via a septum into the bag; this can be done using a calibrated rotameter. Then add a known volume of carbon dioxide gas through a septum and add more air to a total accurately known volume of

between 3-4 liters. It is necessary to know accurately the volume of carbon dioxide added and the total volume of air to determine concentration in ppm. The concentration in ppm is equal to the volume of carbon dioxide divided by the sum of the volume of carbon dioxide and the volume of air.

- 9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ppm versus peak area. Corrections for the unknown carbon dioxide concentration in the filtered air must be made if necessary. The carbon dioxide correction factor can be determined by filling an evacuated bag with 3-4 liters of the filtered air used for preparing the calibration standards. This "blank" air is analyzed under the same conditions as the calibration standards and the samples. The "blank" area thus determined is subtracted from the peak area of each calibration standard. A calibration curve is established by plotting concentration in ppm versus corrected peak area.

Note: Calibration standards should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in detector response.

10. Calculations

- 10.1 Read the concentration in ppm, corresponding to each peak area from standard curve.
- 10.2 Another method of expressing concentration is mg/cu m (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{mg/cu m} = \text{ppm} \times \frac{\text{MW}}{24.45} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, KLCD. to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.2 Backup Data Report for Carbon Dioxide, prepared under NIOSH
Contract No. 210-76-0123.

S249-6

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: CO

CARBON MONOXIDE

2ND EDITION METHOD #: S340

DATE ISSUED: 04/07/72

M.W.: 28.01

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 35 ppm; C 200 ppm
NIOSH: TWA 35 ppm; C 200 ppm
ACGIH: TWA 50 ppm; STEL 400 ppm
(1 ppm = 1.15 mg/m³ @ NTP)

PROPERTIES: gas; poisonous;

sp. gr. (liquid) 0.79;
BP -102 °C;
VP >101 kPa (>760 mm Hg) @ 20 °C

SYNONYMS: CAS #630-08-0

SAMPLER: gas sampling bag, five-layer

FLOW RATE: 0.050 L/min

RECOMMENDED VOLUME: 5 L

MEASUREMENT TECHNIQUE: electrochemical analysis

FIELD BLANKS OR MEDIA BLANKS: not required

RECOMMENDED MEASUREMENT OPTIONS: portable electrochemical monitor may be used for direct measurements of the concentration of carbon monoxide

MEASUREMENT CALIBRATION: bag standards made from a known volume of air and a known volume of a carbon monoxide standard in the range 1 to 120 ppm

ESTIMATED LIMIT OF DETECTION (LOD): 0.4 ppm

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method is specific for carbon monoxide

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Goldbaum, L.R., P.H. Chase and N.T. Lappas. Determination of Carbon Monoxide in Blood by Gas Chromatography Using a Thermal Conductivity Detector. *J. Forensic Sci.*, **31**(2), 133-142 (1989).
- [3] Fuchs, P. Fast Analysis of Argon, Oxygen, Methane, Carbon Monoxide, Carbon Dioxide with Capillary Gas Chromatographs. *Anal. Chem.*, **333**(7), 738 (1989).
- [4] NIOSH Manual of Analytical Methods, 2nd Ed., V. 1, P&CAM 112, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157A (1977).

8/15/90

NIOSH Manual of Analytical Methods

Carbon Monoxide

Analyte:	Carbon Monoxide	Method No.: S340
Matrix:	Air	Range: 24.7 - 115.4 ppm
OSHA Standard:	50 ppm (57 mg/cu m)	Precision ($\overline{CV}_T$): 0.0146
Procedure:	Collection in gas sampling bag, electro-chemical analysis	Validation Date: 4/15/77

1. Principle of the Method

- 1.1 A known volume of air is collected in an evacuated five-layer gas sampling bag by means of a low flow rate personal sampling pump capable of filling a bag.
- 1.2 The carbon monoxide content of the samples is determined by electrochemical analysis.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 24.7-115.4 ppm at an atmospheric temperature of 23°C and atmospheric pressure of 750 mm Hg using a 3.5-liter sample volume. The working range of the method is estimated to be 5-120 ppm, under the experimental conditions cited.
- 2.2 The instrument specifications indicate that the response of the analyzer is linear up to 600 ppm. However, no studies have been conducted at this higher concentration range.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that several gaseous pollutants (e.g., NO, NO₂, SO₂) when in excess of 25 ppm can cause an interference equivalent to 1 ppm CO or greater (see Manufacturer's Specifications).
- 3.3 If the possibility of interference exists, the magnitude must be determined by further experimentation.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 24.7-115.4 ppm was 0.0146. This value corresponds to a 0.7-ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 There was no bias in the analytical method since the average recovery from the bags was 1.015. A collection efficiency of 100% is assumed since the collection medium is an impermeable gas sampling bag whose integrity and storage stability have been confirmed. By independent verification (Reference 11.2), the CO concentration obtained at the OSHA standard level using the overall sampling and analytical method was found to be 1% lower than the "true" concentration for a limited number of laboratory experiments. Any difference between the "found" and "true" concentration may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages

- 5.1 The sampling device is portable, and involves no liquids. Interferences are minimal but may not be easily corrected. The gas samples are analyzed by means of a quick and portable instrumental method.
- 5.2 One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.

6. Apparatus

- 6.1 Personal Sampling Pump. A personal sampling pump capable of filling a bag at approximately 0.05 liter per minute is required. This pump should be calibrated to within $\pm 5\%$.
- 6.2 Gas Sampling Bag. 5-liter capacity; only the five-layer sampling bags manufactured by Calibrated Instruments, Inc., (731 Saw Mill Road, Ardsley, New York 10502) were tested for sample collection and storage for at least 7 days. The bag is fitted with a metal valve and hose bib. For the preparation of calibration standards in the laboratory, 5-liter Saran or Tedlar bags could be used.

- 6.3 Ecolyzer - such as an electrochemical analyzer, Series 2000, manufactured by Energetics Science Inc., or equivalent.
- 6.4 Recorder. Any suitable laboratory recorder with a range of 2 V full scale.
- 6.5 Gas-tight syringes. 500 μ l and other convenient sizes for making standards.
- 6.6 Calibrated rotameters of convenient sizes for making standards.
- 7. Reagents
 - 7.1 Carbon monoxide, 99.5% or higher purity.
 - 7.2 Air, zero grade (<1 ppm CO).
- 8. Procedure
 - 8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the closure mechanism and bleeding out the air sample. The use of a vacuum pump is recommended, although this procedure can be carried out by manually flattening the bags. The bags are then flushed with carbon monoxide-free air and evacuated. This procedure is repeated at least twice.

Bags may be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Observe for any discernable leaks and any volume changes or slackening of the bag, preferably over at least a one-hour period.
 - 8.2 Calibration of Personal Pumps. Each personal pump should be calibrated to minimize errors associated with uncertainties in the sample volume collected. Although sample volume is not actually used in this determination, the pump should be calibrated to avoid over filling the bags; i.e., a maximum sampling time can be determined based on flow rate and sample volume which should be limited to approximately 80% of the volume-capacity of the bag (ca. 4 liters for a 5-liter bag).
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, attach a small piece of Tygon or plastic tubing to the hose bib of the five-layer gas sampling bag.
 - 8.3.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump.

- 8.3.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required.
- 8.3.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liters per minute or less, but not less than 0.01 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.6 The gas sampling bag should be labeled appropriately and sealed tightly.
- 8.3.7 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of puncture during shipping.

8.4 Analysis of Samples

- 8.4.1 Electrochemical Analysis. Open the valve and attach the gas sampling bag to the inlet port of the "Ecolyzer" via a short piece of tubing. Turn the instrument "on" and allow the sample to be automatically pumped through the electrochemical cell until an equilibrium is attained. Record the instrument output on a laboratory recorder. While the instrument's meter can be used to read the concentration directly, the recorder allows the measurement of concentrations slightly in excess of 100 ppm CO (full scale meter reading) since the calibration curve is linear up to about 120 ppm.
- 8.4.2 Measurement of Peak Height. The peak height is measured directly from the chart recorder. The peak height reaches its maximum (constant) level after pumping the sampling bag about 1.5 minutes. The results are read from a standard curve as discussed in Section 9.

9. Calibration and Standards

- 9.1 Completely evacuate a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Introduce a known volume (3-4 liters) of zero air via a septum into the bag. This can be done by using an air cylinder equipped with a calibrated rotameter. Then add a known volume of carbon monoxide gas through a septum using a gas tight syringe. Knead the bag to ensure complete mixing. It is necessary to know accurately the volume of carbon monoxide added

and the total volume of zero air to determine concentration in ppm. The concentration in ppm is equal to the volume of carbon monoxide divided by the volume of air (volume of CO is negligible).

- 9.2 The instrument is zeroed as per the manufacturer's instructions and then the instrument is calibrated using a span gas standard with a concentration of about 90-100 ppm CO. The instrument should be rezeroed and recalibrated with the span gas standard several times. Due to a slow, diffusion-limited return to zero, this process may take up to an hour. However, once completed, the instrument is stable within 1% full scale during at least 12 hours.

Note: Calibration standards should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in cell response.

10. Calculations

- 10.1 Read the concentration in ppm, corresponding to each peak area from standard curve.
- 10.2 Another method of expressing concentration is mg/cu m (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{mg/cu m} = \text{ppm} \times \frac{\text{MW}}{24.45} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Carbon Monoxide, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Parker, C.D., and Strong, R.B., "Evaluation of Portable Direct-Reading Carbon Monoxide Meters", prepared by Research Triangle Institute under NIOSH Contract No. HSM-99-73-1 (T.O. No. 1), September, 1974.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_{10}H_{10}Cl_8$ (avg.)

CHLORINATED CAMPHENE

2ND EDITION METHOD #: S67

DATE ISSUED: 02/14/75

M.W.: 414 (avg.)

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; MP 70 °C to 95 °C

OSHA: TWA 0.5 mg/m³; (skin) STEL 1 mg/m³

BP (760 mm Hg) decomposes;

NIOSH: TWA 0.5 mg/m³; (skin) STEL 1 mg/m³;

sp. gr. 1.63;

potential occup. carcinogen, LOQ 0.01 mg/m³ [1]

VP 0.03 to 0.05 kPa

ACGIH: TWA 0.5 mg/m³; (skin) STEL 1 mg/m³

(0.2 to 0.4 mm Hg) @ 20 °C

SYNONYMS: toxaphene; CAS #8001-35-2

SAMPLER: filter, 0.8-µm cellulose ester membrane

FLOW RATE: 1 L/min

RECOMMENDED VOLUME: 15 L

MEASUREMENT TECHNIQUE: gas chromatography, ECD (⁶³Ni)

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION:

standard solutions of chlorinated camphene in petroleum ether;

measure total peak area under the envelope of peaks

ESTIMATED LIMIT OF DETECTION (LOD): 0.14 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: [2]

APPLICABILITY: pesticides such as aldrin, parathion, dieldrin, DDT and its metabolites, and PCB's elute in the retention time band for chlorinated camphene

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH Testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, (August 1, 1988).

[2] NIOSH Health Hazard Technical Report #HETA-81-400-1242, NIOSH (unpublished, 1981).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Service Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

Chlorinated Camphene
(Toxaphene)

Analyte:	Chlorinated Camphene	Method No.: S67
Matrix:	Air	Range: 0.225-1.155 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$): 0.076
Procedure:	Filter collection, petroleum ether extraction, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.
- 1.2 The filter is transferred to a screw cap bottle and extracted with petroleum ether.
- 1.3 An aliquot of the extract is analyzed by electron capture gas chromatography.
- 1.4 The area of the sample peaks is determined and compared with areas obtained from standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.225-1.155 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 15-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m for 15-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for chlorinated camphene was considered to be 1.00 ± 0.01 when sampled for 15 minutes at 1 liter per minute from a test atmosphere containing 1 mg/cu m.

3. Interference

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method and a high electron capture cross section is an interference.
- 3.3 Chlorinated camphene is composed of a mixture of compounds, which chromatograph over a range of retention times. Any compound with an electron capture response in this retention time band will interfere. This would include pesticides, such as aldrin, parathion, dieldrin, DDT and its metabolites, and PCB's.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.225-1.155 mg/cu m was 0.076. This value corresponds to a standard deviation of 0.038 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which analytical method recovery corrections were made. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.
- 5.2 Other volatile compounds which give an electron capture response that are dispersed as particulates, are likely to interfere.

6. Apparatus

- 6.1 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
 - 6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm 3-piece cassette filter holder. Do not use tenite filter holders.
 - 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

- 6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.
- 6.3 Screw cap bottles. Within 1 hour after the sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping.
- 6.4 Gas chromatograph equipped with an electron capture detector.
- 6.5 Column (6-ft X 1/4-in glass) packed with 3% OV-1 on 100/120 mesh Gas-Chrom Q.
- 6.6 An electronic integrator or some other suitable method for measuring peak areas.
- 6.7 Sample extraction equipment.
 - 6.7.1 Beakers, 50 ml.
 - 6.7.2 Volumetric flasks, 10 ml.
 - 6.7.3 Tweezers and funnels.
- 6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.
- 6.9 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

- 7.1 Petroleum ether, 30° to 60°C boiling range, suitable for pesticide residue analysis, Mallinckrodt Nanograde[®] or equivalent.
- 7.2 Chlorinated camphene (toxaphene), reagent grade.
- 7.3 Purified nitrogen.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the screw cap bottles should be detergent washed and thoroughly rinsed with tap water and distilled water, dried, and then rinsed with petroleum ether.
- 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

- 8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.
- 8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.
- 8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.3.4 A sample size of 15 liters is recommended. Sample at a flow of 1.0 liter per minute. The flow rate should be known with an accuracy of $\pm 5\%$.
- 8.3.5 Turn the pump on and begin sample collection. 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, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.
- 8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.
- 8.3.8 Carefully record sample identity and all relevant sampling data.
- 8.3.9 With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. Care must be taken to handle the filter only with clean tweezers. Open the screw cap

bottle, remove the filter, and place the filter in a 50-ml beaker. Rinse the screw cap bottle with 3 ml petroleum ether. Pour the solvent into the beaker. Swirl the solvent over the filter, then decant the extract into a 10-ml volumetric flask. Repeat this process two more times. Dilute the combined extracts to a total of 10 ml with petroleum ether, stopper, and mix.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 250°C detector temperature
3. 230°C injector temperature
4. 205°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for determination. It is anticipated that the extraction scheme is dependent on operator skill and perhaps on the formulation used to disperse the analyte. Thus, it is necessary to determine the recovery of the analyte.

8.5.2 Procedure for determining analytical method recovery. A known amount of petroleum ether solution containing 1.74 mg/ml of chlorinated camphene, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. An amount of the analyte equivalent to that present in a 15 liter sample at the selected level is used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 10 ml of petroleum ether with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/10 ml petroleum ether, because samples are extracted in this amount of petroleum ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the electron capture response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak areas from the standard curve. No volume corrections are needed, because the standard curve is based on mg/10 ml of petroleum ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: CH₂ClCHO

CHLOROACETALDEHYDE

2ND EDITION METHOD #: S11

DATE ISSUED: 08/03/79

M.W.: 78.50

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 1.236 g/mL @ 20 °C;

OSHA: C 1 ppm

sp. gr. (40% aq. soln.) 1.19;

NIOSH: C 1 ppm

BP 85 °C; VP 13.3 kPa (100 mm Hg);

ACGIH: C 1 ppm

flash point 88 °C (closed cup)

(1 ppm = 3.21 mg/m³ @ NTP)

SYNONYMS: 2-chloroacetaldehyde; 2-chloroethanal; CAS #107-20-0

SAMPLER: silica gel tube, 520 mg/260 mg

FLOW RATE: 0.05 to 0.2 L/min; 0.2 L/min for 15 min
ceiling sample

RECOMMENDED VOLUME: 3 L

MEASUREMENT TECHNIQUE: gas chromatography, ECD

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION:

standard solutions of chloroacetaldehyde in 50% aqueous methanol
in the range 0.1 to 30 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.1 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: the method is not able to distinguish between chloroacetaldehyde, the
monomer hydrate, and dimer hydrate forms of chloroacetaldehyde

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] Williams, R.G., Determination of Chloroacetaldehyde in Air by Differential Pulse Polarography
Anal Chem., 54(12), 2121-2122 (1982).



Chloroacetaldehyde

Analyte:	Chloroacetaldehyde	Method No.: S11
Matrix:	Air	Range: 1.8-6.4 mg/cu m
OSHA Standard:	1 ppm (3 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$): 0.060
Procedure:	Collection on silica gel, desorption with 50% aqueous methanol, GC/ECD	Validation Date: 8/3/79

1. Synopsis

- 1.1 A known volume of air is drawn through a glass tube containing silica gel to trap chloroacetaldehyde vapor.
- 1.2 Chloroacetaldehyde is desorbed from the silica gel with 50% aqueous methanol and the resulting sample is analyzed by gas chromatography using electron capture detection.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 1.8-6.4 mg/cu m at an average atmospheric temperature of 20°C and atmospheric pressure of 761 mm Hg, using a 3-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent upon the adsorptive capacity of the silica gel. This capacity may vary with the concentrations of other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 520 mg of silica gel) reaches 5% of the concentration in the test gas mixture. In the validation study breakthrough occurred after sampling chloroacetaldehyde at 5.16 mg/cu m for 118 minutes at a sampling rate of approximately 0.2 liter/minute and relative humidity of 80% and temperature of 17°C.
- 2.3 Under the instrumental conditions used in the validation study, a sensitivity of approximately 300 mv sec/ μ g of chloroacetaldehyde was obtained.
- 2.4 The limit of detection is estimated to be 8 pg per injection or 100 ng chloroacetaldehyde per silica gel tube sample.

3. Interferences

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.
- 3.2 The method will not distinguish between chloroacetaldehyde, the monomer hydrate, and dimer hydrate forms of chloroacetaldehyde.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.8-6.4 mg/cu m was 0.060. This value corresponds to a 0.2 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.
- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit averaged 2% lower than the dynamically generated test concentrations ($n = 18$). The desorption efficiency was determined to be 0.996 for a collector loading of 4.74 micrograms. Storage stability studies on samples collected from a test atmosphere at a concentration of 3.13 mg/cu m (20% relative humidity) and 2.731 mg/cu m (80% relative humidity) indicated that collected samples are stable for at least 7 days. The mean of samples analyzed after 7 days were within 8.3% of the mean of samples analyzed immediately after collection at 20% relative humidity and within 5.3% at 80% relative humidity. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. The tubes are analyzed by means of a quick instrumental method.
- 5.2 A disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of chloroacetaldehyde found on the backup section of the silica gel tube exceeds 25% of that found on the front section, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within +5% at the recommended flow rate is needed. Each personal sampling pump must be calibrated with a representative sampling tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 6.2 Silica Gel Sampling Tubes. These tubes are available from SKC, Inc.* (Catalogue No. 226-15). The sorbent tube consists of a glass tube with both ends flame sealed (8 cm long with a 8-mm O.D. and 6-mm I.D.) packed with 20/40 mesh silica gel. Each tube contains two sections of silica gel, separated by a 2-mm portion of urethane foam. The front adsorbing section contains 520 mg of silica gel and the backup section contains 260 mg. The pressure drop must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute. Equivalent tubes from another supplier may be used.
- 6.3 Gas chromatograph, equipped with an electron capture detector.
- 6.4 Column (6-ft long x 1/4-in I.D. glass) packed with 60/80 mesh Chromosorb 101.
- 6.5 Area Integrator. An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Volumetric Flasks: 25 mL for desorbing samples and suitable sizes for preparing standard solutions.
- 6.7 Erlenmeyer Flasks: 250 mL.
- 6.8 Buret: 10 mL.
- 6.9 Pipets: 1, 5, 10 mL, and other suitable sizes for preparing standards.
- 6.10 Microliter Syringes: 10, 50, and 100 microliter.
- 6.11 Thermometer.
- 6.12 Manometer.
- 6.13 Stopwatch.

7. Reagents

Whenever possible, all reagents used should be ACS reagent grade or better.

- 7.1 Chloroacetaldehyde, 45% in water. This reagent must be standardized (see Section 9.1).

* SKC, Inc., Road 1 #395 Valley View Road, Eighty Four, PA 15330

- 7.2 Methanol.
- 7.3 Water, distilled, deionized.
- 7.4 50% Aqueous methanol. Add 250 mL of methanol into a 500-mL volumetric flask and dilute to the mark with distilled deionized water. Allow the solution to temperature equilibrate.
- 7.5 Stock standard chloroacetaldehyde solution (2.19 mg/mL). Dilute 1 mL of 45% chloroacetaldehyde (density 1.215 g/mL) to 250 mL with distilled deionized water. If the chloroacetaldehyde is assayed to be exactly 45.0%, this stock standard will be 2.19 mg/mL.
- 7.6 Hydrazine sulfate, 5.0%. Weigh 12.5 g of hydrazine sulfate and dilute to 250 mL with distilled deionized water.
- 7.7 Ferric ammonium sulfate solution, saturated, in 1 M HNO_3 .
- 7.8 Ammonium thiocyanate, 0.100 N. Accurately weigh 7.613 g ammonium thiocyanate and dilute to 1 liter with distilled deionized water.
- 7.9 Silver nitrate solution, 0.100 N. Accurately weigh 16.987 g silver nitrate. Dilute to 1 liter with distilled deionized water.
- 7.10 Nitric acid solution. Add 25 mL concentrated nitric acid to 25 mL of water and boil until colorless to remove nitrous acid.
- 7.11 Nitrobenzene.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling, break the ends of the sealed silica gel tube. All tubes must be packed with silica gel from the same manufacturer's lot.
 - 8.2.2 Attach the tubing from the sampling pump to the backup end (small section of silica gel) of the tube. Air being sampled should not pass through any hose or tubing before entering the sorbent tube.
 - 8.2.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.
 - 8.2.4 Set the flow rate as accurately as possible using the manufacturer's directions. A sample size of 3 liters is recommended. Sample at a flow rate between 0.05-0.2 liter/minute. For ceiling measurements, sample for 15 minutes at 0.2 liter/minute.

Record sampling time, flow rate, and type of sampling pump used.

- 8.2.5 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.2.6 The silica gel tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.2.7 With each batch or partial batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this tube as the blank.
- 8.2.8 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.2.9 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the silica gel tubes. A minimum of 18 extra silica gel tubes should be provided for desorption efficiency determinations.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Transfer the glass wool plug and front section of silica gel to a 25-mL volumetric flask. Transfer the backup sorbent section to another clean flask. Label each appropriately for separate analysis.
- 8.3.2 Desorption. Add 50% aqueous methanol, diluting to the 25-mL mark. Stopper the flasks. Shake the mixtures occasionally over a 30-minute period. Samples should be analyzed within one day.
- 8.3.3 Gas Chromatographic Conditions. The typical operating conditions are:
 - 5% Argon/methane flow rate, 50 mL/minute
 - Injection port temperature, 250°C
 - Detector temperature, 300°C
 - Column temperature, 150°C, isothermal
- 8.3.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with distilled water several times to wet the barrel and plunger.

Three microliters of distilled water are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 2.0 microliters to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

A retention time of approximately 5 minutes is to be expected for chloroacetaldehyde under the above conditions, using the column recommended in Section 6.4.

- 8.3.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

- 8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of silica gel.
- 8.4.2 Silica gel sample tubes, as described in Section 6.2, are used to determine desorption efficiency. The silica gel must be from the same batch as that used in obtaining the collected samples. Desorption efficiency samples are prepared by injecting an appropriate amount of a 2.19 mg/mL solution of chloroacetaldehyde in water (Section 7.5) directly into the front section of silica gel to represent 3-liter air samples at 0.5X, 1X, and 2X the OSHA standard.

Six tubes at each of three levels are prepared in this manner and allowed to stand at least overnight to ensure complete adsorption of the aldehyde onto the silica gel. Standards are prepared by spiking identical amounts of the analyte into 25 mL of 50% methanol. The samples and a parallel blank tube should be desorbed and analyzed in exactly the same manner as described in Section 8.3.

- 8.4.3 The desorption efficiency (D.E.) equals the average weight in μg recovered from the tube divided by the weight in μg added to the tube, or

$$\text{D.E.} = \frac{\text{Average weight recovered } (\mu\text{g}) - \text{Blank } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

The desorption efficiency may be dependent on the amount of chloroacetaldehyde collected on the silica gel. Plot the desorption efficiency versus weight of chloroacetaldehyde found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

- 9.1 The calibration curve is prepared using standardized 45% chloroacetaldehyde solution. The following procedure is used to standardize the 45% solution (Reference 11.3). The method is based upon the reaction of chloroacetaldehyde with hydrazine sulfate to convert bound chlorine to chloride ion. A measured excess of standard silver nitrate solution is added to the sample and the excess silver is titrated by a standard solution of thiocyanate, using ferric ion as an indicator to show when excess thiocyanate is present.
- 9.1.1 Weigh 2 mL of the 45% chloroacetaldehyde solution (Section 7.1) into a small stoppered flask. Transfer to a 250-mL erlenmeyer flask and dilute to the mark with distilled deionized water.
- 9.1.2 Pipet 5-mL aliquots of the above solution into 2 separate 250-mL erlenmeyer flasks. Add 10 mL of 2.5% hydrazine sulfate to one of the flasks and allow to sit 10 minutes with occasional swirling. The other flask will serve as a blank and will determine any free halide ion already present.
- 9.1.3 Add 10 mL of 0.100 N silver nitrate solution, 5 mL of the nitric acid solution, and 2 mL ferric ammonium sulfate solution to each flask. Swirl and then add 2 mL nitrobenzene. The nitrobenzene forms an oily coating on the particles of precipitated silver chloride and prevents their undesired reaction with the thiocyanate ion.
- 9.1.4 Titrate each flask with 0.1 N ammonium thiocyanate to a faint orange - brown color change which is permanent on shaking. The endpoint color is due to the formation of the complex $\text{Fe}(\text{SCN})_6^{-3}$ ion.
- 9.1.5 Compute the volume of standard silver solution in excess of that used by the liberated chloride.

$$V_S = V_T \times \frac{N_T}{N_S}$$

where:

- V_S = volume of silver solution in excess
- V_T = volume of standard thiocyanate solution titrated
- N_T = normality of NH_4SCN solution
- N_S = normality of AgNO_3 solution

9.1.6 Compute the net volume of silver solution required for the precipitation of the liberated chloride.

$$V_N = 10 - V_S$$

where:

- V_N = net volume of silver solution used in precipitation of chloride (in mL)
- V_S = volume of silver solution in excess (in mL) (computed in Section 9.1.5)

9.1.7 Corrections for the blank must be made for each sample.

$$mL = V_N - V_N (\text{blank})$$

where:

- V_N = milliliters of silver solution required for precipitation of chloride in sample (computed in Section 9.1.6).

- $V_N (\text{blank})$ = milliliters of silver solution required for precipitation of any chloride in blank. The blank is the flask to which no hydrazine sulfate is added.

9.1.8 Calculate the weight of chloroacetaldehyde present in the aliquot. One milliliter of 0.100 N silver nitrate solution is equivalent to 0.00785 g chloroacetaldehyde. This factor must be adjusted or determined accordingly on the basis of the exact normality of the standard silver nitrate solution.

9.1.9 The concentration of chloroacetaldehyde in the initial solution can be expressed in percent.

$$\% \text{ chloroacetaldehyde} = \frac{W_C}{W_S} \times \frac{250}{5} \times 100$$

where:

- W_C = weight of chloroacetaldehyde present in the aliquot (computed in Section 9.1.8)
- W_S = weight of the initial 2-mL aliquot

- 9.2 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for chloroacetaldehyde, is prepared and analyzed under the same chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in $\mu\text{g}/25\text{ mL}$ versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the electron capture detector response.
- 9.3 From the stock standard solution (Section 7.5) appropriate aliquots are withdrawn and dilutions are made with 50% aqueous methanol. Prepare at least 6 working standards to cover the range of 0.948-28.4 micrograms/25 mL. This range is based on a 15-minute (3-liter) sample at the ceiling standard.
- 9.4 Prepare a standard calibration curve by plotting micrograms/25 mL chloroacetaldehyde versus peak area.

10. Calculations

- 10.1 Read the weight, in μg , corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on $\mu\text{g}/25\text{ mL}$ chloroacetaldehyde and the volume of sample injected is identical to the volume of the standards injected.

- 10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\begin{aligned}\mu\text{g sample} &= \mu\text{g found in front section of the sample tube} \\ \mu\text{g blank} &= \mu\text{g found in front section of the blank tube}\end{aligned}$$

A similar procedure is followed for the backup section.

- 10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.4.3) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

- 10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

- f = flow rate sampled (liters/min)
- t = sampling time (min)
- P₁ = pressure during calibration of sampling pump (mm Hg)
- P₂ = pressure of air sampled (mm Hg)
- T₁ = temperature during calibration of sampling pump (°K)
- T₂ = temperature of air sampled (°K)

10.6 The concentration of chloroacetaldehyde in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

- P = pressure (mm Hg) of air sampled
- T = temperature (°C) of air sampled
- 24.45 = molar volume (liters/mole) at 25°C and 760 mm Hg
- M.W. = molecular weight (g/mole) of chloroacetaldehyde
- 760 = standard pressure (mm Hg)
- 298 = standard temperature (°K)

11. References

- 11.1 Documentation of the NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Backup Data Report No. S11 for Chloroacetaldehyde, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Satanovskaya, Ts. I. and B. G. Yasnitskii, "Quantitative Analysis of Chloroacetaldehyde," Metody Poluch Khim. Reaktiv Prep., No. 21, (1970), 118-20.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: C₆H₅ClO

p-CHLOROPHENOL

2ND EDITION METHOD #: P&CAM 337

DATE ISSUED: 09/19/80

M.W.: 128.56

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: crystals; d 1.224 g/mL @ 20 °C;

MP 43.2 - 43.7 °C; BP 220 °C;

OSHA: no PEL

VP 0.013 kPa (0.1 mm Hg) @ 20 °C;

NIOSH: no REL

flash point 121 °C (closed cup)

ACGIH: no TLV

SYNONYMS: 4-chlorophenol; CAS #106-48-9

SAMPLER: solid sorbent tube, silica gel, 150 mg/75 mg

FLOW RATE: 0.05 to 0.2 L/min

RECOMMENDED VOLUME: ≤40 L

MEASUREMENT TECHNIQUE: high performance liquid chromatography, UV detector

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples; media blanks, 9 to 12 for desorption efficiency

RECOMMENDED MEASUREMENT OPTIONS: reverse-phase liquid chromatographic column, C₁₈ bonded to silica may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of p-chlorophenol in 30% (v/v) acetonitrile in water in the range 2.5 to 50 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2.5 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: phenol and various substituted phenols can be separated under the conditions of the method

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] Dillon, L.H. et al., Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds, Research Report for p-Chlorophenol, NIOSH Contract No. 210-78-0012 (1980).
- [2] Korhonen, I.O., Separation of Chlorophenol Isomers on Quartz Columns, J. Chromatogr., 303 (1), 197-205 (1984).
- [3] Buisson, R.S.K. et al., Determination of Chlorinated Phenols by Capillary GC/ECD, J. Chromatogr. Sci., 22 (8), 399-42 (1984).
- [4] Lee, H.B. et al., Determination of Chlorinated Phenolics in Pulp and Paper Effluents, J. Assoc. of Anal. Chem., 72(6), 979-84 (1989).

p-CHLOROPHENOL
Methods Research Branch
Analytical Method

Analyte:	<u>p</u> -Chlorophenol	Method No.:	P&CAM 337
Matrix:	Air	Range:	0.910-23.4 mg/m ³
Procedure:	Adsorption on silica gel, desorption with acetonitrile, high performance liquid chromatography	Precision:	0.06

Date Issued: 9/19/80

Date Revised: Classification: B (Accepted)

1. Synopsis

- 1.1 A known volume of air is drawn through a silica gel tube to adsorb the p-chlorophenol vapor present.
- 1.2 The silica gel in the tube is transferred to a small vial where the p-chlorophenol is desorbed with 1 mL of acetonitrile. Two mL of H₂O is added to the extract.
- 1.3 An aliquot of the resulting solution is injected into a high performance liquid chromatograph.
- 1.4 The area of the resulting peak for p-chlorophenol is determined and compared with the peak areas obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The overall method was evaluated by collecting 3-L samples of test atmospheres containing p-chlorophenol in the range of 0.910-23.4 mg/m³ at 29°C and a relative humidity of greater than 80%. The amounts of p-chlorophenol collected ranged from 2.6-64 µg per 150-mg bed of silica gel. For the maximum allowable sampling volume of 40 L, the range is 0.064-1.6 mg/m³.

- 2.2 The slope of the analytical calibration curve was 62 area counts/ng of p-chlorophenol with an HP 1084B liquid chromatograph.
- 2.3 The lowest analytically quantifiable level for this method was determined to be about 2.5 μg of p-chlorophenol per sorbent sample extracted with 1.00 mL of acetonitrile and then diluted to 3.00 mL with 2.00 mL of distilled, deionized water. The instrumental detection limit was about 0.1 $\mu\text{g/mL}$, a concentration of p-chlorophenol in 30% acetonitrile in water that gave a response that was about twice the noise level under the operating conditions specified below.
- 2.4 The breakthrough volume of the sorbent tube was found to be approximately 60 L with a sampling rate of 0.2 L/min at a p-chlorophenol concentration of about 70 mg/m^3 , a sampling temperature of 43°C, and a relative humidity of greater than 80%.
3. Interferences
- 3.1 The chromatographic operating conditions described below will separate phenol, o-chlorophenol; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dichlorophenol; o- and p-nitrophenol; 2,4-dimethylphenol; 2,4,5-trichlorophenol; 4-chloro-3-methylphenol; 2,4-dinitrophenol; 4,6-dinitro-2-methylphenol; and pentachlorophenol can be achieved; with comparable concentrations of the two in solution, the resolution was found to be 0.91.
- 3.2 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of p-chlorophenol.
- 3.3 Any substance that has the same retention time as p-chlorophenol with the chromatographic operating conditions described in this method can interfere with the analysis. Therefore, retention time data cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, changing the separation conditions (column type or temperature, solvent flow rate, solvent programming rate, etc.) may circumvent the problem.
4. Precision and Accuracy
- 4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for the replicate measurements was 6.1% over the range of 0.910–24.3 mg/m^3 . The pooled RSD for the analytical method was 2.4% for 18 sorbent samples spiked with 2.54–48.0 μg of p-chlorophenol and stored for 24 hours.

- 4.2 The concentration of p-chlorophenol in test atmospheres was determined in control experiments by impinger sampling. The determinations with sorbent sampling gave values that averaged 98% of those determined by impinger sampling.
- 4.3 Samples of p-chlorophenol on silica gel were found to be stable at 25°C for seven days and for 29 days if stored at 0°C after the seventh day.
5. Advantages and Disadvantages
- 5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.
- 5.2 One disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.
6. Apparatus
- 6.1 Personal sampling pump capable of accurate performance ($\pm 5\%$) at 0.05–0.2 L/min and calibrated with a representative tube in the line.
- 6.2 Sorbent tubes. Pyrex tubes, 7-cm long with a 6-mm o.d. and a 4-mm i.d., flame-sealed at both ends. Each tube contains two sections of 20/40 mesh silica gel -- a 150-mg sorbing section and a 75-mg backup section. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.4 in H₂O (350 kPa) at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty-Four, PA); its catalog number is 226-10.
- 6.3 High performance liquid chromatograph, such as the Hewlett-Packard 1084B or equivalent, with ultraviolet absorption spectrophotometric detector.
- 6.4 Reverse-phase liquid chromatographic column, C₁₈ bonded to silica, such as the Varian MicroPak MCH-5, 5- μ m particle size, 4-mm i.d. by 30-cm long.
- 6.5 Centrifuge tubes, 12-mL, glass with screw caps.

- 6.6 Vials, 1-mL, with crimp-on caps containing Teflon-lined silicone rubber septa.
- 6.7 Pipets, 1- and 2-mL, and convenient sizes for making dilutions.
- 6.8 Ultrasonic bath.
- 6.9 Centrifuge for 12-mL tubes.
- 7. Reagents
 - 7.1 p-Chlorophenol, 99+% pure.
 - 7.2 Acetonitrile, distilled in glass.
 - 7.3 Water, distilled, deionized.
 - 7.4 Hexane, distilled in glass.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, and distilled water (in that order). The glassware should then be dried.
 - 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling, break open the ends of the tube to provide openings that are at least 2-mm in diameter.
 - 8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of silica gel is the backup layer and is positioned nearer the sampling pump.
 - 8.2.3 Place the silica gel tube in a vertical position during sampling to prevent channeling through the tube.
 - 8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.
 - 8.2.5 Sample the air at 0.05-0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 40 L at 0.2 L/min.
 - 8.2.6 Record the temperature and pressure of the air being sampled and measured.

- 8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps.
 - 8.2.8 To obtain a blank sample, process one unused silica gel tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit one blank sample tube for every ten samples with a minimum of three blank tubes.
 - 8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.
 - 8.2.10 Ship nine to twelve unopened silica gel tubes so that desorption efficiency studies can be performed on the same type and lot of silica gel used for sampling.
 - 8.2.11 Log samples as soon as they are received in the laboratory.
 - 8.2.12 Refrigerate all samples stored longer than seven days.
- 8.3 Analysis of Samples
- 8.3.1 Preparation of Samples. Remove the silica gel tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of silica gel in a sorbent tube to a separate 12-mL centrifuge tube. Add the glass wool plug near the sorbent tube inlet to the centrifuge tube containing the sorbing section; add the two urethane foam plugs to the centrifuge tube containing the backup section.
 - 8.3.2 Desorption of Samples. After the two sections of a sorbent tube are transferred, pipet 1 mL of acetonitrile into each centrifuge tube. Cap each tube immediately after the acetonitrile has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature. Then add 2 mL of distilled, deionized water to each tube. Cap the tubes and mix the solutions well. Centrifuge the solutions for 10 min. Then transfer about 1 mL of the supernatant liquid in each tube to a separate 1-mL vial and seal the vial with a Teflon-lined septum.

8.3.3 Operating Conditions for the High Performance Liquid Chromatograph.

Solvent flow rate: 1 mL/min.
Solvent A: Distilled, deionized water.
Solvent B: Acetonitrile.
Solvent program: 30% B to 80% B in 20 min.
Column temperature: 30°C.
UV detector: Analytical wavelength, 280 nm;
reference wavelength, 430 nm.
Injection volume: 100 µL.
Under these conditions, the analyte elutes in approximately 11 min.
Column cleanup procedure: At the end of each working day, flush the column with approximately 50 mL of acetonitrile (Solvent B) at a flow rate of 1 mL/min.

8.3.4 Determination of Concentration. Determine the concentration of p-chlorophenol in the sample solution by comparing the peak area to the peak areas obtained with standard solutions as discussed in Section 9. Peak heights may also be used.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of silica gel. Also, for a given batch of silica gel the desorption efficiency may vary with the weight of contaminant adsorbed. The silica gel used for the study of this method gave an average desorption efficiency of 0.960 with a pooled RSD of 2.4% for loadings of 2.54-48.0 µg of p-chlorophenol on 150-mg beds of sorbent material.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve p-chlorophenol in hexane to give stock solutions with concentrations such that 2.5-48.0 µg of p-chlorophenol will be injected onto the sorbent in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution into the front sorbing section of a sorbent tube while sampling 6 L of analyte-free air through the tube at 0.2 L/min. Cap the

tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 3 mL of 30% (v/v) acetonitrile in water. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of *p*-chlorophenol found in a sample versus the desorption efficiency.

9. Calibration and Standardization

To make a stock solution, add 500 mg of *p*-chlorophenol to 25 mL of 30% (v/v) acetonitrile in water. By serial dilution with 30% CH₃CN/H₂O, prepare a series of working standards varying in concentration over the range of 0.5–100 µg/mL. Follow the dilution scheme presented below.

<u>Initial concentration</u>	<u>Aliquot volume, mL</u>	<u>Final diluted volume, mL</u>	<u>Final concentration</u>
20.0 mg/mL	1	10	2.0 mg/mL
2.0 mg/mL	5	10	1.0 mg/mL
1.0 mg/mL	1	10	100.0 µg/mL
100.0 µg/mL	5	10	50.0 µg/mL
100.0 µg/mL	1	10	10.0 µg/mL
10.0 µg/mL	1	10	1.0 µg/mL
1.0 µg/mL	5	10	0.5 µg/mL

Prepare fresh working standards daily; the same stock solution may be used indefinitely if stored in an airtight container. Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak area.

10. Calculations

10.1 Determine the sample weight in µg from the standard curve.

10.2 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_S - W_b$$

where: W_F = corrected amount (μg) on the front section of the silica gel tube.

W_S = amount (μg) found on the front section of the silica gel tube.

W_b = amount (μg) found on the front section of the blank silica gel tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (μg) in the front section.

W_F = amount (μg) after blank correction.

D = desorption efficiency corresponding to the weight, W_F .

10.4 Express the concentration, C , of p-chlorophenol in the air sampled in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{L}$.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (μg) of p-chlorophenol found on front section.

M_B = corrected amount (μg) of p-chlorophenol found on backup section.

V = volume (L) of air sampled.

10.5 If desired, the results may be expressed in ppm by volume at 25°C (298 K) and 760 torr.

$$C(\text{ppm}) = C(\mu\text{g}/\text{L}) \times \frac{24.45}{128.56} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature ($^\circ\text{C}$) of air sampled.

24.45 = molecular volume (L/mol) at 25°C and 760 torr.

128.56 = molecular weight of p-chlorophenol.

11. Reference

- 11.1 Dillon, H. K.; Emory, M. B. "Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for p-Chlorophenol"; NIOSH Contract 210-78-0012; Southern Research Institute: Birmingham, Alabama; September, 1980.

H. Kenneth Dillon
Merry B. Emory
Southern Research Institute
NIOSH Contract No. 210-78-0012

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{CH}=\text{CHCHO}$

CROTONALDEHYDE

2ND EDITION METHOD #: P&CAM 285

DATE ISSUED: 10/28/77

M.W.: 70.09

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 2 ppm

NIOSH: TWA 2 ppm

ACGIH: TWA 2 ppm

(1 ppm = 2.87 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.85 g/mL @ 20 °C;

BP 104 °C;

VP 0.26 kPa (20 mm Hg) @ 20 °C;

vapor density (air=1) 2.4

SYNONYMS: crotonic aldehyde; trans-2-butenal; CAS #4170-30-3

SAMPLER: midget bubbler containing buffered (formate) hydroxylamine solution

FLOW RATE: 0.1 to 0.2 L/min

RECOMMENDED VOLUME: 12 L

MEASUREMENT TECHNIQUE: differential pulse polarography of crotonaldehyde oxime

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples; media blanks, at least one

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of crotonaldehyde in the range
6 to 280 µg per sample.

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: if not refrigerated, samples must be analyzed within 4 hours of sampling.
Other volatile aldehydes (e.g., acrolein, formaldehyde, benzaldehyde) may
interfere

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Aldehydes Screening, Method #2539, NIOSH Manual of Analytical Methods, 3rd Ed., Third Supplement, May 15, 1989.
- [3] Spingham, A.L. GC/MS Analytical Method for Priority Pollutants Including Crotonaldehyde, *J. Chromatogr. Sci.*, 20(6), 286-288 (1982).

Crotonaldehyde

Analyte:	Crotonaldehyde oxime	Method No.: P&CAM 285
Matrix:	Air	Range: 2.9-23.4 mg/cu m
OSHA Standard:	2 ppm (6 mg/cu m)	Precision ($\overline{CV}_T$): 0.061
Procedure:	Bubbler collection, derivatization with hydroxylamine, polarog- raphy	Date Issued: 10/28/77 Classification: E (Proposed)
Date Issued:	7/2/79	
Date Revised:		

1. Synopsis

- 1.1 A known volume of air is drawn through a midjet bubbler containing a buffered solution of hydroxylamine. Crotonaldehyde is derivatized with hydroxylamine to form crotonaldehyde oxime.
- 1.2 The crotonaldehyde oxime derivative is measured by polarography.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was studied over the range of 2.9-23.4 mg/cu m at an atmospheric temperature and pressure of 21°C and 766 mm Hg, using a 12-liter sample.
- 2.2 The upper limit of the method is dependent on the concentration of hydroxylamine. While collection efficiency has not been tested outside of the method range, a 50-fold molar excess of hydroxylamine should be maintained over the total amount of crotonaldehyde sampled.

3. Interferences

- 3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Other volatile aldehydes such as acrolein, formaldehyde, and benzaldehyde may cause significant interference.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.9-11.6 mg/cu m was 0.061. This corresponds to a 0.4 mg/cu m standard deviation at 1X the OSHA standard. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 The average concentrations obtained from analysis of samples collected from test atmospheres at 0.5X, 1X, 2X, and 4X the OSHA standard were 10.0% lower, 2.1% lower, 3.7% higher, and 0.3% higher, respectively, than the "true" concentrations. The difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no uncorrected bias. The Coefficient of Variation is a good measure of the accuracy of the method provided samples are refrigerated after collection. Storage stability studies on samples collected from a test atmosphere at a concentration of 5.80 mg/cu m indicate that collected samples are stable for at least 7 days at 8°C. Collection efficiency of the midget bubbler was determined to be 0.96 for an average of 24 samples and a correction must be applied.

5. Advantages and Disadvantages

- 5.1 The sample is not stable unless stored at cold temperatures (8°C). If samples are analyzed within 4 hours after collection, no refrigeration is required.
- 5.2 Collected samples are analyzed by a quick instrumental method.
- 5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 A glass midget bubbler.
- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing. Each sampling pump must be calibrated with a representative bubbler and trap in the line to minimize errors associated with uncertainties in the volume sampled.

- 6.3 Thermometer.
 - 6.4 Manometer.
 - 6.5 Volumetric Flasks: 1-liter and other convenient sizes for preparing standard solutions.
 - 6.6 Pipets: Convenient sizes for preparing stock standard solutions and for measuring the collection medium.
 - 6.7 Syringes: Convenient sizes for preparing spiked standard samples.
 - 6.8 Polarograph which is capable of differential pulse polarography with reference to a saturated calomel electrode.
 - 6.9 China marker.
 - 6.10 Teflon tubing (15 cm x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.
7. Reagents
- All reagents used must be ACS reagent grade or better.
- 7.1 Hydroxylamine hydrochloride.
 - 7.2 Sodium hydroxide, 0.1 M.
 - 7.3 Formic acid.
 - 7.4 Sodium formate.
 - 7.5 Hydroxylamine collection solution. Dissolve 0.68 g of hydroxylamine hydrochloride in 1 liter of deionized water. Adjust the pH to 5 with 0.1 M sodium hydroxide.
 - 7.6 Formic acid-sodium formate buffer. Add 3.4 g sodium formate and 2 mL formic acid into a 500-mL volumetric flask. Bring to volume with deionized water.
 - 7.7 Crotonaldehyde, 85%.
 - 7.8 Crotonaldehyde stock solutions: Prepare solutions containing 17.19 mg/mL and 1.719 mg/mL of crotonaldehyde in deionized water.
8. Procedure
- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried. All midget bubblers should be heated in an oxidizing atmosphere at a temperature of approximately 580°C. A glassblower's annealing oven is satisfactory for this purpose. This procedure will remove organic contaminants.

8.2 Collection and Shipping of Samples

- 8.2.1 Rinse each bubbler with 10 mL of the hydroxylamine solution. Pipet 10 mL of hydroxylamine solution buffered at a pH of 5 into each midget bubbler. Mark the liquid level on the bubbler with a china marker. Make sure the bubbler frit is covered.
- 8.2.2 The outlet of the midget bubbler is attached to the pump's inlet or a trap which may be used to protect the pump during personal sampling. The trap is a midget impinger or bubbler with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
- 8.2.3 Air being sampled should not be passed through any hose or tubing before entering the midget bubbler. (Polyvinyl chloride tubing is known to give interferences in the method).
- 8.2.4 A sample size of 12 liters is recommended. Sample at a flow rate of 0.2 liter/minute or less. Do not sample at a flow rate of less than 0.1 liter/minute.
- 8.2.5 Turn the pump on and begin sample collection. Periodically check the pump rotameter and adjust the flow as needed. Terminate sampling at the predetermined time and record sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.
- 8.2.6 The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber or polyvinyl chloride tubing. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. Care should be taken to minimize spillage or loss of sample by evaporation at all times.
- 8.2.7 The bubblers should be shipped in a suitable container designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible. If samples cannot be analyzed within four hours after collection, they must be refrigerated during shipping and until the time of analysis at 8°C.
- 8.2.8 With each batch or partial batch of five samples, submit one bubbler containing 10 mL of the collection medium prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

- 8.2.9 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the bubblers.
- 8.2.10 Do not ship the material in the trap. If more than 1 mL of material is collected in the trap after sampling, the sample should be considered invalid, otherwise, it can be discarded.

8.3 Analysis of Samples

- 8.3.1 Sample analysis should be done in a room with a fairly stable temperature. Each sample and blank is analyzed separately. Remove the bubbler stem and tap the stem lightly against the flask to drain the contents into the bubbler flask. If necessary, bring the liquid volume to the 10-mL mark with distilled water. Add 5 mL of the formic acid-sodium formate buffer. Swirl the bubbler flask to mix the contents well.
- 8.3.2 Transfer the mixed solution to a clean, dry polarographic receptacle which contains a small amount of mercury (approximately 0.3 mL) on the bottom. Place the receptacle on the polarograph and purge the sample for 3 minutes with oxygen-free nitrogen at a flow rate of 200 mL/minute.
- 8.3.3 Analyze the sample by differential pulse polarography using the following conditions:
- Drop Time: 1 second
Scan Rate: 5 mV/second
Scan from -0.6 V to -1.2 V versus a saturated calomel electrode.
- 8.3.4 Rinse the electrodes with distilled water between samples.
- 8.3.5 Measure the resultant diffusion current from the reduction of the crotonaldehyde oxime. The half-wave potential, $E_{1/2}$, of the crotonaldehyde oxime is -1.03 V vs. a saturated calomel electrode. The concentration of crotonaldehyde in the sample is determined by referring to the calibration curve prepared as described below.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 4 times the OSHA standard for the sample under study, is prepared and analyzed under the same polarographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/15 mL versus diffusion current. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations. Sample analysis and standards calibration should be done in a room with a fairly stable temperature.

- 9.1 From the stock solutions (Section 7.8), appropriate aliquots are withdrawn (less than 100 microliters) and added to 10 mL of the hydroxylamine solution. Five milliliters of formic acid/sodium formate buffer is added. The mixture should be swirled occasionally and after 15 minutes. Prepare at least 6 working standards to cover the range of 6-280 micrograms/sample.
- 9.2 Prepare at least one blank and analyze it at the same time as the standards.
- 9.3 Prepare a standard calibration curve by plotting micrograms/15 mL crotonaldehyde versus diffusion current.

10. Calculations

- 10.1 Read the weight, in micrograms, corresponding to each sample current from the standard curve. No volume correction is needed, because the standard curve is based on micrograms/15 mL of solution.
- 10.2 Corrections for the blank must be made for each sample.

$$\text{micrograms} = \text{microgram sample} - \text{microgram blank}$$

where:

$$\begin{aligned} \text{microgram sample} &= \text{micrograms found in sample bubbler} \\ \text{microgram blank} &= \text{micrograms found in blank bubbler} \end{aligned}$$

- 10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

$$\begin{aligned} f &= \text{flow rate sampled} \\ t &= \text{sampling time} \\ P_1 &= \text{pressure during calibration of sampling pump (mm Hg)} \\ P_2 &= \text{pressure of air sampled (mm Hg)} \\ T_1 &= \text{temperature during calibration of sampling pump (°K)} \\ T_2 &= \text{temperature of air sampled (°K)} \end{aligned}$$

- 10.4 The concentration of crotonaldehyde in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \text{micrograms/liter} = \frac{\text{Corrected micrograms}}{\text{Corrected air volume sampled (liters)}}$$

- 10.5 The collection efficiency of the midget bubblers was determined to be 0.96. The concentration of crotonaldehyde should be corrected for collection efficiency.

$$\text{Corrected mg/cu m} = \frac{\text{mg/cu m (Section 10.4)}}{0.96}$$

- 10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{70.09} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (L/mole) at 25°C and 760 mm Hg
70.09 = molecular weight (g/mole) of crotonaldehyde
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Backup Data Report for Crotonaldehyde, prepared under NIOSH Contract No. 210-76-0123.

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SRI International
Contract No. 210-76-0123

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(\text{CH}_3)_2\text{NNH}_2$

1,1-DIMETHYLHYDRAZINE

2ND EDITION METHOD #: S143

DATE ISSUED: 07/04/75

M.W.: 60.10

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.78 g/mL @ 25 °C;

BP 63.9 °C;

OSHA: TWA 0.5 ppm (skin)

VP 21 kPa (157 mm Hg) @ 25 °C;

NIOSH: carcinogen; C (120 min) 0.06 ppm

flash point -15 °C (closed cup)

ACGIH: TWA 0.5 ppm (skin), Suspected Human Carcinogen

(1 ppm = 2.44 mg/m³ @ NTP)

SYNONYMS: N,N-dimethylhydrazine; dimazine; CAS #57-14-7

SAMPLER: midget bubbler, glass, containing 15 mL of 0.1 M hydrochloric acid

FLOW RATE: ≤1 L/min

RECOMMENDED VOLUME: 100 L

MEASUREMENT TECHNIQUE: visible spectrophotometry, 730 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION:

standard solutions of 1,1-dimethylhydrazine in 0.1 M hydrochloric acid in the range 2 to 250 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: other hydrazines may interfere

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] Criteria for a Recommended Standard....Occupational Exposure to Hydrazines, DHEW (NIOSH), Publ. No. 78-122 (1978).
- [2] 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.
- [3] Kestner, P.E. and Danielson, N.D., Chromatographia, 18 (3), 125-128 (1984).
- [4] Holtzclaw, J.R. et al., Anal. Chem., 56(14), 2952-2956 (1984).

1,1-Dimethylhydrazine

Analyte:	1,1-Dimethylhydrazine	Method No.: S143
Matrix:	Air	Range: 0.506-2.22 mg/cu m
OSHA Standard:	0.5 ppm (1 mg/cu m) - skin	Precision (CV _T): 0.062
Procedure:	Bubbler collection, colorimetric	Validation Date: 7/4/75

1. Principle of the Method (Reference 11.1)

- 1.1 1,1-Dimethylhydrazine is collected in a midget bubbler containing 0.1 M hydrochloric acid.
- 1.2 The resulting solution is reacted with phosphomolybdic acid to form a bluish green colored complex.
- 1.3 The strong absorption maximum at 730 nm is used as a quantitative measure of 1,1-dimethylhydrazine.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.506-2.22 mg/cu m, at an atmospheric temperature and pressure of 23°C and 760 mm Hg. The probable range of the method is 0.1-10 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted with hydrochloric acid prior to color development to extend the upper limit of the range.
- 2.2 A concentration of 0.020 mg/cu m of 1,1-dimethylhydrazine can be determined in a 100-liter air sample based on a 0.025 absorbance using a 1-cm cell.

3. Interferences

Potential interferences result from agents that can reduce the phosphomolybdic acid to form the blue oxide and hence, give an elevated reading--including stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide. Interferences from oxidation of the 1,1-dimethylhydrazine giving a diminished reading may occur with halogens and oxygen (especially in presence of Cu (I) ions). Other hydrazine derivatives will also interfere (elevating the reading) and hydrogen dioxide will possibly reoxidize the blue oxide giving a lower reading (References 11.2, 11.3, 11.4, and 11.5).

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.506-2.22 mg/cu m was 0.062. This value corresponds to a 0.062 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.6.
- 4.2 A collection efficiency of 0.991, standard deviation of 0.002, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The samples, collected in bubblers, are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 Glass bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 Sampling Equipment. The sampling method for the bubbler collection method consists of the following components:
- 6.1.1 A glass, midget bubbler with a stem which has a fritted glass end and containing 10 ml of 0.1 M hydrochloric acid (Section 7.1). The fritted end should have porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter).
- 6.1.2 A pump suitable for sampling at least 1.0 liter per minute for 100 minutes. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.

- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.
- 6.2 Spectrophotometer. This instrument should be capable of measuring the developed color at 730 nm.
- 6.3 Matched glass cells or cuvettes, 1-cm path length.
- 6.4 Assorted laboratory glassware -- pipets, volumetric flasks, large test tubes, and graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

- 7.1 Collection Medium. 0.1 M hydrochloric acid. Fill a 1000-ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated hydrochloric acid, mix, and bring volume to the 1000-ml mark.
- 7.2 Phosphomolybdic acid solution (PMA). Dissolve 15 grams PMA in 500 ml distilled water, allow to stand one day, and filter before use through a fluted paper filter.
- 7.3 1,1-Dimethylhydrazine, reagent grade.
- 7.4 1,1-Dimethylhydrazine standard solution. (500 mg of 1,1-dimethylhydrazine in 100 ml 0.1 M hydrochloric acid solution.)

8. Procedure

- 8.1 Cleaning of equipment. No specialized cleaning of glassware is required.
- 8.2 Calibration of personal pump. Personal sampling pump should be calibrated using integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Pour 10 ml of the 0.1 M hydrochloric acid (Section 7.1) into each bubbler.
 - 8.3.2 Connect a bubbler with a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

- 8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.0 liter per minute or less. A sample size of 100 liters is recommended.
- 8.3.4 After sampling, the bubbler stems are lifted out of the bubbler bottom and rinsed with approximately 2 ml 0.1 M hydrochloric acid. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation at all times.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 Blank. With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 50-ml volumetric flask.
- 8.4.3 Rinse the bubbler three times with 2 ml 0.1 M hydrochloric acid and add rinses to the volumetric flask.
- 8.4.4 Add 10 ml phosphomolybdic acid solution to the volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.
- 8.4.5 Bring solution to the 50-ml mark with 0.1 M hydrochloric acid.
- 8.4.6 Transfer solution to a large test tube and heat in a water bath at 98°C for 1 hour. Cool solution under running tap water.
- 8.4.7 Read at 730 nm within 30 minutes in the spectrophotometer against a blank prepared from the 0.1 M hydrochloric acid in the same fashion as the samples.

9. Calibration and Standards

- 9.1 To six 50-ml volumetric flasks, add 10 ml 0.1 M hydrochloric acid using a graduated cylinder.
- 9.2 Carefully pipet 10, 20, 30, 40, and 50 microliters of the standard solution into the flasks (Section 7.4). Process one flask as a blank.
- 9.3 Add to this mixture 10 ml of phosphomolybdic acid solution (Section 7.2) using a 10-ml graduated cylinder.
- 9.4 Bring the solution to the 50-ml mark with 0.1 M hydrochloric acid.
- 9.5 Transfer the solution to a large test tube and heat it in a water bath at 98°C for 1 hour. Cool the solution under running tap water.
- 9.6 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.
- 9.7 Read the blank in the sample cell, then read the samples at 730 nm.
- 9.8 Construct a calibration curve by plotting absorbance against milligrams of 1,1-dimethylhydrazine in the color developed solution.

10. Calculations

- 10.1 Subtract the absorbance of the blank from the absorbance of each sample.
- 10.2 Determine from the calibration curve (Section 9.8) the mg of 1,1-dimethylhydrazine present in each sample.
- 10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg 1,1-dimethylhydrazine (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

- 10.4 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

- 11.1 Leo Feinsilver, Joseph Perregrino, and Courtney Smith, Jr.,
"Estimation of Hydrazine and Three of Its Methyl Derivatives,"
Industrial Hygiene Journal, 20, February 1959, 26-31.
- 11.2 Comprehensive Treatise on Inorganic and Theoretical Chemistry,
J. W. Mellor (Longmans, N. Y.), 1948, Vol. VII and XI.
- 11.3 Inorganic Chemistry, Heslop and Robinson (Elsevier, N. Y.), 1967.
- 11.4 Advanced Inorganic Chemistry, Cotton and Wilkinson, (Interscience,
N. Y.), 1966.
- 11.5 Inorganic Chemistry, T. Moeller (Wiley and Sons, N. Y.), 1963.
- 11.6 Documentation of NIOSH Validation Tests, NIOSH Contract No.
CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_7H_3(NO_2)_2OH$

DINITRO-o-CRESOL

2ND EDITION METHOD #: S166

DATE ISSUED: 12/23/77

M.W.: 198.14

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; MP 87.5 °C;

VP 0.7×10^{-5} kPa (5.2×10^{-5} mm Hg)
@ 20 °C

OSHA: TWA 0.2 mg/m^3 (skin)

NIOSH: TWA 0.2 mg/m^3 (skin)

ACGIH: TWA 0.2 mg/m^3 (skin)

SYNONYMS: 2-methyl-4,6-dinitrophenol; CAS #534-52-1

SAMPLER: filter, 0.8- μm cellulose ester membrane backed with a bubbler containing 10 mL ethylene glycol

FLOW RATE: 1.5 L/min

RECOMMENDED VOLUME: 180 L

MEASUREMENT TECHNIQUE: high pressure liquid chromatography, UV detector

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: C-18 column may be used for better sensitivity

MEASUREMENT CALIBRATION: standard stock solutions of dinitro-o-cresol in methanol;
working standards in ethylene glycol-isopropanol in the
range 3 to 180 μg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 3 μg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method may be adapted to other nitrocresol compounds with changes in chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Tripathi, A. M. et al., Determination of 2,6- and 4,6-Dinitro-o-Cresols by High Pressure Liquid Chromatography on a beta-Cyclodextrin Bonded Column, J. Chromatogr., **460**, 442 (1989).
- [3] Krause, R. T. et al., Oxidative Detection of Coulometrically Reduced Organonitro Pesticides in Reversed-Phase High Pressure Liquid Chromatography, J. Chromatogr., **459**, 151 (1988).

8/15/90

NIOSH Manual of Analytical Methods

Dinitro-o-cresol

Analyte:	4,6-Dinitro-2-methyl phenol	Method No.:	Sl66
Matrix:	Air	Range:	0.070-0.62 mg/cu m in a 180-liter sample
OSHA Standard:	0.2 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.075
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date:	12/23/77

1. Synopsis

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 10 mL of ethylene glycol to collect dinitro-o-cresol.
- 1.2 The filter and bubbler are disconnected. The filter is removed from the cassette holder and added to the bubbler flask. Five milliliters of 2-propanol are added to the flask before analysis.
- 1.3 The resulting sample is analyzed by high pressure liquid chromatography.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was validated over the range of 0.070-0.62 mg/cu m at an atmospheric temperature of 24°C and pressure of 761 mm Hg, using 180-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the mixed cellulose ester membrane filter connected in series to the midget bubbler.

3. Interferences

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Any compound that has the same retention time as dinitro-o-cresol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.070-0.62 mg/cu m was 0.075. This value corresponds to a standard deviation of 0.015 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true" value on the average 95% of the time over the validation range. The concentrations obtained at 0.5X, 1X, and 2X the OSHA environmental limit were 2% lower than the dynamically generated test concentrations ($n = 17$). In these experiments the average analytical method recovery was 1.037 for a loading of 17.98-71.9 micrograms of dinitro-o-cresol on the filter. A correction was applied for this recovery. In storage stability studies, the mean of samples analyzed after 7 days were within 5% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 Collected samples are analyzed by means of a quick, instrumental, method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 Filter unit: The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37-mm two-piece cassette filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.
- 6.2 A glass midget bubbler.
- 6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative filter cassette, bubbler,

and trap in the line to minimize errors associated with uncertainties in the volume sampled. The sampling pump is protected from splash-over or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.

6.4 Manometer.

6.5 Thermometer.

6.6 High pressure liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 50-microliter external sample loop.

6.7 Column (300 mm x 3-mm I.D. stainless steel) packed with μ -Bondapak C-18. This column is available from Waters Associates, Milford, Massachusetts.

6.8 An electronic integrator or some other suitable method for measuring peak areas.

6.9 Tweezers.

6.10 Microliter Syringe: 10-microliter.

6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.

6.12 Pipets: Convenient sizes for preparing standard solutions and 5-mL and 10-mL pipets for measuring the extraction medium.

6.13 Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

Whenever possible, all reagents used should be ACS reagent grade or better.

7.1 4,6-Dinitro-o-cresol.

7.2 Ethylene glycol.

7.3 2-Propanol.

7.4 Methanol, distilled in glass.

7.5 Water, deionized and distilled.

7.6 Prepare a 9.00 mg/mL dinitro-o-cresol stock standard solution by dissolving 225 mg dinitro-o-cresol in methanol and diluting to 25 mL in a volumetric flask.

7.7 Glacial acetic acid.

7.8 Toluene.

7.9 Mobile phase for HPLC: 65% methanol/35% water/0.175% acetic acid (% by volume).

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Assemble each filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel screen. Secure the cassette holder together with tape or shrinkable band.

8.2.2 Pour 10 mL of ethylene glycol into a midget bubbler, and mark the liquid level before inserting the bubbler frit. Be sure that the bubbler frit is completely immersed in the ethylene glycol. If the ethylene glycol does not cover the frit, do not use the bubbler. Dinitro-o-cresol will not be collected efficiently unless the bubbler frit is completely immersed in the ethylene glycol.

8.2.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet of the midget bubbler to either the pump's inlet or the trap's inlet. When a trap is used, it is attached to the pump by tape or a holder. The outlet of the trap is connected by tubing to the pump's inlet. Material collected in the trap must never be returned to the midget bubbler. If more than 1 mL of material is collected in the trap after sampling, the sample should be considered invalid, otherwise, it can be discarded. The bubbler must be maintained in a vertical position during sampling.

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.

8.2.6 Turn the pump on and begin sample collection. 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, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

- 8.2.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.
- 8.2.8 After sampling, disconnect the filter and bubbler. Remove the bubbler stem, and remove the filter from the filter cassette with clean tweezers and add it to the bubbler. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of dinitro-o-cresol from the filter by vaporization may occur.
- 8.2.9 With each batch or partial batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.
- 8.2.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.3 Analysis of Samples

- 8.3.1 Remove the bubbler stem from the bubbler. Allow ethylene glycol to drain from the frit into the bulk of the solution in the bubbler. If the sample volume is less than 10 mL, add ethylene glycol until the volume reaches the 10-mL mark. If the sample volume is more than 10 mL, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1. Absorption of water would cause the volume in the bubbler to increase.
- 8.3.2 Add 5 mL of 2-propanol to each sample and mix the solution by swirling.
- 8.3.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 3230 psi
Flow Rate: 1.6 mL/minute
Mobile Phase: 65% methanol/35% water/0.175% acetic acid
Detector: uv photometer at 254 nm
Retention Time: 6 minutes

8.3.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 50-microliter sample loop. Flush this loop thoroughly with the sample (300 microliters), and inject the sample.

8.3.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Analytical Method Recovery

8.4.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of dinitro-o-cresol from the mixed cellulose ester membrane filter. The analytical method recovery should be determined over the concentration range of interest.

8.4.2 Procedure for Determining Analytical Method Recovery. An appropriate aliquot of a 9.00 mg/mL solution of dinitro-o-cresol in toluene is added to a 37-mm MCE filter. The amount added is equal to the amount of dinitro-o-cresol collected in a 180-liter sample at 2X, 1X, and 0.5X the OSHA standard level. Six spiked samples are prepared at each level along with six blanks. The filters are allowed to stand for 2-3 minutes to allow evaporation of toluene. The filter is transferred to a container containing 10 mL of ethylene glycol and 5 mL 2-propanol. The resulting sample is mixed well and allowed to stand for 1 hour before analysis.

Standards are prepared as discussed in Section 9 and analyzed with the samples.

Analytical Method Recovery (A.M.R.) equals the weight in μg found on the filter divided by the weight in μg added to the filter, or

$$\text{A.M.R.} = \frac{\text{Average weight recovered } (\mu\text{g}) - \text{Blank } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/15 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

9.1 From the stock solution (Section 7.6), appropriate aliquots are withdrawn and added to 10 mL ethylene glycol and 5 mL 2-propanol. Prepare at least 5 working standards to cover the range of 3.6-108 micrograms/15 mL. This range is based on a 180-liter sample. Analyze samples as described in Section 8.3.

9.2 Prepare a standard calibration curve by plotting concentration of dinitro-o-cresol in $\mu\text{g}/15\text{ mL}$ versus peak area.

10. Calculations

10.1 Read the weight, in μg , corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on $\mu\text{g}/15\text{ mL}$ of ethylene glycol/2-propanol and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample}$$

$$\mu\text{g blank} = \mu\text{g found in blank}$$

10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected } \mu\text{g/sample} = \frac{\mu\text{g (Section 10.2)}}{\text{A.M.R.}}$$

10.4 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.5 The concentration of dinitro-o-cresol in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \mu\text{g/L} = \frac{\mu\text{g (Section 10.3)}}{\text{Corr. Air Volume Sampled (L) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Dinitro-o-cresol prepared under NIOSH Contract No. 210-76-0123.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{COOCH}_2\text{CH}_3$

ETHYL ACETATE

2ND EDITION METHOD #: S49

DATE ISSUED: 01/17/75

M.W.: 88.08

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.895 g/ml @ 25 °C;

BP 77 °C;

VP 9.7 kPa (73 mm Hg) @ 20 °C

OSHA: TWA 400 ppm

NIOSH: TWA 400 ppm

ACGIH: TWA 400 ppm

(1 ppm = 3.60 mg/m³ @ NTP)

SYNONYMS: acetic acid ethyl ester; CAS #141-78-6

SAMPLER: coconut shell charcoal tube, 100 mg/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: ≤6 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: 30-m, 0.32-mm ID DB-Wax/Stabilwax capillary column or DB-1 capillary column may be used for better resolution [1]

MEASUREMENT CALIBRATION: standard solutions of ethyl acetate in carbon disulfide in the range 7 µg to 1000 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 7 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: The method was modified with the use of capillary column for better sensitivity and resolution [2]

APPLICABILITY: this is similar to NIOSH method 1450 [3] and can be used for other esters with appropriate changes in chromatographic conditions

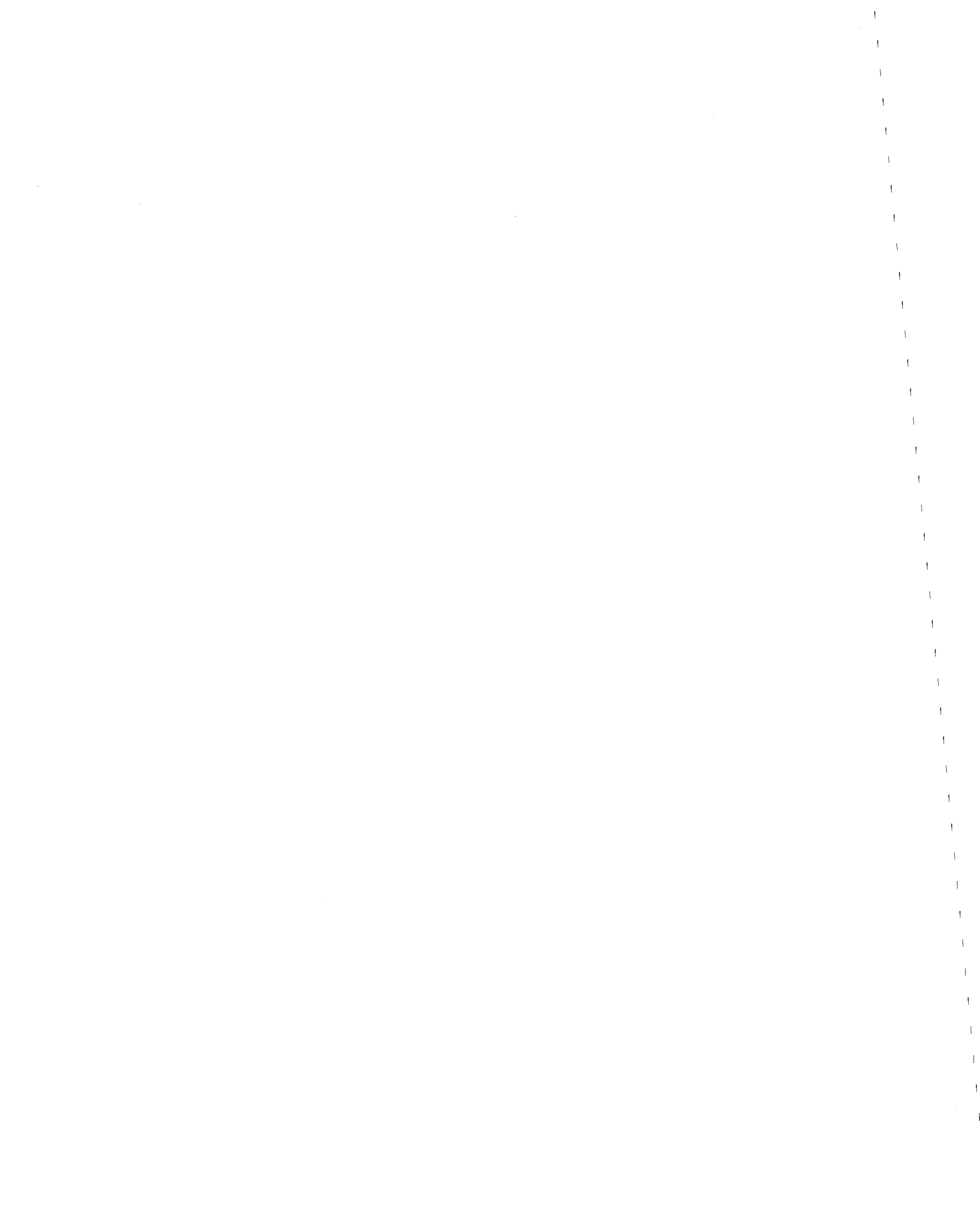
OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Pendergrass, S.M., Method Development Efforts, Measurement Research Support Branch, DPSE, NIOSH (unpublished 1990).

[2] Analytical Sequence # 5580, 5375 and 5276, Measurement Research Support Branch, DPSE, NIOSH (unpublished, 1990).

[3] NIOSH Manual of Analytical Methods, 3rd ed., Method No. 1450, Department of Health and Human Services, U.S. Government Printing Press, Washington D.C. (1984).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.



Ethyl Acetate

Analyte:	Ethyl Acetate	Method No.: S49
Matrix:	Air	Range: 704-2950 mg/cu m
OSHA Standard:	400 ppm (1400 mg/cu m)	Precision ($\overline{CV}_T$): 0.058
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 1/17/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 704-2950 mg/cu m at an atmospheric temperature and pressure of 23 °C and 759 mm Hg, using a 6 liter sample. Under the conditions of sample size (6 liters) the probable useful range of this method is 140-4200 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 25 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 25 mg of analyte when a test atmosphere containing 2950 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 45 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 704-2950 mg/cu m was 0.058. This value corresponds to an 81 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 1.4% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Ethyl Acetate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 6 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 30 ml/min (60 psig) Helium carrier gas flow
 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 3. 400 ml/min (60 psig) Air flow to detector
 4. 225°C injector temperature
 5. 250°C manifold temperature (detector)
 6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 6 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: HCOOCH2CH3

ETHYL FORMATE

2ND EDITION METHOD #: S36

DATE ISSUED: 12/06/74

M.W.: 74.08

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.92 g/mL @ 20 °C;
BP 54.5 °C; MP 81 °C; VP 25.9 kPa
(194 mm Hg) @ 20 °C;
vapor density (air=1) 2.56

OSHA: TWA 100 ppm

NIOSH: TWA 100 ppm

ACGIH: TWA 100 ppm

(1 ppm = 3.03 mg/m³ @ NTP)

SYNONYMS: formic acid ethyl ester; CAS #109-94-4

SAMPLER: coconut shell charcoal tube, 100 mg/50 mg

FLOW RATE: ≤0.2 L/min

RECOMMENDED VOLUME: ≤10 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of ethyl formate in carbon disulfide in
the range 0.1 to 6 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not estimated

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, Backup Data Report for Ethyl Formate, Publication No. DHEW (NIOSH) 77-185, 1977.
- [2] 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.
- [3] Kacpura, B., Determination of Ethyl Formate by Gas Chromatography, Pr. Cent. Inst. Ochr. Pr., 34 (123), 243-250 (1984).

8/15/90

NIOSH Manual of Analytical Methods

Ethyl Formate

Analyte:	Ethyl Formate	Method No:	S36
Matrix:	Air	Range:	171-666 mg/cu m
OSHA Standard:	100 ppm (300 mg/cu m)	Precision (CV _T):	0.0782
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 171-666 mg/cu m at an atmospheric temperature and pressure of 23°C and 766 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9 mg. sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 9.5 mg of analyte when a test atmosphere containing 666 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 75 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 171-666 mg/cu m was 0.0782. This value corresponds to a 23.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 4.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Ethyl Formate, reagent grade.

7.3 Nonane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 30 ml/min (60 psig) Helium carrier gas flow
 - 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 - 3. 400 ml/min (60 psig) Air flow to detector
 - 4. 225°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 65 °C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: CH ₂ (NH)CH ₂	2ND EDITION METHOD #: P&CAM 300	ETHYLENIMINE
M.W.: 43.07		DATE ISSUED: 05/02/79
		CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: liquid; d 0.832 g/mL @ 20 °C;
	BP 56 °C;
OSHA: carcinogen; no PEL	VP 21.3 kPa (160 mm Hg) @ 30 °C;
NIOSH: carcinogen; no REL	vapor density (air=1) 1.5
ACGIH: 0.5 ppm (skin)	

SYNONYMS: aziridine; CAS #151-56-4

SAMPLER: midget bubbler containing 15 mL Folin's Reagent

FLOW RATE: 0.2 L/min

RECOMMENDED VOLUME: ≤48 L

MEASUREMENT TECHNIQUE: HPLC, UV detection, 254 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples; media blanks, 125 mL

RECOMMENDED MEASUREMENT OPTIONS: a uBondapak CN column gave an LOD of 0.3 µg per sample. [2]

MEASUREMENT CALIBRATION: standard solutions of ethylenimine derivative
(4-(1-aziridinyl)-1,2-naphthoquinone) in chloroform in the
range 0.7 to 800 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.3 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH analytical sequence #3680 [2]

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
 - [2] NIOSH Health Hazard Evaluation Report No. HHE 82-287 and NIOSH Analytical Sequence No. 3680, DPSE, Measurement Research Support Branch, Cincinnati, Ohio, NIOSH, unpublished (1982).
 - [3] Koval'chuk, T.V. Methods for Analysis of Ethylenimine Derivative Pharmaceuticals, Farmatsiya (Moscow), 52(6), 77-79 (1983).
 - [4] De Haan, P.E. et al. Determination of Volatile Amines by Capillary Gas Chromatography, J. High Resolut. Chromatogr., 12(9), 604-607 (1989).
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ETHYLENIMINE

Measurements Research Branch

Analytical Method

Analyte:	Ethylenimine (Aziridine)	Method No:	P&CAM 300
Matrix:	Air	Range:	0.16-20 mg/m ³
Procedure:	Collection in Folin's reagent/bubbler, extraction with chloroform, analysis by HPLC.	Precision:	7%
Date Issued:	5/2/79		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

- 1.1 A known volume of air is drawn through a bubbler containing an aqueous buffered solution of 1,2-naphthoquinone-4-sulfonate (Folin's Reagent) which reacts with ethylenimine to produce 4-(1-aziridinyl)-1,2,-naphthoquinone.
- 1.2 The reaction product is extracted with chloroform.
- 1.3 An aliquot of the extract is injected into a high performance liquid chromatograph (HPLC).
- 1.4 Peak areas are electronically determined and compared with a calibration curve obtained from injections of standard solutions of 4-(1-aziridinyl)-1,2-naphthoquinone.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was evaluated over the range 1.2 to 795 µg/sample (24-15,900 µg/m³ for a 50 L air sample) when using 15 mL of reagent and 10-µL injections into the HPLC. It can probably be extended down to 0.7 µg/sample as a lower limit.
- 2.2 Tests to determine breakthrough of ethylenimine indicated less than 0.1% in back-up bubblers when challenge concentrations of 204 µg/L were sampled for 26 minutes and 20.6 µg/L for 270 minutes. Air flows were maintained at approximately 0.15 L/min.

2.3 The limit of detection is 0.3 $\mu\text{g}/\text{sample}$.

3. Interferences

- 3.1 In solutions containing ethylenimine at 17 $\text{ng}/\mu\text{L}$, the following compounds were found not to interfere when their concentrations were 2 $\text{ng}/\mu\text{L}$: methylamine, diethylamine, butylamine, ethanolamine, dihexylamine, dicyclohexylamine, benzylamine, dibenzylamine, and aniline. Propylenimine and 2-bromoethylamine interfere. The latter compound and its chloro analogue can be expected to interfere since they are probably converted to ethylenimine in the alkaline reagent solution.
- 3.2 Any compound collected with ethylenimine and having or forming a derivative which has the same retention time as the analyte will interfere with the analysis. This type of interference often can be eliminated by changing the mobile phase composition, solvent programming, or changing the chromatographic column. Compounds, such as ammonia, which consume Folin's reagent can be considered interferences if they prevent ethylenimine from reacting with the reagent. The ammonia derivative is not extracted into the chloroform.

4. Precision and Accuracy

- 4.1 The precision of the overall method is 7% relative standard deviation for samples collected from dry air at room temperature. This value is based on the collection and analysis of 52 samples of laboratory generated atmospheres containing ethylenimine at the levels 0.16-21 mg/m^3 and sampling at approximately 0.2 L/min. The range of volumes sampled was 2.6-39 L such that the range of sample sizes was 1-800 μg .
- 4.2 Folin's reagent spiked with 1.67 and 16.7 μg of ethylenimine and stored at 23 °C yielded recoveries of 86-99% after seven days and 56-60% after 28 days. Samples stored at 5 °C yielded recoveries of 94-95% after seven days and 86-94% after 28 days. It is recommended that samples be refrigerated until analyses can be conducted.
- 4.3 The method was evaluated with up to 800 μg of ethylenimine. Although Folin's reagent is present in sufficient excess to react with larger amounts of ethylenimine, it is not known whether the reaction will be quantitative.
- 4.4 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

- 5.1 The samples, collected in bubblers, are analyzed by means of a quick, instrumental method.

- 5.2 The derivative formed between ethylenimine and Folin's reagent is indicative of the intact imine rather than its hydrolysis product.
- 5.3 A disadvantage of the method is the awkwardness in using bubblers for collecting personal samples. If the employee's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 This method has not been field tested.

6. Apparatus

- 6.1 Personal air sampling pump that can be maintained for four hours at a flow rate of 0.2 L/min with the sampler in line. Each pump should be calibrated with a representative sampler in line to minimize errors in volume measurements. A bubble flow meter or other suitable flow measuring device may be used. The pump should be protected from splashover or solvent condensation by a 5-cm long x 6-mm i.d. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.2 Spillproof bubblers, with fritted glass stems (I-1143-87 body and I-1143-89 bubbler, Ace Glass, Inc., Vineland, New Jersey, or equivalent) containing the collection solution (reagent) described in Section 7.11. The bubblers should be wrapped in aluminum foil to prevent photochemical decomposition of the analyte.
- 6.3 High performance liquid chromatograph equipped with an ultraviolet detector (254 nm) and injection valve.
- 6.4 Lichrosorb DIOL column, or equivalent, (10- μ m), 4.6-mm i.d. x 25-cm.
- 6.5 Potentiometric strip chart recorder.
- 6.6 Electronic integrator.
- 6.7 Analytical balance.
- 6.8 Desiccator.
- 6.9 Glass syringes, 10- μ L.
- 6.10 Pipettes of convenient volumes for the preparation of standard solutions.
- 6.11 Volumetric flasks, low actinic glass, of convenient volumes for the preparation of standard solutions. Ten-milliliter flasks are required for the sample extracts.

- 6.12 Pipette bulb.
- 6.13 Separatory funnels with Teflon stopcocks, 60-mL and 1-L.
- 6.14 Funnels, 25-mm i.d. x 40-mm stem and 75-mm i.d. x 75-mm stem.
- 6.15 Beakers, 50-mL and 2-L.
- 6.16 Aluminum foil.
- 6.17 Filter paper (Whatman 42), 12.5 cm diameter.

7. Reagents

- 7.1 Chloroform with 1% ethanol preservative, UV grade, distilled in glass.
- 7.2 Hexane, UV grade, distilled in glass.
- 7.3 2-Propanol, UV grade, distilled in glass.
- 7.4 Methyl alcohol, UV grade, distilled in glass.
- 7.5 Acetone, UV grade, distilled in glass.
- 7.6 Ethylenimine.
- 7.7 1,2-Naphthoquinone-4-sulfonic acid, sodium salt (Pfaltz & Bauer).
- 7.8 0.1N Sodium hydroxide (NaOH).
- 7.9 0.1M Potassium dihydrogen phosphate (KH_2PO_4).
- 7.10 Buffer solution, pH 7.7; Mix 100 mL of 0.1M KH_2PO_4 with 93.4 mL of 0.1N NaOH.
- 7.11 Folin's reagent: Dissolve 0.40 grams of 1,2-naphthoquinone-4-sulfonic acid sodium salt in 100 mL of buffer solution. Dilute to 500 mL with distilled water in a volumetric flask. Wrap the flask with aluminum foil and store in a refrigerator. Discard the reagent after five days.
- 7.12 4-(1-Aziridiny1)-1,2-naphthoquinone: Wrap a 1-L separatory funnel with aluminum foil and add 2 g of the sodium salt of 1,2-naphthoquinone-4-sulfonic acid dissolved in 250 mL of distilled water. Add 25 mL of 0.5M trisodium phosphate, shake and check that the pH is between 10.5 and 11.5. Add 0.3 mL ethylenimine and shake intermittently for ten minutes.

CAUTION: Ethylenimine has been identified as a carcinogen. Appropriate precautions must be taken in handling the compound to avoid personnel exposure and area contamination.

Extract the 4-(1-aziridinyl)-1,2-naphthoquinone formed with six 200-mL portions of chloroform. Place the combined extracts in a 2-L beaker wrapped in aluminum foil. Cover the beaker with aluminum foil in which three holes have been made. Evaporate the chloroform with a nitrogen purge. Transfer the dry residue to a 50-mL beaker wrapped with aluminum foil. Add 35 mL of methyl alcohol and 1 mL of chloroform to the residue and stir briefly. Not all of the residue will dissolve. Place the beaker in an ice-water bath for ten minutes and then filter the precipitate through Whatman 42 filter paper. Rinse the precipitate in the filter with 4 mL of chilled methyl alcohol and discard the filtrates. Dry the precipitate with a nitrogen purge, transfer it to a brown-glass bottle and purge again. Dry the compound overnight in a desiccator containing Drierite. The melting point of the compound is 173-175 °C. The compound is to be used for making standard solutions for calibration purposes. The 4-(1-aziridinyl)-1,2-naphthoquinone should be stored in a freezer until standard solutions are to be prepared.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis is washed with detergent and rinsed with tap water, distilled water, and methyl alcohol.

8.2 Collection and Shipping of Samples

8.2.1 Pour 15 mL of Folin's reagent into each midget bubbler.

8.2.2 Connect the 5-cm glass tube containing the glass wool plug to the personal sampling pump and then to the bubbler using short sections of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler. The bubbler should be maintained in a vertical position during sampling.

8.2.3 The atmosphere is sampled at a flow rate of 0.2 L/min for four hours. The flow rate and sampling time, or the volume of sampled air, must be measured as accurately as possible.

8.2.4 The temperature, pressure and, if possible, humidity of the atmosphere being sampled are measured and recorded, along with other pertinent data such as location, date, and time of sampling.

8.2.5 After sampling, use a pipet bulb to force air through the bubbler stem to dislodge the derivatized product and recover as much of the sampling solution as possible. Wash the stem with 2 mL of chloroform, adding the wash to the bubbler. The bubbler is sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed.

- 8.2.6 Whenever possible, hand-delivery of the samples is recommended. Otherwise, transfer liquid to a 20-mL scintillation vial with polyseal cap (Kimble No. 74515 or equivalent) and seal with a 24 to 20-mm shrink band (Walter H. Jelly Co., Franklin Park, Illinois, or equivalent).
- 8.2.7 Care should be taken to minimize spillage or loss by evaporation. Refrigerate samples if analysis cannot be conducted within a day.
- 8.2.8 Blank samples are obtained by handling random bubblers in the same manner as in sampling (fill, seal, and transport) except that no air is drawn through them.
- 8.2.9 If samples of bulk material associated with the process under investigation are to be shipped to the laboratory, they should not be placed in the same container as the air samplers or blanks.
- 8.3 Analysis of Samples
- 8.3.1 Transfer the collection solution from each bubbler into individual 60-mL separatory funnels.
- 8.3.2 Rinse the bubbler with 4 mL of chloroform and add the rinse to the separatory funnel.
- 8.3.3 Cap and moderately shake the funnel for about 15 seconds. Allow the liquid phases to separate.
- 8.3.4 With the aid of a small funnel, collect the chloroform extract in a 10-mL actinic glass volumetric flask.
- 8.3.5 Repeat extraction and collection procedures with another 4-mL chloroform extract.
- 8.3.6 Dilute the volumetric flask to 10 mL with chloroform and shake.
- 8.3.7 Liquid chromatographic conditions (23 °C, 585 mm Hg).

Column:	Lichrosorb DIOL (25-cm x 4.6-mm i.d.)
Mobile Phase:	Hexane/chloroform (with 1% ethanol)/ 2-propanol, 59.5/40/0.5 (v/v).
Flow Rate:	1.3 mL/min, 300 psi
Detector:	UV (254 nm), 0.04 AUFS
Injection Vol.:	10 µL
Efficiency:	1936 theoretical plates

Capacity Ratio: 0.9

Retention Vol.: 6.3 mL

8.3.8 Injection. Flush the 10- μ L syringe first with acetone (to insure its cleanliness and to wet the barrel and plunger) and then with the sample solution. Draw 10 μ L of sample solution into the syringe and inject the aliquot into the liquid chromatograph.

8.3.9 Measure the peak area and read the amount of analyte from the calibration curve.

8.4 Efficiency of Sample Recovery

8.4.1 Importance of Determination. The recovery of the ethylenimine derivative can vary from one laboratory to another. The fraction recovered may also vary with the amount of ethylenimine present. Determinations should, therefore, be made for at least three levels in the range of anticipated sample sizes. Recovery should be at least 90%.

8.4.2 Procedure for Determining Recovery. To each bubbler containing 15 mL of Folin's reagent, add a known amount of an ethylenimine chloroform solution. Five bubblers are thus prepared at each of three different levels in the range of interest. Place the stem-caps on the bubblers immediately and shake intermittently for five minutes. Treat a parallel blank in the same manner adding only an equal volume of chloroform. Allow them to stand overnight in a refrigerator. Analyze the samples as described in section 8.3. The sample recovery (R) is given by the average amount found, corrected for the blank if necessary, divided by the amount added.

9. Calibration and Standardization

9.1 For accuracy in preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at a high concentration. The initial standard is prepared by weighing a selected amount of 4-(1-aziridinyl)-1,2-naphthoquinone (e.g., 125 mg) into a 250-mL volumetric flask (low actinic glass) and adding chloroform to the calibration mark. Dilutions encompassing the concentration range of interest down to 0.3 ng/ μ L are then made from the stock solution. Solutions should be stored in a refrigerator when not in use. Prepare fresh standards every five days.

9.2 The standard solutions should be analyzed under the same liquid chromatographic conditions and during the same time period as the samples. This will minimize inaccuracy due to day-to-day variations in the setting of instrumental conditions.

- 9.3 Calibration curves for 4-(1-aziridinyl)-1,2-naphthoquinone are prepared by plotting the peak areas for the standards against their concentration in $\mu\text{g}/10\text{ mL}$.

10. Calculations

- 10.1 In the event that the blank produces a peak with the same retention time as the analyte, the analyst should determine the source of the interference and eliminate or compensate for it.
- 10.2 Read the weight (W_1) in μg of 4-(1-aziridinyl)-1,2-naphthoquinone present in the sample from the calibration curve.
- 10.3 The total weight (W_t) is determined by

$$W_t = \frac{W_1}{R}$$

where R is the recovery factor.

- 10.4 The concentration of ethylenimine in air (C , $\mu\text{g}/\text{m}^3$) is given by

$$C = \frac{W_t}{V} \times 10^3 \times 0.216$$

where V is the volume of air sampled in liters, 10^3 is the factor to convert from liters to m^3 , and 0.216 is the gravimetric factor to convert the weight of 4-(1-aziridinyl)-1,2-naphthoquinone to that of the ethylenimine collected.

- 10.5 The concentration can also be expressed in ppm.

$$\text{ppm} = \frac{\mu\text{g}/\text{m}^3}{10^3} \times \frac{24.45}{43.08} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

10^3 = factor to convert $\mu\text{g}/\text{m}^3$ to mg/m^3
 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
 43.08 = molecular weight (g/mole) of ethylenimine
 760 = standard pressure (mm Hg)
 P = pressure (mm Hg) of air sampled
 T = temperature ($^\circ\text{C}$) of air sampled
 298 = standard temperature ($^\circ\text{K}$)

11. References

Raul Morales, J. F. Stampfer, Jr., R. E. Hermes, E. E. Campbell and H. J. Ettinger, "Development of a Sampling and Analytical Method for Ethylenimine, January 1, 1978 - October 31, 1978," Los Alamos Scientific Laboratory Progress Report LA-7978-PR, National Technical Information Service, Springfield, Virginia, 1979.

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NIOSH-1A-78-11

FLUORIDES, aerosol and gas

METHOD: 7902

ISSUED: 2/15/84

REVISION #1: 8/15/90

PROPERTIES: HF: liquid; BP 19.5 °C; fluoride salts liberate HF in presence of acids

ACGIH: 2.5 mg/m³ (fluorides); 3 ppm (HF)
(1 ppm HF = 0.78 mg/m³ @ NTP)

SYNONYMS: sodium fluoride (CAS #7681-49-4), hydrogen fluoride, hydrofluoric acid (CAS #7664-39-3), cryolite, sodium hexafluoroaluminate (CAS #13775-53-6).

SAMPLING	MEASUREMENT
SAMPLER: PREFILTER + TREATED PAD (0.8- μm cellulose ester membrane followed by a Na_2CO_3 -treated cellulose pad)	! !TECHNIQUE: ION-SPECIFIC ELECTRODE ! !ANALYTE: fluoride ion (F^-) !
FLOW RATE: 1 to 2 L/min	!FILTER (particulate F^-): fuse in NaOH, dissolve in ! 50 mL water + TISAB !
VOL-MIN: 12 L @ 2.5 mg/ m^3 -MAX: 800 L @ 2.5 mg/ m^3	!TREATED FILTER (gaseous F^-): extract in 50 mL ! water + TISAB !
SHIPMENT: routine	!CALIBRATION: standard F^- solutions in TISAB !
SAMPLE STABILITY: stable	!RANGE: 0.03 to 1.2 mg F^- per sample !
BLANKS: 2 to 10 field blanks per set	!ESTIMATED LOD: 0.003 mg F^- per sample [2] !
	!PRECISION (s_r): 0.017 @ 0.055 to 0.22 mg per ! sample [3] !
	!
RANGE STUDIED: not studied	!
BIAS: none identified	!
OVERALL PRECISION (s_r): not evaluated	!

APPLICABILITY: The working range is 0.12 to 8 mg/m³ for a 250-L air sample. The method applies to mining samples, aluminum reduction, ceramic, glass etching, electroplating, semiconductor, and fluorochemical industries. If other aerosols are present, gaseous fluoride may be underestimated due to sorption onto or reaction with particles, with concurrent overestimation of particulate/gaseous fluoride ratio [4-9].

INTERFERENCES: In samples containing cryolite, aluminum is sufficiently concentrated to give erroneous fluoride concentrations [4]. Hydroxide ion greater than 1/10 of the fluoride level will interfere positively. Fe^{+3} , Si^{+4} and Al^{+3} give a negative interference. Concentrations $>8 \mu\text{g/mL}$ cannot be suppressed [10]. The TISAB suppresses up to $500 \mu\text{g/mL}$ Fe^{+3} and up to $90 \mu\text{g/mL}$ Si^{+4} .

OTHER METHODS: This revises method 7902 [11] which was withdrawn on 5/15/89. Method 7903 [12] is an alternative method for HF. Ion chromatography is an alternative measurement technique.

REAGENTS:

1. Sodium carbonate (Na_2CO_3).
2. Glycerol.
3. Potassium chloride (KCl).
4. Sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$).
5. Cyclohexylene diamine tetraacetic acid (CDTA).
6. Hydrochloric acid, 1:1 (v/v).
7. Sodium fluoride (NaF).*
8. Deionized (DI) water.
9. Fixative solution. Dissolve 25 g Na_2CO_3 in deionized water. Add 20 mL glycerol. Dilute to 1 L.
10. Total ionic strength activity buffer (TISAB), pH 5.5. Dissolve 37 g KCl , 68 g sodium acetate and 346 g CDTA in H_2O . Adjust to pH 5.5 ± 0.2 with 1:1 HCl . Dilute to 1 L.
11. Calibration stock solution, 100 $\mu\text{g F}^-/\text{L}$. Dissolve 0.2211 g NaF (dried at 105 °C for 2 hrs) in DI H_2O ; dilute to 1 L.
12. Sodium hydroxide, 20% (w/v). Dissolve 200 g NaOH in DI water to make 1 L solutions.

EQUIPMENT:

1. Sampler: Two filter cassettes in line, connected with a short piece of PVC tubing:
 - a. Prefilter: 37-mm, 0.8- μm cellulose ester membrane filter and porous plastic backup pad (Nuclepore Part #220800, or equivalent).
 - b. Treated pad: cellulose backup pad which has been moistened with 0.8 mL fixative solution and dried at 105 °C for 30 to 45 minutes.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Crucibles, nickel or Inconel, 20-mL.
4. Bunsen or Meaker burner.
5. Tripod.
6. Triangle, ceramic-covered.
7. Volumetric flasks, 50- and 100-mL, and 1-L.
8. Pipets, appropriate sizes for standards.
9. Beakers, plastic, 100-mL or 150-mL.
10. Magnetic stirrer.
11. PTFE-coated stirring bars.
12. Fluoride ion selective electrode (ISE), combination or with calomel-type reference electrode.
13. pH/ion meter with millivolt readout and pH electrode.

*see SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Fluorides are extremely corrosive to skin, eyes and mucous membranes [13]. Perform all fusions in fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 12 to 800 L. Do not exceed 2 mg total dust loading on the filter.
3. Separate and cap the two filter cassettes for shipment.

SAMPLE PREPARATION:

4. Prefilter (particulate fluoride).
 - a. Transfer the membrane filter to a crucible containing 5 mL 20% NaOH .
 - b. Evaporate to dryness.
 - c. Heat residue to fusion temperature, hold 1 to 2 min, cool and dissolve in ca. 5 mL DI H_2O .
 - d. Transfer sample into 100-mL plastic beakers.
 - e. Rinse crucible with 25 mL of TISAB then with a few drops of 1:1 HCl .
 - f. Adjust to pH 5.5 ± 0.2 using 1:1 HCl .
 - g. Transfer to 50-mL volumetric flask; dilute to volume with DI H_2O .

NOTE 1: Water-soluble particulate fluorides may be extracted by the procedure for gaseous fluorides. Insoluble particles require fusion.

NOTE 2: For ion chromatographic analysis, follow steps a to c, but do not add water at step c. Instead, transfer sample to 150 mL plastic beaker, add 100 mL of DI water using volumetric pipet, and then place in an ultrasonic bath for 15 to 20 minutes. Withdraw an aliquot of this solution, dilute 1:40 with DI water, and filter into sample vials for analysis.

5. Treated pad (gaseous fluoride).

- Open cassettes and transfer treated pads to 100-mL plastic beakers.
- Add 25 mL TISAB and 25 mL deionized water.
- Soak pad for 30 min with sufficient stirring to reduce it to pulp.

NOTE: For ion chromatographic analysis, place sample into 150 mL beaker and add only 100 mL deionized water (do not add TISAB). Place in an ultrasonic bath for 15 to 20 minutes. Filter into sample vials for analysis.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 0.003 to 1.2 mg F⁻ per sample.

- Add known amounts of calibration stock solution to 25 mL TISAB and 5 mL 20% NaOH (particulate fluoride) or 25 mL TISAB (gaseous fluoride) in 100-mL beakers.
 - Adjust pH to 5.5 ± 0.2 with 1:1 HCl.
 - Transfer to 50-mL volumetric flasks. Dilute to the mark with DI water.
- NOTE: Working standards are stable at least one month in polyethylene bottles at 4 °C.
- Analyze together with samples and blanks (steps 7 through 10).

- Prepare separate calibration graphs (mV vs. log F⁻ concentration) for particulate and gaseous fluorides.

NOTE 1: Calibration curve is not linear below 0.1 µg/mL or above 25 µg/mL.

NOTE 2: For ion chromatography, prepare calibration samples by addition of known amounts of stock fluoride solution to deionized water. Filter into vials. Use multi-anion standard, containing fluoride and acetate, to ensure that these ions are resolved. Analyze these standards together with the blanks and samples.

MEASUREMENT:

7. Bring sample and standard solutions to room temperature.

NOTE: Temperature of samples and standards must be equal (± 2 °C) for accurate results.

8. Pour ca. 20 mL of each solution into plastic beakers.

9. Add magnetic stir bar, insert electrodes and gently stir on magnetic stirrer.

10. Record potential (mV) after 2 min.

NOTE 1: If measured concentration of F⁻ is >25 µg/mL, dilute with appropriate matrix (step 6), reanalyze and apply dilution factor in calculations.

NOTE 2: Samples can be analyzed by ion chromatography (IC) using 5 mM tetraborate (Na₂B₄O₇) eluent, at 2 mL/min, with a fast run anion separator column (Dionex AG4A, or equivalent), and an anion suppressor (Dionex AMMS, or equivalent). Measure peak height using a conductivity detector set at 10 µS full scale, for each sample injection (50 µL).

CALCULATIONS:

- Using the proper calibration graph (particulate or gaseous), convert potential (mV) to solution fluoride concentration, C_s (µg/mL), in the solution volume, V_s (mL).
- Calculate the concentration of fluoride, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{C_s V_s}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Measurement precision, s_p , in the range 0.055 to 0.22 mg HF per sample averaged 0.017 with average recovery of 100.0% [3]. Analytical results on field samples report detection limits of 3 μg per sample for both gaseous and particulate fluorides [2]. Reported collection ranges for gaseous fluoride and particulate fluorides were 4 to 61 μg per sample and 4 to 410 μg per sample, respectively [11].

NOTE: With ion chromatographic analysis the following performance criteria were determined. The limit of detection (LOD) for the front (particulate fluoride) section was estimated at 120 μg fluoride per sample, with a range of 0.12 to 10 mg fluoride per sample. The LOD for the rear (gaseous fluoride) section was estimated at 3 μg fluoride per sample, with a range of 0.003 to 0.25 mg fluoride per sample. The precision (s_p) was determined to be 0.019 over the range 13 to 250 μg per sample for the rear treated pad. The precision (s_p) for the front filter was estimated to be 0.066 at 250 μg per sample.

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- [12] NIOSH Manual of Analytical Methods, 3rd. Ed., Method No. 7903 (Acids, Inorganic), Vol. 2 (1984).
- [13] NIOSH/OSHA Occupational Health Guidelines to Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY: Charles Lorberau, NIOSH/DPSE, and originally written by M. E. Cassinelli, NIOSH/DPSE.

FORMULA: HCOOH

FORMIC ACID

2ND EDITION METHOD #: S173

DATE ISSUED: 05/12/78

M.W.: 46.03

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 5 ppm

NIOSH: TWA 5 ppm

ACGIH: TWA 5 ppm

(1 ppm = 1.88 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.22 g/mL @ 20 °C;

BP 108 °C;

VP 4.4 kPa (33 mm Hg) @ 20 °C;

vapor density (air=1) 1.6

SYNONYMS: CAS #64-18-6

SAMPLER: two solid sorbent tubes in series, Chromosorb 103, 50 mg per tube

FLOW RATE: 0.05-0.2 L/min

RECOMMENDED VOLUME: ≤ 25 L

MEASUREMENT TECHNIQUE: ion chromatography, conductivity detection

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: Dionex HPIC-AS4A column may be used for high-efficiency anion separations; gradient elution techniques may produce better separations of early-eluting peaks

MEASUREMENT CALIBRATION: standard solutions of formic acid in high-purity water in the range 2 to 400 µg formate ion per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 µg formate ion per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: NIOSH is investigating the use of silica gel instead of Chromosorb as sorbent for the sampling to improve the breakthrough capacity [1]

OTHER METHODS AND/OR LITERATURE REFERENCES:

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- [4] Beine, H. Method for Continuous Automatic Determination of Formic Acid in Industrial Emissions, Essen, 57, 26-30 (1983).
- [5] Kawamura, K., et al. Determination of Volatile Organic Acids in the Atmosphere, Environ. Sci. Technol., 19(11), 1082-86 (1985).

Formic Acid

Analyte:	Formate Ion	Method No.: S173
Matrix:	Air	Range: 4.4-21.6 mg/cu m
OSHA Standard:	5 ppm (9 mg/cu m)	Precision ($\overline{CV}_T$): 0.073
Procedure:	Adsorption on Chromosorb 103, desorption with deionized water, ion chromatography/electrolytic conductivity detection	Validation Date: 5/12/78

1. Synopsis

- 1.1 A known volume of air is drawn through two glass tubes connected in series containing Chromosorb 103 to trap formic acid vapors. A Teflon prefilter is connected in front of the Chromosorb 103 tubes to remove interfering formate salts.
- 1.2 Formic acid is desorbed from the Chromosorb 103 with deionized water and the sample is analyzed by ion chromatography using electrolytic conductivity detection.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 4.4-21.6 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 759 mm Hg, using a 24-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Chromosorb 103. This capacity may vary with the concentrations of formic acid and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 50 mg of Chromosorb 103) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 302 minutes at an average sampling rate of 0.18 liter/minute and relative humidity of 85% and temperature of 22°C. The breakthrough test was conducted at a concentration of 25 mg/cu m.

S173-1

- 2.3 The sensitivity of the method for the instrumental conditions used during the validation study was 7 $\mu\text{mho/cm}/\mu\text{g}$ formate ion. In other words, a 100-microliter injection of a 22 microgram/mL solution of formic acid gave a peak whose height was 50% of full scale on a 1-volt recorder when the ion chromatograph was set on range 30 $\mu\text{mho/cm}$.
- 2.4 The detection limit of the analytical method is estimated to be 2 micrograms formic acid/sample tube. This corresponds to a 100-microliter aliquot of a 0.2 microgram/mL standard.

3. Interferences

- 3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Any compound that has the same retention time as the formate ion at the operating conditions described in this method is an interference. Retention time data cannot be considered proof of chemical identity.
- 3.3 Formate esters may interfere only if collected by the sorbent and subsequently hydrolyzed to formic acid.
- 3.4 A Teflon prefilter is connected in front of the sampling tubes to remove formate salts which may interfere in the analysis of formic acid.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 4.4-21.6 mg/cu m was 0.073. This value corresponds to a 0.7 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.
- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5X, 1X, and 2X the OSHA environmental limit averaged 3.8% lower than the dynamically generated test concentrations (n=16). The desorption efficiency was determined to be 1.002 for a collector loading of 106.4 micrograms. In storage stability studies, the mean of samples analyzed after 7 days were within 8.5% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions or by use of the prefilter in front of the collection tubes. The tubes are analyzed by means of a quick, instrumental method.

- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of formic acid found on the backup Chromosorb 103 tube exceeds 25% of that found on the front tube, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one set of tubes only.

6. Apparatus

- 6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate is needed. Each personal sampling pump must be calibrated with a representative prefilter, front and backup Chromosorb 103 tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 6.2 Prefilter Unit. The prefilter unit is used to collect interfering formate salts. It consists of a 13-mm filter holder and a 13-mm diameter/5-micrometer pore size Teflon filter.
- 6.3 Chromosorb 103 Tubes. Glass tube with both ends unsealed, 7-cm long with a 6-mm O.D. and a 4-mm I.D., containing 60/80 mesh Chromosorb 103*. The tube contains 50 mg of Chromosorb 103. A plug of silylated glass wool is placed at each end of the tube to retain the sorbent. Two tubes connected in series with a short piece of polyvinyl chloride tubing are used for sampling. The pressure drop across the prefilter and tubes must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.
- Immediately prior to packing, the empty glass tubes should be rinsed with acetone and dried to eliminate the problem of Chromosorb 103 adhering to the walls of the glass tubes. The tubes are capped with plastic caps at each end.
- 6.4 Ion chromatograph** equipped with a 100-microliter sample loop and an electrolytic conductivity detector.
- 6.5 Columns: 3-mm I.D. x 150-mm long anion precolumn; 3-mm I.D. x 500-mm long anion analytical column; 6-mm I.D. x 250-mm long anion suppressor column.**

* Chromosorb 103 is a polymeric gas chromatographic column packing material which is manufactured by Johns-Manville Corp., Ken-Caryl Ranch, Denver, Colorado.

** Dionex Corp., Model 10 or 14, 1228 Titan Way, Sunnyvale, CA.

- 6.6 Filtration unit for protection of the anion analytical column from particulate contamination: 13-mm diameter/0.8 micrometer pore size cellulose ester membrane filter and holder.
- 6.7 Syringes: 10-mL with luer-lock or luer-slip connection.
- 6.8 Scintillation Vials: 20 mL.
- 6.9 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.10 Volumetric Pipets: Convenient sizes for preparing standard solutions.
- 6.11 Ruler with mm graduations.
- 6.12 Stopwatch.
- 6.13 Manometer.
- 6.14 Thermometer.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

- 7.1 Acetone.
- 7.2 Formic acid, 88%.
- 7.3 Sodium formate. This reagent is used to standardize the formic acid stock solution. Sodium formate should be dried in an oven at approximately 110°C for 4 hours and stored in a desiccator.
 - 7.3.1 Prepare a stock solution containing 1.503 g sodium formate/liter deionized water. This solution contains 995 micrograms formate ion/mL.
 - 7.3.2 From the stock solution prepare at least 3 working standards in the range of 9.95-39.8 µg/mL formate ion.
 - 7.3.3 Analyze the working standards as described in Sections 8.3.3-8.3.8.
 - 7.3.4 Prepare a standard calibration curve by plotting concentration of formate ion in µg/mL versus peak height. This curve is used to determine the concentration of the formic acid stock solution.
- 7.4 Deionized water.
- 7.5 Dioxane.

- 7.6 Formic acid stock solution (~~1.074~~ ^{1.078} mg/mL formic acid in water). Add 1 mL of 88% formic acid to a 100-mL volumetric flask and make to volume with deionized water. This solution must be prepared fresh daily. To accurately determine the concentration of this solution, analyze this solution as described in Sections 8.3.3-8.3.8. Read the concentration from the calibration curve prepared in Section 7.3.4.
- 7.7 Formic acid solution for determining desorption efficiency (~~27~~ ⁵¹ mg/mL formic acid in dioxane). Pipet 6 mL of 88% formic acid into a 125-mL volumetric flask and make to volume with dioxane. Prepare fresh daily.
- Note: All standards must be prepared fresh daily. Loss of formic acid was observed after 24 hours. Pipetting below the liquid level of the standard will minimize loss of formic acid from evaporation. If loss of formic acid is suspected, the formic acid standard should be standardized against sodium formate as described above.
- 7.8 Ion chromatograph eluant, 0.0025 M Na₂B₄O₇·10 H₂O. Add 3.82 g Na₂B₄O₇·10 H₂O to 4 liters of deionized water. Dissolve the salt, then filter to remove particles which are greater than 1 micrometer.
- 7.9 0.1 M Na₂B₄O₇·10 H₂O. Add 145 g Na₂B₄O₇·10 H₂O to 4 liters of deionized water. Filter the solution to remove particles greater than 1 micrometer. This is used to clean the analytical column.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and deionized water, and dried.
- 8.2 Collection and Shipping of Samples
- 8.2.1 Immediately before sampling, remove the caps from the ends of the Chromosorb 103 tubes. All tubes must be packed with Chromosorb 103 from the same manufacturer's lot.
- 8.2.2 Two tubes connected in series are used for sample collection. The tubes are connected with a short piece of polyvinyl chloride tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The tube nearest the sampling pump is the backup tube. A prefilter is connected in front of the sampling train to remove interfering formate salts.
- 8.2.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Chromosorb 103.
- 8.2.4 Air being sampled should not be passed through any hose or tubing before entering the prefilter.

- 8.2.5 A sample size of 24 liters is recommended. Set the flow rate as accurately as possible using the manufacturer's directions. Sample at a flow rate between 0.05 and 0.2 liter/minute. Do not sample at a flow rate less than 0.05 liter/minute. Record sampling time, flow rate, and type of sampling pump used.
- 8.2.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.2.7 The Chromosorb 103 tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Chromosorb 103 tube with the corresponding backup Chromosorb 103 tube. The prefilter should be removed from the filter cassette and discarded. The filter cassettes should be cleaned and saved for future use.
- 8.2.8 With each batch or partial batch of ten samples, submit one set of tubes (two Chromosorb 103 tubes) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label these tubes as the blanks.
- 8.2.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Chromosorb 103 tubes. A minimum of 18 extra Chromosorb 103 tubes should be provided for desorption efficiency determinations.

8.3 Analysis of Samples

- 8.3.1 Desorption of Formic Acid. Remove the plastic caps from both ends of the front Chromosorb 103 tube and transfer the entire contents of the tube to a 20-mL scintillation vial. This is accomplished by pushing the contents out of the tube with a clean glass rod. Pipet 10 mL of deionized water through the empty tube into the vial. Cap the vial.

The backup Chromosorb 103 tube should be handled in a similar manner, using a separate vial. The two samples are analyzed separately.

- 8.3.2 Shake the sample vigorously. Desorption is complete in 5 minutes. Analysis should be completed the same day the formic acid is desorbed.

- 8.3.3 Ion Chromatograph Conditions. The typical operating conditions for the ion chromatograph are:

Column Temperature: Ambient
Pump: 25% of total capacity
Column Pressure: 400 psig
Flow Rate: 165 mL/hr
Mobile Phase: 0.0025 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$

- 8.3.4 Filtration and Injection. The sample is drawn into a 10-mL syringe. The filtration unit with filter is attached to the syringe and about 1 mL of the sample is flushed through the sample loop of the ion chromatograph. The sample is then injected onto the ion exchange columns. The syringe and filter unit should be rinsed with deionized water between injections. The filter should be changed when the pressure required to expel the sample through the filter unit increases.
- 8.3.5 The columns are flushed with 0.1 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ for one minute after the formate ion has eluted. This procedure removes later eluting ions quickly from the column. The eluting solvent is then replaced with the normal 0.0025 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ solution. The ion chromatograph is ready for the next sample when a baseline is reestablished.
- 8.3.6 The peak height of the sample peak is measured in mm with a ruler and the results are read from a standard curve prepared as discussed in Section 9. It is not recommended to quantitate sample peaks using an electronic area integrator. The output of the ion chromatograph is not compatible with most electronic integrators and reproducible results cannot be obtained.
- 8.3.7 Concentration levels that exceed the range of the calibration curve should be diluted appropriately.
- 8.3.8 Sample blanks must be analyzed following the same procedure as that used for the samples.

8.4 Determination of Desorption Efficiency

- 8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 103 to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Chromosorb 103.
- 8.4.2 Chromosorb 103 sample tubes, prepared as described in Section 6.3 are used to determine desorption efficiency. The Chromosorb 103 must be from the same batch as that used in obtaining the samples. A known amount of a dioxane solution of formic acid containing 27 mg/mL (Section 7.7) is injected

directly into the Chromosorb 103 with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 24-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the formic acid onto the Chromosorb 103. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

8.4.3 To prepare standards at each level, add approximately 7 mL of deionized water to each of three 10-mL volumetric flasks. Deliver 2, 4, and 8 microliters of the 27 micrograms/mL stock solution to each flask under the surface of the water, then bring the volume to 10 mL.

8.4.4 The desorption efficiency (D.E.) equals the average weight in micrograms recovered from the tube divided by the weight in micrograms added to the tube, or

$$\text{D.E.} = \frac{\text{Average weight recovered } (\mu\text{g}) - \text{Blank } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

The desorption efficiency may be dependent on the amount of formic acid collected on the Chromosorb 103. Plot the desorption efficiency versus weight of formic acid found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

- 9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same ion chromatograph conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/10 mL versus peak height. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done.
- 9.2 From the stock standard solution of formic acid in deionized water (Section 7.6), appropriate aliquots are withdrawn and dilutions are made in deionized water. Prepare at least 5 working standards to cover the range of 20-650 micrograms/10 mL. This range is based on a 24-liter sample.
- 9.3 Analyze the standards as described in Section 8.3.
- 9.4 Prepare a standard calibration curve by plotting concentration of formic acid in micrograms/10 mL versus peak height.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak height from the standard curve. No volume corrections are needed because the standard curve is based on micrograms/10 mL deionized water and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front sample tube}$$

$$\mu\text{g blank} = \mu\text{g found in front blank tube}$$

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.4) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled (liters/min)

t = sampling time (min)

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.6 The concentration of formic acid in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liters/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of formic acid
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Backup Data Report for Formic Acid, prepared under NIOSH Contract No. 210-76-0123.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{Cl}_2\text{C}=\text{CCl}-\text{CCl}=\text{CCl}_2$

HEXACHLOROBUTADIENE

2ND EDITION METHOD #: P&CAM 307

DATE ISSUED: 06/28/79

M.W.: 260.76

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 1.665 g/mL @ 20±5 °C;

BP 217 °C;

VP 2.9 kPa (22 mm Hg) @ 100 °C

OSHA: TWA 0.02 ppm

NIOSH: carcinogen; TWA 0.02 ppm (skin)

ACGIH: TWA 0.02 ppm (skin); Susp. Human Carcinogen

(1 ppm = 10.67 mg/m³ @ NTP)

SYNONYMS: perchlorobutadiene; CAS #87-68-3

SAMPLER: XAD-2 tube, 100 mg/50 mg

FLOW RATE: 0.05 to 0.2 L/min

RECOMMENDED VOLUME: ≤100 L

MEASUREMENT TECHNIQUE: gas chromatography, ⁶³Ni electron capture detector

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples;

media blanks, 6 to 12 for desorption efficiency study

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION:

standard solutions of hexachlorobutadiene in hexane in the range 0.02 to 6 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.02 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH health hazard evaluations [1], all work done on 7 cmx4 mm charcoal tubes containing 100 mg in front section and 50 mg in back section

APPLICABILITY: other chlorinated compounds such as perchloroethylene and hexachloroethane which are likely to be present along with hexachlorobutadiene in air can be separated under the same conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH/DPSE, Analytical Sequence Nos. 5188, 5207, 5266, 5781, Measurement Research and Support Branch, Cincinnati, Ohio, NIOSH (unpublished 1986-87).

[2] Dillon, K.H., Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds, NIOSH Contract No. 210-78-0012 (1980).

[3] U.S. EPA Method No. 625, A Gas Chromatography/Mass Spectrometric Method for the Analysis of Hexachloro-1,3-Butadiene, 40 CFR, 136 (1987).

HEXACHLOROBUTADIENE

Measurements Research Branch

Analytical Method

Analyte:	Hexachlorobutadiene	Method No.:	P&CAM 307
Matrix:	Air	Range:	10 to 2000 $\mu\text{g}/\text{m}^3$ in 3 L of air
Procedure:	Adsorption on Amberlite XAD-2, desorption with hexane, GC-ECD	Precision:	9%
Date Issued:	6/28/79		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

- 1.1 A known volume of air is drawn through an XAD-2 tube to trap the hexachlorobutadiene present.
- 1.2 The XAD-2 in the tube is transferred to a small vial where the hexachlorobutadiene is desorbed with hexane.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The height of the resulting peak is determined and compared with the peak heights obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The sampling and analytical method was tested with nominal sample loadings of 20 to 6000 ng of hexachlorobutadiene per 100-mg bed of XAD-2. The samples were collected from atmospheres containing hexachlorobutadiene in the approximate range of 10 to 2000 $\mu\text{g}/\text{m}^3$ at 25 to 28 °C and at a relative humidity of 90% or greater.
- 2.2 The slope of the analytical calibration curve was 5×10^{-3} A/pg when peak heights were plotted as a function of the amount of hexachlorobutadiene injected. (There was a slight curvature in the calibration curve. See Section 9.)
- 2.3 The lowest analytically quantifiable level for this method was determined to be 20 ng of hexachlorobutadiene per sorbent sample extracted with 2.00 mL of hexane. At this level, the relative standard deviation for replicate samples was found to be less than 3%, and desorption was quantitative. The instrumental detection limit was

0.8 ng/mL of hexachlorobutadiene in hexane; the relative standard deviation of replicate determinations of standards at this level was 10%.

3. Interferences

- 3.1 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of hexachlorobutadiene.
- 3.2 Any substance that has the same retention time as hexachlorobutadiene with the gas chromatographic operating conditions described in this method is an interferent. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.
- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, carrier flow, detector, etc.) must be changed to circumvent the problem.
- 3.4 The gas chromatographic operating conditions described below will separate tetrachloroethylene, hexachloroethane, 1,2,4-trichlorobenzene, hexachlorocyclopentadiene, octachlorocyclopentene, and 4-chlorobiphenyl from hexachlorobutadiene. These compounds are among those likely to be collected along with hexachlorobutadiene in air (see Reference 11.1).

4. Precision and Accuracy

- 4.1 For the overall sampling and analytical method, the pooled relative standard deviation was 9% for 24 sorbent samples collected in the approximate range of 10 to 2000 $\mu\text{g}/\text{m}^3$. The pooled relative standard deviation for the analytical method was 3.0% for 18 sorbent samples spiked with 4 to 33 ng of hexachlorobutadiene. For six sorbent samples spiked with 3000 ng, the relative standard deviation for the analytical results was 0.8%.
- 4.2 The concentration of hexachlorobutadiene in test atmospheres was determined in control experiments by sampling the bubblers containing hexane and subsequently analyzing the bubbler solutions by gas chromatography. The determinations with sorbent sampling gave values that averaged 85 to 100% of those found by bubbler sampling over the range of the method.
- 4.3 The breakthrough volume of the sorbent tube was found to be greater than 100 L with a sampling rate of 0.2 L/min at a hexachlorobutadiene concentration of 10 mg/m^3 , a sampling temperature of 25 to 28 °C, and a relative humidity greater than 90%. Elevation of the sampling temperature to 38 °C significantly reduced the capacity; however, the breakthrough volume of a 100-mg sorbing section was still estimated to be greater than 100 L at a hexachlorobutadiene concentration of about 1 mg/m^3 and a relative humidity of about 50%.

- 4.4 Samples of hexachlorobutadiene on XAD-2 were found to be stable at 25 °C for 7 d and for 28 d if stored at 0 °C after the seventh day. These samples were stored in the dark.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the gas chromatographic procedure. The samples are analyzed by means of a quick instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the XAD-2 tube. When the sample value obtained for the backup section of the XAD-2 tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage the analyte may migrate throughout the tube until equilibrium is reached; however, no migration of 20- to 30-ng amounts of hexachlorobutadiene was observed after storage for 28 d when the samples were refrigerated (0 °C) after the seventh day.
- 5.3 Another disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 Personal sampling pump capable of accurate performance ($\pm 5\%$) at 0.05 to 0.2 L/min and calibrated with a representative tube in the line.
- 6.2 XAD-2 tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d. containing two sections of Amberlite XAD-2 (35/50 mesh)—a 100-mg sorbing section and a 50-mg backup section—held in place with three silylated glass wool plugs. The tubes are constricted slightly about 1 cm from the outlet end to facilitate the packing of the tube with sorbent material. The ends of the tubes are sealed with Teflon tape and then with plastic caps to prevent contamination during storage. The pressure drop across a typical sorbent tube is less than 4 in. H₂O at 25 °C, 1.0 kPa, at a sampling rate of 0.2 L/min. During the preparation of sorbent tubes, avoid undue agitation of the sorbent particles. A static charge can be induced that will cause the particles to agglomerate. This may reduce the capacity of the sorbent tube.
- 6.3 Purified XAD-2 (available from Applied Science Laboratories, Inc.) is used to pack the tubes without further treatment. If the purified XAD-2 is unavailable, gram quantities of the XAD-2 should be cleaned by Soxhlet extraction as follows:
- Extract with an acetone-methanol mixture (80:20) for 4 h.
 - Extract with hexane for 4 h.

- Dry the sorbent material under vacuum at 50 to 75 °C overnight.
- Cool and store in a clean dessicator.

(If 2-mL hexane extracts of 100-mg amounts of the washed XAD-2 yield anomolous peaks in the GC analysis procedure, repeat the cleaning procedure.)

- 6.4 Gas chromatograph equipped with a ^{63}Ni electron capture detector.
- 6.5 Glass GC column (4 mm i.d. by 2 m long) packed with 3% OV-1 on Gas-Chrom Q (100/120 mesh).
- 6.6 Vials, 5 mL, with serum caps containing Teflon-lined silicone rubber septa.
- 6.7 Microliter syringes, 10 μL and convenient sizes for making dilutions.
- 6.8 Pipets 1.00 mL, 2.00 mL, and convenient sizes for making dilutions.
- 6.9 Glass wool, silanized.
- 6.10 Ultrasonic bath.

7. Reagents

All reagents used should be ACS Reagent Grade or better.

- 7.1 Hexane, spectroquality.
- 7.2 Hexachlorobutadiene, 98% or purer.
- 7.3 A mixture of 5% methane and 95% argon (or other appropriate carrier and purge gas for the electron capture detector).

8. Procedure

- 8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, distilled water, acetone, and hexane (in that order).
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling, open the ends of the tube by removing the plastic caps and Teflon tape. Examine the ends of the tube to ensure that the openings are at least one-half the internal diameter of the tube (2 mm).
 - 8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of XAD-2 is the backup layer and is positioned nearest the sampling pump.

- 8.2.3 Place the XAD-2 tube in a vertical position during sampling to prevent channeling through the tube.
- 8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.2.5 Measure and report the flow rate and time or volume sampled. The sample is taken at 0.05 to 0.2 L/min. The maximum volume sampled should not exceed 100 L at 0.2 L/min at temperatures near 25 °C. At high humidity (>90%) accompanied by temperatures near 40 °C, do not sample more than about 50 L.
- 8.2.6 The temperature and pressure of the air being sampled are measured and reported.
- 8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps and store the tubes in the dark.
- 8.2.8 For every 10 samples taken, process one XAD-2 tube not exposed to hexachlorobutadiene in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank.
- 8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.
- 8.2.10 Ship 6 to 12 unopened XAD-2 tubes so that desorption efficiency studies can be performed on the same type and lot of XAD-2 used for sampling.
- 8.2.11 Log and refrigerate samples as soon as they are received in the laboratory.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Remove the XAD-2 tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of XAD-2 in a tube to a separate 5-mL vial. Add the glass wool plug near the tube inlet to the vial containing the sorbing section; add the other two glass wool plugs to the vial containing the backup section.
- 8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 2.00 mL of hexane into the vial containing the sorbing section and 1.00 mL into the vial containing the backup layer. Crimp a serum cap into place immediately after the hexane has been added. Extract the sealed sorbent samples by ultrasonification for 1 h at room temperature.

8.3.3 GC Conditions

- Carrier flow, 30 mL/min.
- Purge flow, 80 mL/min.
- Injection port temperature, 150 °C.
- Detector temperature, 250 °C.
- Column temperature, 135 °C.

8.3.4 Injection. Inject a 5- μ L aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 μ L of hexane as the solvent flush. Maintain a 1- μ L air gap between the solvent flush and the 5- μ L aliquot.

8.3.5 Measurement of Peak Height. Multiply the peak height by the attenuator setting necessary to keep the peak on scale. Determine the apparent concentration from a standard curve prepared as discussed in Section 9. If the peak height indicates an apparent concentration above 100 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of XAD-2. Also, for a given batch of XAD-2 the desorption efficiency may vary with the weight of contaminant adsorbed. (The XAD-2 used for the study of this method gave a desorption efficiency of 1.000 for a loading of 16.7 ng of hexachlorobutadiene on a 50-mg bed of sorbent material.)

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve hexachlorobutadiene in hexane to give stock solutions with concentrations such that 20 to 6000 ng of hexachlorobutadiene will be injected onto the sorbent in no more than 5 μ L of a stock solution. Place XAD-2 in an amount equivalent to that found in the larger section of the tube (100 mg) in a small vial and cap the vial. Inject an aliquot of the appropriate stock solution into the vial. Allow each vial to stand overnight to assure complete adsorption of hexachlorobutadiene onto the XAD-2. Prepare standards by injecting an identical amount of hexachlorobutadiene solution into 2.00 mL of hexane. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of hexachlorobutadiene found in a sample versus the desorption efficiency.

9. Calibration and Standardization

CAUTION: Hexachlorobutadiene has been identified as a suspect carcinogen. Precautions must be taken while handling this compound to prevent contamination of personnel and the working area.

To make a stock standard solution, dilute 1.00 mL (1.67 g) of hexachlorobutadiene to 100 mL with hexane. By serial dilution with hexane prepare a series of working standards varying in concentration over the range of 1-100 ng/mL. Follow the dilution scheme presented below:

<u>Initial concn</u>	<u>Aliquot volume, mL</u>	<u>Final diluted volume, mL</u>	<u>Final concn</u>
1.67 g/mL	1	100	16.7 mg/mL
16.7 mg/mL	1	100	167 µg/mL
167 µg/mL	1	100	1.67 µg/mL
1.67 µg/mL	1	10	167 ng/mL
167 µg/mL	1	10	16.7 ng/mL
167 µg/mL	2	10	33.4 ng/mL
167 µg/mL	4	10	66.8 ng/mL
167 µg/mL	6	10	100.2 ng/mL
16.7 ng/mL	2	25	1.34 ng/mL
16.7 ng/mL	5	10	8.35 ng/mL

Analyze the standard solutions under the same GC conditions and during the same time period as the samples. Alternate standards and samples during the analysis. To establish a calibration curve plot the concentration of the standards in ng/2 mL (or ng/sample) versus peak height. The plot has a slight curvature but the deviation from linearity is small below a concentration of 100 ng/mL (200 ng/2 mL). To ensure accurate analyses, determine standards at concentrations about 25% above and below the apparent sample concentration.

10. Calculations

10.1 Read the sample weight in ng from the standard curve.

10.2 Blank corrections are not expected to be necessary but, if the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (ng) on the front section of the XAD-2 tube.

W_s = amount (ng) found on the front section of the XAD-2 tube.

W_b = amount (ng) found on the front section of the blank XAD-2 tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (ng) in the front section.

W_F = amount (ng) after blank correction.

D = desorption efficiency corresponding to the weight W_F .

Calculate the corrected amount on the backup section, M_B , similarly.

10.4 Express the concentration, C , of hexachlorobutadiene in the air sampled in $\mu\text{g}/\text{m}^3$, which is numerically equal to ng/L.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = amount (ng) of hexachlorobutadiene found on front section.

M_B = amount (ng) of hexachlorobutadiene found on backup section.

V = volume (L) of air sampled.

10.5 If desired, the results may be expressed in ppb at 25 °C (298 °K) and 760 torr.

$$C(\text{ppb}) = C(\text{ng/L}) \times \frac{24.45}{260.76} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature (°C) of air sampled.

24.45 = molar volume (L/mol) at °C and 760 torr.

260.76 = molecular weight (M_r) of hexachlorobutadiene.

11. References

- 11.1 "Backup Data Report for Hexachlorobutadiene," prepared under NIOSH Contract No. 210-78-0012.
- 11.2 Taylor, D. G.; Kupel, R. E.; Bryant, J. M., "Documentation of the NIOSH Validation Tests"; National Institute for Occupational Safety and Health; Cincinnati, Ohio, April 1977. DHEW (NIOSH) Publication No. 77-185.

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Southern Research Institute
NIOSH Contract No. 210-78-0012

HYDROGEN CYANIDE

M.W.: 27.03

METHOD: 6010

ISSUED: 5/15/89

REVISION #1: 8/15/90

OSHA: STEL 4.7 ppm
NIOSH: STEL 4.7 ppm [1]
ACGIH: 10 ppm/10 min (skin)
(1 ppm = 1.11 mg/m³ @ NTP)

PROPERTIES: gas; d 0.94 (air = 1.00) g/mL @ 26 °C;
d(liq) 0.69 g/mL @ 20 °C; BP 26 °C;
VP 82.7 kPa (620 mm Hg) @ 20 °C;
explosive range 5 to 40% v/v in air

SYNONYMS: hydrocyanic acid, prussic acid; CAS #74-90-8

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (soda lime, 600 mg/200 mg)	! TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION !
FLOW RATE: 0.05 to 0.2 L/min	! ANALYTE: cyanide ion complex !
VOL-MIN: 0.6 L @ 5 ppm -MAX: 90 L	! DESORPTION: 10 mL deionized water; stand 60 min !
SHIPMENT: routine	! COLOR DEVELOPMENT: N-chlorosuccinimide/ succinimide oxidizing agent and barbituric acid/pyridine coupling agent; absorption @ 580 nm in 1-cm cuvette !
SAMPLE STABILITY: at least 2 weeks @ 25 °C [2]	!
FIELD BLANKS: 10% of samples	! CALIBRATION: standard solutions of KCN in 0.1 N NaOH !
	! RANGE: 3 to 300 µg CN ⁻ per sample [2] !
<u>ACCURACY</u>	! ESTIMATED LOD: 1 µg CN ⁻ per sample [2] !
RANGE STUDIED: 2 to 15 mg/m ³ [2] (3-L samples)	! PRECISION (s_p): 0.041 @ 10 to 50 µg per sample [2] !
BIAS: Not significant [2]	!
OVERALL PRECISION (s_p): 0.076 [2]	!

APPLICABILITY: The working range is 1 to 260 mg/m³ (0.9 to 235 ppm) for a 3-L air sample. The method is applicable to STEL measurements. Particulate cyanides are trapped by the glass fiber membrane. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904. The method was used to determine HCN in firefighting environments [3].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference.

OTHER METHODS: This is based on the method of Lambert, et al. [4]. NIOSH Method 7904 uses an ion specific electrode for measurement. This replaces Method 6010 (issued 5/15/89).

REAGENTS:

1. Potassium cyanide*, reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectrophotometric quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, concentrated, reagent grade.
8. Sodium hydroxide (NaOH), reagent grade.*
9. Soda lime (CaO + 5-20% NaOH), reagent grade (Aldrich #26,643-4 or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
10. Water, deionized-distilled.
11. Sodium hydroxide solution, 0.1 N.*
12. Calibration stock solution, 1 mg CN⁻/mL. Dissolve 0.125 g KCN in 0.1 N NaOH in a 50-mL volumetric flask. Dilute to mark with 0.1 N NaOH.
13. Hydrochloric acid solution, 0.15 N.
14. N-Chlorosuccinimide/succinimide oxidizing reagent. Dissolve 10.0 g succinimide in about 200 mL distilled water. Add 1.00 g N-chlorosuccinimide. Stir to dissolve. Adjust volume to 1 liter with distilled water. Stable 6 months when refrigerated.
15. Barbituric Acid/Pyridine Reagent. Add about 30 mL distilled water to 6.0 g barbituric acid in a 100 mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust the volume to 100 mL with water. Stable 2 months when refrigerated.

EQUIPMENT:

1. Sampler, glass tube, 9 cm long, 7-mm OD, 5-mm ID, with plastic caps, containing two sections (front = 600 mg; back = 200 mg) granular soda lime 10/35 mesh, separated and contained with silanized glass wool plugs, with a 5-mm diameter glass fiber filter disk placed before the plug on inlet side. The sampler tube is available commercially.
2. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm light path.
3. Personal sampling pump, 0.05 to 0.2 L/min., with flexible connecting tubing.
4. Pipets, volumetric 0.1-, 0.5-, 1.0-, 2.0-, 10.0-mL.
5. Vials, glass or plastic, 15-mL with PTFE-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Syringes, 10 µL, readable to .1 µL.
9. Flask, Erlenmeyer, 100 mL.
10. Syringes, 10-mL, polyethylene with luer tip.
11. Filter cassette, with membrane filter, 13-mm diameter, 0.45-µm pore size, with luer fitting.

*See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS:

HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [5]. Soda lime and NaOH are very caustic [5]. Use gloves and a fume hood for handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
4. Cap tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line. Remove and discard glass fiber plugs.

NOTE: Particulate cyanides will be trapped on the glass fiber filter disc at the front of the sampler. An estimate of their concentrations may be obtained by carrying the glass fiber filter disc through the following procedure. However, no evaluation data are available for particulate cyanides determined in this manner.

6. Transfer glass fiber filter discs and front and back sorbent sections to separate vials.
7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section. Add 10.0 mL 0.1 N NaOH to each vial containing a glass fiber filter disc. Cap each vial.
8. Allow to stand 60 minutes, with occasional agitation. Transfer to a 10-mL plastic syringe fitted with an in-line 0.45- μ m filter. Collect the filtrate in a clean vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 3 to 300 μ g CN⁻ per sample.
 - a. Prepare a working standard solution, 1.00 μ g CN⁻/mL, by diluting 100 μ L of calibration stock solution to 100 mL with 0.1 N NaOH.
 - b. Pipet 0.5-, 1.00-, 1.50-, 2.00- and 2.50-mL of the working standard solution into 25-mL volumetric flasks to make 0.50-, 1.00-, 1.50-, 2.00- and 2.50- μ g CN⁻ standards.
 - c. Analyze together with field samples and blanks (steps 12 through 19).
 - d. Prepare calibration graph (absorbance vs. μ g CN⁻).
10. Determine desorption efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
 - (a) Remove and discard back sorbent section of a blank sampler.
 - (b) Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
 - (c) Cap, and allow to stand overnight.
 - (d) Desorb (steps 5 through 8) and analyze together with working standards (steps 12 through 19).
 - (e) Prepare a graph of DE vs. μ g CN⁻ recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Pipet a sample aliquot estimated to contain 0.5 to 2.5 μ g CN⁻ into a 25-mL volumetric flask. Alternately, pipet 0.5-, 1.00-, and 3.00-mL aliquots into separate 25-mL vol. flasks for each field sample. Larger or smaller aliquots may be taken, based on prior knowledge of expected analyte level.
13. Pipet 0.5 mL 0.1 N NaOH into a 25-mL volumetric flask for reagent blank.
14. Add one drop phenolphthalein solution to each standard or sample.

NOTE: A little deionized-distilled water added increases volume for easier mixing. All solutions should be alkaline (pink) at this point.
15. Starting with the reagent blank, add dropwise 0.15 N HCl, with mixing, until pink color just disappears. CAUTION: HCN may be produced. Work in hood.

NOTE: To avoid possible loss of HCN perform step 16 before proceeding to the next sample.
16. Immediately add 1.0 mL N-chlorosuccinimide/succinimide oxidizing reagent. Mix and let stand. Do not prepare more samples than can be analyzed within the 30-minute maximum time for color development.

17. After at least 5 min. standing (but not longer than 15 min), starting with the reagent blank, add 1.0-mL barbituric acid-pyridine coupling reagent. Mix.
18. Adjust sample volume to 25 mL with deionized-distilled water and allow to stand at least 12 min (but not longer than 30 min) for color development.
19. Read absorbance at 580 nm on a spectrophotometer. If sample absorbance is outside the range of the calibration standards, take an aliquot, re-analyze (steps 12 through 19), and apply the appropriate aliquot factor in calculations.

CALCULATIONS:

20. Calculate the mass, μg , of CN^- in aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, μg , of CN^- in the original 10-mL solution.
21. Determine the mass, μg CN^- (corrected for DE), found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections. If $W_b > W_f/10$, report breakthrough and possible sample loss.
22. Calculate concentration, C, of HCN in the air volume sampled, V(L).

$$C = \frac{(W_f + W_b - B_f - B_b) \times 1.039}{V}, \text{ mg/m}^3$$

where 1.039 = conversion factor, CN^- to HCN

EVALUATION OF METHOD:

The method was evaluated by sampling test atmospheres of HCN generated from a compressed mixture of HCN in nitrogen [2]. The range of HCN concentration was equivalent to 2 to 15 mg/m^3 for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision s_p of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at the flow rate of 0.2 L/min at an HCN concentration of 148 mg/m^3 . Sample tubes spiked with solutions of KCN and analyzed after storage, indicated that the samples of cyanide ions were stable on the tube for at least 2 weeks. Analysis of 22 tubes which were spiked with KCN standard solutions in the range 10 to 50 μg indicated a recovery of nearly 100% with a pooled precision of 0.041.

REFERENCES:

- [1] NIOSH Testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
- [2] Williamson, George. "Method Development Protocol and Backup Data Report on Hydrogen Cyanide" Internal NIOSH/MRSB Report, (Unpubl., NIOSH 1988).
- [3] Williamson, George. "Analysis of Air Samples on Project 166/Firesmoke" Sequence NIOSH/MRSB-6366A, (unpublished, NIOSH, 1988).
- [4] Lambert, J. L., Ramasamy, J., and J. V. Paukstelis, "Stable Reagents for the Colorimetric Determination of Cyanide by Modified Konig Reactions," *Anal. Chem.*, **47**, 916-918 (1975).
- [5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 form NTIS, Springfield, VA 22161.
- [6] Merck Index, 10th ed., Merck & Co. (Rahway, NJ, 1983).

METHOD WRITTEN BY: George Williamson, NIOSH/DPSE.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: H₂S

HYDROGEN SULFIDE

2ND EDITION METHOD #: P&CAM 296

DATE ISSUED: 08/29/80

M.W.: 34.08

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: gas; d (liquid) 1.54 g/mL;
BP -60 °C; VP 20 atm @ 25 °C;
vapor density (air=1) 1.19

OSHA: TWA 10 ppm; STEL 15 ppm

NIOSH: C (10 min) 10 ppm

ACGIH: TWA 10 ppm; STEL 15 ppm

(1 ppm = 1.39 mg/m³ @ NTP)

SYNONYMS: sulfuretted hydrogen; hydrosulfuric acid; hepatic gas; CAS #7783-06-4

SAMPLER: molecular sieve; 400 mg/200 mg

FLOW RATE: 0.15 to 0.2 L/min

RECOMMENDED VOLUME: 5 L

MEASUREMENT TECHNIQUE: gas chromatography, thermal desorption, FPD in sulfur mode

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better sensitivity and specificity

MEASUREMENT CALIBRATION: standard mixtures of H₂S in air or N₂ prepared in Tedlar bags from pure H₂S in the range 14 to 280 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 14 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method may be adapted to other sulfur containing gases

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Kangas, J., and Ryosa, H. The Analysis of Reduced Sulphur Gases in Ambient Air of Workplaces, Chemosphere, 17, 905-914 (1988).
- [3] McKee, E.S., McConnaughey, P.W. Laboratory Evaluation of a Passive Length of Stain Dosimeter for Hydrogen Sulfide, Am. Ind. Hyg. Assoc. J., 47, 475-481 (1986).
- [4] Septon, J.C., Wilczek, T.J. Evaluation of Hydrogen Sulfide Detector Tubes, Appl. Ind. Hyg., 1, 196-198 (1986).

HYDROGEN SULFIDE

Measurements Research Branch

Analytical Method

Analyte:	Sulfide	Method No:	P&CAM 296
Matrix:	Air	Range:	15-60 mg/m ³
Procedure:	Adsorption on molecular sieve, thermal desorption GC-FPD	Precision:	0.066
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

- 1.1 A known volume of air is drawn through a desiccant tube containing sodium sulfate to remove water vapor, followed by a tube containing molecular sieve to trap hydrogen sulfide.
- 1.2 Hydrogen sulfide is desorbed from the molecular sieve using thermal desorption, and the sample is analyzed by gas chromatography.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was evaluated over the range of 15-60 mg/m³ at an atmospheric temperature of 25°C and an atmospheric pressure of 745 mm Hg, using a 5-L sample. This sample size is based on both the capacity of molecular sieve to trap hydrogen sulfide and the sensitivity of the flame photometric detector. The method is capable of measuring smaller amounts, with satisfactory desorption efficiency. (Ref. 11.1) Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the method depends on the adsorption capacity of the molecular sieve. This capacity may vary with the concentrations of hydrogen sulfide and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 400 mg of molecular sieve) reaches 5% of the concentration in the test gas

mixture. A breakthrough test was conducted at a concentration of 17.1 mg/m³ and 85% relative humidity. Breakthrough occurred in 173 minutes at an average sampling rate of 0.137 L/min. This corresponds to a breakthrough capacity of 0.359 mg and volume of 23.7 L.

3. Interferences

- 3.1 Humidity is the single largest interference in this method. It is advantageous to record the relative humidity of a sampling site if possible. Use of the recommended desiccant tube eliminates the effects of humidity when sampling for hydrogen sulfide.
- 3.2 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 Any sulfur containing compound that has the same retention time as hydrogen sulfide at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The relative standard deviation for the total analytical and sampling method in the range of 7.5-30 mg/m³ was 0.066. This value corresponds to a 1.9 mg/m³ standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2.
- 4.2 The relative standard deviation is a good measure of accuracy of the method. Experiments performed in development studies are described in Reference 11.3. In these experiments the desorption efficiency was greater than 0.988 for a loading of 0.1-0.4 mg on the sorbent. On the average, the concentrations obtained at 0.5X, 1X, and 2X the OSHA standard level were 0.07% lower than the "true" concentration for 18 samples collected from dynamically generated test atmospheres. This difference could represent the random variation from the experimentally determined "true" concentration. Storage stability studies indicated that the mean concentration of samples analyzed after seven days was 20% lower than the mean concentration of samples analyzed immediately after collection. Thus, storage represents a source of bias that would need to be corrected in the method.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be

eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

- 5.2 Thermal desorption eliminates the use of desorbing liquids and hence the background disturbance they cause. In doing so, thermal desorption improves sensitivity. In addition, thermal desorption eliminates any lengthy desorption time period.
- 5.3 One disadvantage of the method is the fact that hydrogen sulfide is not stable on molecular sieve. In addition, the capacity of molecular sieve is dramatically reduced in the presence of water vapor (humidity). Use of the recommended desiccant tube eliminates the humidity problem.
- 5.4 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for using one tube only.

6. Apparatus

- 6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the desired flow rate. Each personal sampling pump must be calibrated with a representative molecular sieve and desiccant tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 6.2 Molecular sieve tubes. Glass tube with both ends flame sealed, 7 cm long with a 8-mm O.D. and 6-mm I.D., containing two sections of molecular sieve, 5-angstrom, separated by a 2-mm portion of urethane foam. The adsorbing section contains 400 mg of molecular sieve, the backup section contains 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2.5 inch of mercury at a flow of 0.2 L/min.
- 6.3 Desiccant tubes. The desiccant tube was a 7-cm long Teflon tube with 13-mm I.D. containing 9.0 g of anhydrous sodium sulfate.
- 6.4 Gas chromatograph equipped with a flame photometric detector in the sulfur mode.
- 6.5 Column (36' x 1/8" FEP Teflon) packed with 40/60 mesh Chromosorb T coated with 12% polyphenyl ether and 0.5% H_3PO_4 .

- 6.6 Glass lined thermal desorption unit with a sample splitter or a glass lined thermal desorption unit and a 500-mL evacuated glass vessel with a septum port.
- 6.7 An electronic integrator or some other suitable method of determining peak areas.
- 6.8 Milliliter syringes, 5-mL and other convenient sizes for preparing standards.
- 6.9 Mercury Manometer (if evacuated vessel from 6.6 is used).
- 6.10 Tedlar bags of varying size for H₂S standard preparation.
7. Reagents
 - 7.1 Nitrogen, or equivalent, pre-purified with 99.995% minimum purity.
 - 7.2 Air, or equivalent, dry.
 - 7.3 Hydrogen, or equivalent, pre-purified with 99.995% minimum purity.
 - 7.4 H₂S, or equivalent, 95.5% minimum purity.
 - 7.5 H₂S permeation tube, or equivalent, 230 cm, standard emission from Metronics, Inc.
8. Procedure
 - 8.1 Collection and Shipping of Samples
 - 8.1.1 Immediately before sampling, break the ends of the molecular sieve tube to provide an opening at least one-half the internal diameter of the tube. Uncap the ends of the desiccant tube. The molecular sieve tubes must be from the same manufacturer's lot.
 - 8.1.2 The smaller section of molecular sieve is used as a backup and should be positioned nearer the sampling pump. The dessiccant tube should be connected to the molecular sieve tube (at the end of the tube with the larger amount of molecular sieve) with the shortest possible piece of tubing.
 - 8.1.3 The desiccant and molecular sieve tubes should be placed in a vertical direction during sampling to minimize channeling through the molecular sieve.
 - 8.1.4 Air being sampled should not be passed through any hose or tubing before entering the desiccant tube.

- 8.1.5 A sample size of 5 L is recommended. Sample at a known flow rate of 0.15-0.2 L/min. Record the sampling time, flow rate, and type of sampling pump used.
- 8.1.6 The temperature, pressure and relative humidity of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.1.7 The molecular sieve tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.1.8 With each batch or partial batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.
- 8.1.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Hydrogen sulfide samples must be shipped immediately and in cold storage, if possible, because H₂S does not store well on molecular sieve.

8.2 Analysis of Samples

- 8.2.1 Preparation of Samples. In preparation for analysis, each molecular sieve tube is scored with a file in front of the first section of molecular sieve and broken open. The glass wool is removed and discarded. The molecular sieve in the first (larger) section is transferred to the appropriate housing in the thermal desorption unit. The separation section of foam is removed and discarded; the second section is transferred to a 2-mL stoppered sample vial. These two sections are analyzed separately.
- 8.2.2 Desorption of Samples. The samples are positioned in the thermal desorption unit. One of two steps is taken:
 - 1. For small concentrations, the sample can desorb directly into the gas chromatograph for separation and analysis.
 - 2. For samples of large concentration, the sample must go through a sample splitter or be desorbed into an evacuated vessel of known volume.

The temperature for thermal desorption of H₂S is 180°C.

8.2.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

50 mL/min (50 psig) nitrogen carrier gas flow;
170 mL/min (30 psig) hydrogen gas flow to detector;
200 mL/min (60 psig) air flow to detector;
100°C injector temperature;
50°C column temperature.

A retention time of 2-3 minutes can be expected for H₂S under these conditions and using the column recommended in 6.5.

8.2.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. With thermally desorbed samples, the injection may be carried out in one of two manners:

1. directly from the thermal desorption unit via a heated 3-mL gas sampling loop; or
2. via 3 mL gas-lock syringe injection if the sample was thermally desorbed into the evacuated vessel mentioned in 6.6

Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.2.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.3 Determination of Desorption Efficiency

In practical application, thermal desorption is 100% efficient.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1-2 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/3.0 mL versus peak area. NOTE: Since no internal standard is used in this method, standard gases must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FPD response.

- 9.1 From a gas cylinder of pure hydrogen sulfide and clean, dry air or nitrogen, bag standards should be made up to cover the range of 3 mg/m³ to 70 mg/m³. At least five working standards should be prepared.
- 9.2 Analyze the standards as per Section 8.3.
- 9.3 Prepare a standard calibration curve by plotting concentration of hydrogen sulfide in mg/3.0 mL versus peak area.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based upon mg/3.0 mL hydrogen sulfide and the volume of the sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for blank must be made for each sample.

$$M = M_S - M_b$$

where: M = weight of H₂S in mg
 M_S = mg found in front section of sample tube
 M_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the weights found in the front and backup sections to determine the total mass of the sample, M_T .
- 10.4 The concentration hydrogen sulfide in the air sampled can be expressed in mg/m³.

$$C_M = \frac{M_T}{V_C} \text{ (Section 10.3) } \times 1000 \text{ (L/m}^3\text{)}$$

where: C_M = concentration in mg/m³
 M_T = total mass of sample in mg
 V = volume of air sampled

- 10.5 Another method of expressing concentration is ppm.

$$C_A = \frac{C_M \times 24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: C_A = air concentration in ppm
P = pressure (mm Hg) of air sampled
T = temperature ($^{\circ}$ C) of air sampled
24.45 = molar volume (L/mole) at 25 $^{\circ}$ C and 760 mm Hg
MW = molecular weight (g/mole) of hydrogen sulfide
760 = standard pressure (mm Hg)
298 = standard temperature ($^{\circ}$ K)

11. References

- 11.1 Black, M.S., R.P. Herbst, and D.R. Hitchcock: Solid Adsorbant Preconcentration and Gas Chromatographic Analysis of Sulfur Gases. Anal. Chem. 50: 848-851 (1978).
- 11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2

Mary Lynn Woebkenberg
Measurements Systems Section

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$

ISOPROPYL ACETATE

2ND EDITION METHOD #: 550

DATE ISSUED: 01/17/75

M.W.: 102.13

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.87 g/mL @ 20°C;

BP 89.4°C; VP 5.7 kPa (43 mm Hg)
@ 20°C

OSHA: TWA 250 ppm; STEL 310 ppm

NIOSH: no recommended exposure limit

ACGIH: TWA 250 ppm; STEL 310 ppm

(1 ppm = 4.18 mg/m³ @ NTP)

SYNONYMS: CAS #108-21-4

SAMPLER: charcoal tube, 100 mg/50 mg

FLOW RATE: ≤ 0.2 L/min

RECOMMENDED VOLUME: ≤ 9 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of isopropyl acetate in carbon disulfide in the range 0.01 to 15 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.01 mg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Shamp, N. and Dirinck, P. Gas Chromatography/Mass Spectrometry of Volatile Substances, Chem. Foods and Beverages, Recent Dev., 25-47 (1982).
- [3] Gentry, S.J. and Walsh, P.T. Eight-hour TWA personal Monitoring Using a Diffusion Sampler and Short-term Stain-Tube, Am. Ind. Assoc. Hyg. J., 48(3), 287-92 (1987).

8/15/90

NIOSH Manual of Analytical Methods

Isopropyl Acetate

Analyte:	Isopropyl Acetate	Method No.: S50
Matrix:	Air	Range: 446-1870 mg/cu m
OSHA Standard:	250 ppm (950 mg/cu m)	Precision ($\overline{CV}_T$): 0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 1/17/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 446-1870 mg/cu m at an atmospheric temperature and pressure of 23°C and 770 mm Hg, using an 8 liter sample. Under the conditions of sample size (8 liters) the probable useful range of this method is 95-2850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 23 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 26 mg of analyte when a test atmosphere containing 1870 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 72 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 446-1870 mg/cu m was 0.067. This value corresponds to a 63.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 0.4% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Isopropyl Acetate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 9 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 30 ml/min (60 psig) Helium carrier gas flow
 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 3. 400 ml/min (60 psig) Air flow to detector
 4. 225°C injector temperature
 5. 250°C manifold temperature (detector)
 6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 9 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

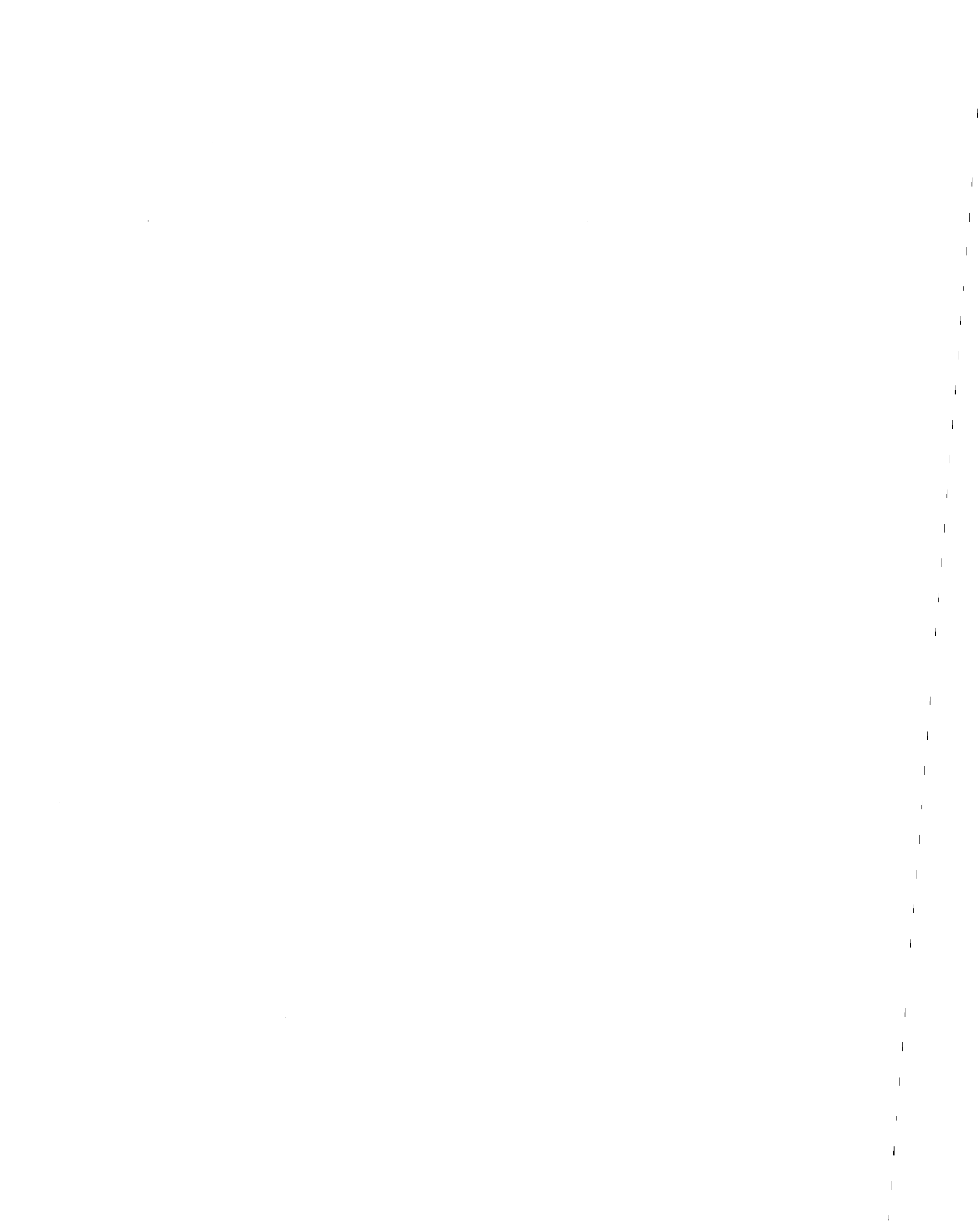
$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.



SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$ ISOPROPYL ETHER

2ND EDITION METHOD #: S368

DATE ISSUED: 05/21/76

M.W.: 102.18

CURRENT DATE: 08/21/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: 500 ppm

NIOSH: 500 ppm

ACGIH: 250 ppm; STEL 310 ppm

(1 ppm = 4.18 mg/m³ @ NTP)

PROPERTIES: liquid; easily forms peroxides;

d 0.723 g/mL @ 20 °C; BP 67.5 °C;

VP 15.8 kPa (119 mm Hg) @ 20 °C

SYNONYMS: diisopropyl ether; CAS #108-20-3

SAMPLER: solid sorbent tube, charcoal, 100 mg/50 mg

FLOW RATE: 0.05 L/min

RECOMMENDED VOLUME: ≤3 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of isopropyl ether in carbon disulfide in the range 0.01 to 12 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402

Isopropyl Ether

Analyte:	Isopropyl Ether	Method No.: S368
Matrix:	Air	Range: 992-4260 mg/cu m
OSHA Standard:	500 ppm (2100 mg/cu m)	Precision ($\overline{CV}_T$): 0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/21/76

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 992-4260 mg/cu m at an atmospheric temperature and pressure of 29°C and 764 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 200-6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 21.9 mg of analyte when a test atmosphere containing 4260 mg/cu m of analyte in air was sampled at 0.198 liter per minute for 26 minutes; i.e., at that time, the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 992-4260 mg/cu m was 0.056. This value corresponds to a 118 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same

sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 80/100 mesh Chromosorb WAW-DMCS.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0-ml type graduated in 0.1-ml increments.
- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Isopropyl ether, reagent grade.
- 7.3 Octane, or other suitable internal standard.
- 7.4 Purified nitrogen.
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 A maximum sample size of 3 liters is recommended. Sample at a rate of 0.05 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
 - 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank. Submit one blank for every 10 samples.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 30 ml/min (60 psig) Nitrogen carrier gas flow
 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 3. 400 ml/min (60 psig) Air flow to detector
 4. 150°C injector temperature
 5. 220°C manifold temperature (detector)
 6. 80°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ

the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame-sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5, 1 and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same amount of analyte into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2S the standard. The analyte concentration in mg per ml is plotted versus the ratio of the area of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (Liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}(\text{O})\text{CH}_2$

ISOPROPYL GLYCIDYL ETHER

2ND EDITION METHOD #: S77

DATE ISSUED: 02/14/75

M.W.: 116.16

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 50 ppm; STEL 75 ppm

NIOSH: C 50 ppm

ACGIH: TWA 50 ppm; STEL 75 ppm

(1 ppm = 4.75 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.924 g/mL;

BP 131-132 °C;

VP 1.25 kPa (9.4 mm Hg) @ 25 °C;

vapor density (air=1) 4.0

SYNONYMS: isopropyl epoxypropyl ether; CAS #4016-14-2

SAMPLER: charcoal tube, 100 mg/50 mg

FLOW RATE: ≤0.2 L/min

RECOMMENDED VOLUME: ≤10 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of isopropyl glycidyl ether in carbon disulfide in the range 1.2 to 4.8 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method not evaluated at current STEL and ceiling standards/recommended levels

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

[2] Levin, J.-O. et al., Solid Sorbent Sampling and Chromatographic Determination of Glycidyl Ethers in Air, *J. Chromatogr.*, 454, 121-128 (1988).

Isopropyl Glycidyl Ether

Analyte:	Isopropyl Glycidyl Ether	Method No.: S77
Matrix:	Air	Range: 121-484 mg/cu m
OSHA Standard:	50 ppm (240 mg/cu m)	Precision ($\overline{CV}_T$): 0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 121-484 mg/cu m at an atmospheric temperature and pressure of 21°C and 763 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 25-720 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of isopropyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 21 mg of isopropyl glycidyl ether

when a test atmosphere containing 480 mg/cu m of isopropyl glycidyl ether in air was sampled at 0.183 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 121-484 mg/cu m was 0.067. This value corresponds to a 16 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 7% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Isopropyl Glycidyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least +5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 205°C injector temperature
 - 5. 270°C manifold temperature (detector)
 - 6. 115°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

FORMULA: Pb

LEAD

M.W.: 207.19 (Pb); 223.19 (PbO)

METHOD: 7105

ISSUED: 8/15/90

OSHA: 0.05 mg/m³
NIOSH: <0.1 mg/m³ [1]
ACGIH: 0.15 mg/m³

PROPERTIES: soft metal;
d 11.3 g/cm³; MP 327.5 °C;
valences +2, +4 in salts

SYNONYMS: vary depending upon the chemical form (elemental lead and lead compounds except alkyl lead); CAS #7439-92-1 (Pb); CAS #1317-36-8 (PbO).

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.8-µm cellulose ester membrane)	! TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE
FLOW RATE: 1 to 4 L/min	! ANALYTE: lead
VOL-MIN: 1 L @ 0.05 mg/m ³ -MAX: 1500 L	! ASHING: conc. HNO ₃ , 3 mL; 30% H ₂ O ₂ , 1 mL; 140 °C
SHIPMENT: routine	! FINAL SOLUTION: 10 mL 5% HNO ₃
SAMPLE STABILITY: stable	! WAVELENGTH: 283.3 nm
FIELD BLANKS: 10% of samples	! GRAPHITE TUBE: pyrolytic coated
	! INJECTION: 20 µL + 10 µL matrix modifier,
	! DRY: 110 °C, 70 sec;
	! CHAR: 800 °C, 30 sec;
	! ATOMIZE: 1800 °C, 5 sec.
	! BACKGROUND CORRECTION: D ₂ , H ₂ or Zeeman
	! CALIBRATION: Pb ⁺⁺ in 5% HNO ₃
	! RANGE: 0.05 to 1.0 µg per sample [2]
	! ESTIMATED LOD: 0.01 µg per sample [2]
	! PRECISION (s _r): not determined

APPLICABILITY: The working range is 0.0002 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 D₂ or H₂ continuum or Zeeman background correction to control molecular absorption. High concentrations of calcium, 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 (3). Method 7300 (ICP-AES) is an alternate analytical method. Method 7505 is specific for lead sulfide. Method 7082 is a flame AA method.

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_2 (w/w), reagent grade.
4. Calibration stock solution, 1000 $\mu\text{g Pb/mL}$. 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 $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.3 g $\text{Mg}(\text{NO}_3)_2$ 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.

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.

*see SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Conc. nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 hrs for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

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:

11. Prepare a series of working standards covering the range 0.005 to 0.1 $\mu\text{g Pb/mL}$ (0.05 to 1.0 $\mu\text{g Pb}$ per sample) by adding 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.
12. Analyze the working standards together with the blanks and samples (steps 17 through 19).
13. Prepare a calibration graph of absorbance vs. solution concentration ($\mu\text{g/mL}$).
14. Analyze a standard for every 10 samples to check for instrument drift.
15. Check recoveries with at least one spiked media blank per 10 samples.

16. 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 AA or ICP.

MEASUREMENT:

17. Set spectrophotometer as specified by the manufacturer and to conditions on page 7105-1.
NOTE: An alternate wavelength is 217.0 nm [6]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, nonatomic absorption is significantly greater at 217.0 nm, making the use of D₂, H₂ continuum, or Zeeman background correction mandatory at that wavelength.
18. Add matrix modifier to samples and standards in proper ratio of 2 to 1 (sample or standard to matrix modifier).
19. 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% HNO₃, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

20. 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.
21. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m³), 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 S341 [5] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m³ for a 180-L air sample, using generated atmospheres of lead nitrate [2]. 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 using flame AAS gave the results [3]:

<u>Species</u>	<u>Digestion Method</u>	<u>Analytical Recovery, %</u>
Pb metal	HNO ₃ only	92 ± 4
Pb metal	HNO ₃ + H ₂ O 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 ₂ O ₂	100 ± 1
Pb in paint*	HNO ₃ only	95 ± 6
Pb in paint*	HNO ₃ + H ₂ O ₂	95 ± 6

*Standard Reference Material #1579, U.S. National Bureau of Standards.

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 [3]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was >97 ± 2%. Overall precision, s_r, was 0.072 for lead nitrate aerosol [2,5] and 0.068 for Pb fume [3].

REFERENCES:

- [1] NIOSH Recommendations for Occupational Safety and Health Standards, NIOSH, Cincinnati, OH (1988).
- [2] Backup Data Report for Method 7105 submitted to NIOSH by DataChem Laboratories, NIOSH (Unpublished, September, 1990).
- [3] 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).
- [4] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation (1976).

METHOD REVISED BY: James B. Perkins, Brent E. Stephens, and Michael P. Beesley, DataChem, Laboratories, Salt Lake City, Utah. S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(CH=O)_2=O$

MALEIC ANHYDRIDE

2ND EDITION METHOD #: P&CAM 302

DATE ISSUED: 05/01/79

M.W.: 98.06

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; sp. gr. 1.43; MP 53 °C;
VP <0.2 kPa (<0.16 mm Hg) @ 20 °C;
vapor density (air=1) 3.38

OSHA: TWA 0.25 ppm

NIOSH: TWA 0.25 ppm

ACGIH: TWA 0.25 ppm

(1 ppm = 4.01 mg/m³ @ NTP)

SYNONYMS: 2,5-furandione; CAS #108-31-6

SAMPLER: midget bubbler containing 15-mL distilled water

FLOW RATE: ≤1.5 L/min.

RECOMMENDED VOLUME: 360 L

MEASUREMENT TECHNIQUE: reverse-phase HPLC, UV detection

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of maleic anhydride in acetone diluted with distilled water in the range 15 to 1000 µg per sample.

ESTIMATED LIMIT OF DETECTION (LOD): 15 µg maleic acid per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Service Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
- [2] Geyer R. and Saunders, G. A. Determination of Maleic Anhydride in Workplace Air by Reverse Phase HPLC J, Chromatogr., 368 (2), 456-458 (1986).
- [3] Kallio, H. Determination of Trace Concentrations of Maleic Anhydride in Workplace Air, Khig. Zdraveopaz, 32 (3), 86-94 (1989).

8/15/90

NIOSH Manual of Analytical Methods



Maleic Anhydride
Measurements Research Branch
Analytical Method

Analyte:	Maleic Acid	Method No.:	P&CAM 302
Matrix:	Air	Range:	0.50-2.14 mg/cu m
Procedure:	Bubbler collection, HPLC	Precision (RSD):	0.063
Date Issued:	5/1/79	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a midget bubbler containing 15 mL of distilled water to collect maleic anhydride.
- 1.2 Maleic anhydride is hydrolyzed to maleic acid in the bubbler.
- 1.3 The resulting sample is analyzed by high pressure liquid chromatography (HPLC) with a uv detector at 254 nm.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was tested over the range of 0.50-2.14 mg/cu m at an atmospheric temperature of 20°C and pressure of 757 mm Hg, using a 360-liter sample.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency of the midget bubbler.
- 2.3 Under the instrumental conditions used in the study, a sensitivity of approximately 0.01 absorbance units/ug maleic anhydride was obtained. The HPLC flow cell path length was 0.8 cm.
- 2.4 The limit of detection is estimated to be 50 ng per injection or 15 ug maleic acid per sample.

3. Interferences

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

- 3.2 Any compound that has the same retention time as maleic acid at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.3 Maleic anhydride is immediately hydrolyzed to maleic acid upon collection. This method will not differentiate between maleic acid and maleic anhydride.

4. Precision and Accuracy

- 4.1 The Relative Standard Deviation (RSD) for the total analytical and sampling method in the range of 0.50-2.14 mg/cu m was 0.063. This value corresponds to a standard deviation of 0.063 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 In the experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true" value on the average 95% of the time over the range tested. The concentrations obtained at 0.5, 1, and 2 mg/cu m were 6.7% lower than the dynamically generated test concentrations ($n = 17$). In these experiments the average analytical method recovery was 1.044 for a loading of 180.7-723 μg of maleic acid in the bubbler. No correction was applied for this recovery. In storage stability studies, the mean of samples analyzed after 7 days were 13% lower than the mean of samples analyzed immediately after collection. Collection efficiency was determined to be at least 0.978 within the range tested; therefore, no correction for collection efficiency is necessary. Experiments performed in the study are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 Collected samples are analyzed by means of a quick, instrumental, method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur. The use of spill-proof impingers is recommended.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one bubbler only.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters because of possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 Glass midget bubblers with fritted glass stems.
- 6.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a bubbler and trap in the line to minimize errors associated with uncertainties in the volume sampled. The sampling pump is protected from splasher or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
- 6.3 Manometer.
- 6.4 Thermometer.
- 6.5 HPLC equipped with a uv detector at 254 nm and a sample injection valve with a 50-microliter sample loop.
- 6.6 HPLC column (300 mm x 3-mm I.D. stainless steel) packed with μ -Bondapak C-18*, or equivalent.
- 6.7 An electronic integrator or some other suitable method for measuring peak areas.
- 6.8 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.9 Pipets: Convenient sizes for preparing standard solutions and 15-mL pipets for measuring the collection medium.
- 6.10 Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

- 7.1 Maleic anhydride, 99+%. Note: Maleic anhydride will slowly hydrolyze in the presence of humid air. Care should be taken to protect it from humid conditions.
- 7.2 Water, deionized and distilled.
- 7.3 Dicyclohexylamine.
- 7.4 Formic acid.

* This column is available from Waters Associates, Milford, Mass.

7.5 Methanol, HPLC grade.

7.6 HPLC Mobile Phase

7.6.1 Add 10 mL of dicyclohexylamine and 10 mL of formic acid to a 100-mL volumetric flask. Bring to volume with distilled water.

7.6.2 Add 10 mL of the solution prepared in Section 7.6.1 and 250 mL of methanol to a 1-liter volumetric flask. Bring this solution to volume with distilled water. Filter and degas prior to use.

7.7 Acetone.

7.8 Stock Maleic Anhydride Standard Solution. Prepare a 1.08 mg/mL stock solution of maleic anhydride in acetone.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Pipet 15 mL of distilled water into a midget bubbler, and mark the liquid level before inserting the bubbler frit. Be sure that the bubbler frit is completely immersed in the water. If the water does not cover the frit, do not use the bubbler. Maleic anhydride will not be collected efficiently unless the bubbler frit is completely immersed in the water.

8.2.2 Connect the outlet of the midget bubbler to the trap's inlet. When a trap is used, it is attached to the pump by tape or a metal holder. The outlet of the trap is connected by tubing to the pump's inlet. Material collected in the trap must never be returned to the midget bubbler. If more than 1 mL of material is collected in the trap after sampling, the sample should be considered invalid, otherwise, the trap material can be discarded. The bubbler must be maintained in a vertical position during sampling.

8.2.3 Air being sampled should not pass through any hose or tubing before entering the bubbler.

8.2.4 A sample size of 360 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.

8.2.5 Turn the pump on and begin sample collection. The pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

- 8.2.6 It may be necessary to replace some of the water in the bubbler during sampling because of evaporation. If the liquid level drops more than 5 mL, add water to the 15-mL mark.
- 8.2.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.
- 8.2.8 After sampling, disconnect the bubbler. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping.
- 8.2.9 With each batch or partial batch of ten samples submit one bubbler containing water from the same lot of bubblers used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.
- 8.2.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.3 Analysis of Samples

- 8.3.1 Remove the bubbler stem from the bubbler. Allow water to drain from the frit into the bubbler. If the sample volume is less than 15 mL, add water until the volume reaches the 15-mL mark.
- 8.3.2 HPLC Conditions. The typical operating conditions for the HPLC are:

Column Temperature: Ambient
Flow Rate: 1.7 mL/minute
Mobile Phase: 1% PIC reagent (Section 7.6.1) / 25%
methanol / 74% distilled water
Detector: uv photometer at 254 nm
Retention Time: 6 minutes

During the experimental study, all samples and blanks contained a peak eluting after maleic acid (at about 8 minutes) which was believed to be phthalic acid.

- 8.3.3 Injection. The first step in the analysis is to inject the sample into the HPLC. The chromatograph is fitted with a sample injection valve and a 50-microliter sample loop. Flush this loop thoroughly with the sample (500 microliters), and inject the sample.
- 8.3.4 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

9. Calibration and Standardization

- 9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1-3 mg/cu m for the sample under study, is prepared and analyzed under the same HPLC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/15 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.
- 9.2 From the stock solution (Section 7.8), appropriate aliquots are withdrawn and diluted with distilled water. Prepare at least 5 working standards to cover the range of 36-1080 micrograms/15 mL. This range is based on a 360-liter sample. Analyze samples as described in Section 8.3.
- 9.3 Prepare a standard calibration curve by plotting concentration of maleic anhydride in micrograms/15 mL versus peak area. Although maleic acid is the actual specie analyzed, all concentrations should be expressed as maleic anhydride.

10. Calculations

- 10.1 Read the weight, in micrograms, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on micrograms/15 mL of distilled water and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 A correction for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\begin{aligned}\mu\text{g sample} &= \mu\text{g found in sample bubbler} \\ \mu\text{g blank} &= \mu\text{g found in blank bubbler}\end{aligned}$$

- 10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P₁ = pressure during calibration of sampling pump (mm Hg)
P₂ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

- 10.4 The concentration of maleic anhydride in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\mu\text{g (Section 10.2)}}{\text{Corr. Air Volume Sampled (L) (Section 10.3)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Backup Data Report No. 302 for Maleic Anhydride prepared under NIOSH Contract No. 210-76-0123

Ellen L. Fernandez
SRI International
NIOSH Contract No. 210-76-0123

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{COOCH}_3$

METHYL ACETATE

2ND EDITION METHOD #: S42

DATE ISSUED: 12/16/74

M.W.: 74.08

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 200 ppm; STEL 250 ppm

NIOSH: TWA 200 ppm; STEL 250 ppm

ACGIH: TWA 200 ppm; STEL 250 ppm

(1 ppm = 3.03 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.934 g/mL @ 20 °C;

BP 56.9 °C; VP 23 kPa (173 mm Hg)

VP 23 kPa (173 mm Hg) @ 20 °C;

vapor density (air = 1) 2.8

SYNONYMS: acetic acid methyl ester; CAS #79-20-9

SAMPLER: coconut shell charcoal tube, 100 mg/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: $\leq 7 \text{ L}$

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: 30-m, 0.32-mm ID, DB-wax polar capillary column or DB-1 capillary column may be used between 35°-150°C; programmed at 10°C/min with 2 min hold at 35°C [1]

MEASUREMENT CALIBRATION: standard solutions of methyl acetate in carbon disulfide in the range 2 μg to 1000 μg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 μg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method may be adapted to other esters of relatively low volatility

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Pendergrass, S.M., Methods Development Efforts, Measurement Research Support Branch, DPSE, NIOSH (unpublished, 1990).

[2] 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.

[3] Tada, D. and Cai, S. X. Determination of Organic Solvents in Air, Div. Work Environ. and Occup. Dis. Instr., 56 (6), 453-457 (1980).

Methyl Acetate

Analyte:	Methyl Acetate	Method No.:	S42
Matrix:	Air	Range:	343-1330 mg/cu m
OSHA Standard:	200 ppm (610 mg/cu m)	Precision (CV _T):	0.0547
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 343-1330 mg/cu m at an atmospheric temperature and pressure of 24°C and 761 mm Hg, using a 7 liter sample. Under the conditions of sample size (7 liters) the probable useful range of this method is 61-1830 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12.8 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 14 mg of analyte when a test atmosphere containing 1330 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 54 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 343-1330 mg/cu m was 0.0547. This value corresponds to a 33.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 8.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
7.2 Methyl Acetate, reagent grade
7.3 Decane, internal standard
7.4 Purified helium
7.5 Prepurified hydrogen.
7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 A maximum sample size of 7 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 30 ml/min (60 psig) Helium carrier gas flow
 - 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 - 3. 400 ml/min (60 psig) Air flow to detector
 - 4. 225°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 7 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_2=\text{CHCOOCH}_3$

METHYL ACRYLATE

2ND EDITION METHOD #: S38

DATE ISSUED: 12/06/74

M.W.: 86.09

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 10 ppm (skin)

NIOSH: TWA 10 ppm (skin)

ACGIH: TWA 10 ppm (skin)

(1 ppm = 3.52 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.956 g/mL @ 20 °C;

BP 80 °C;

VP 9.08 kPa (68.2 mm Hg) @ 20 °C;

vapor density (air=1) 2.95

SYNONYMS: 2-propenoic acid methyl ester; CAS #96-33-3

SAMPLER: coconut shell charcoal tube, 100 mg/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: ≤ 5 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: capillary column or packed column may be used to reduce interferences

MEASUREMENT CALIBRATION: standard solutions of methylacrylate in carbon disulfide with undecane or other suitable internal standard in the range 0.01 to 0.35 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.01 mg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: the probable useful range is 2 to 20 ppm (7 to 70 mg/m³) for a 5-L air sample

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] Gjoes, N. et al., Identification of Methacrylates by Mass Spectrometry, Anal. Chim. Acta, 149, 87-99 (1983).



Methyl Acrylate

Analyte:	Methyl Acrylate	Method No.:	S38
Matrix:	Air	Range:	13.9-58.4 mg/cu m
OSHA Standard:	10 ppm (35 mg/cu m)	Precision ($\overline{CV}_T$):	0.066
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 13.9-58.4 mg/cu m at an atmospheric temperature and pressure of 23°C and 764 mm Hg, using a 6-liter sample. Under the conditions of sample size (5 liters) the probable useful range of this method is 7-70 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.35 mg sample.
- 2.2 The upper limit of the range of the method may be dependent on the absorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 2.7 mg of analyte when a test atmosphere containing 59 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. In this case, the upper range is limited by the reactivity of the monomer on charcoal. It is recommended that this method not be used outside the range stated in Section 2.1.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 13.9-58.4 mg/cu m was 0.066. This value corresponds to a 2.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 12.9% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Methyl Acrylate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 30 ml/min (60 psig) Helium carrier gas flow
 - 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 - 3. 400 ml/min (60 psig) Air flow to detector
 - 4. 225°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 5-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

FORMULA: CH₃OC(CH₃)₃

METHYL tert-BUTYL ETHER

M.W.: 88.15

METHOD: 1615

ISSUED: 8/15/90

OSHA: No permissible exposure limit
NIOSH: No recommended exposure limit
ACGIH: No threshold limit value
(1 ppm = 3.6 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.74 g/mL @ 20 °C;
BP 55.2 °C;
VP 32.6 kPa (245 mm Hg) @ 25 °C

SYNONYMS: MTBE; CAS #1634-04-4

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBES (two charcoal tubes in series; front 400 mg; back 200 mg)	! TECHNIQUE: GAS CHROMATOGRAPHY, FID ! ANALYTE: methyl tert-butyl ether (MTBE) !
FLOW RATE: 0.1 to 0.2 L/min	! DESORPTION: 2 mL CS ₂ , 30 min. !
VOL-MIN: 2 L @ 10 ppm -MAX: 96 L	! INJECTION VOLUME: 1 µL, split ratio 60:1 !
SHIPMENT: routine	! TEMPERATURE - INJECTION: 200 °C ! DETECTOR: 250 °C ! COLUMN: 0 °C for 7 min; 5 °C/min to 25 °C, and then 25 °C/min to 250 °C (hold 5 min) !
SAMPLE STABILITY: at least 5 days @ 25 °C, 3 weeks @ -7 °C (92% recovery) [1]	! CARRIER GAS: He, 1 to 2 mL/min !
FIELD BLANKS: 10% of samples	! COLUMN: fused silica capillary, 50-m x 0.3-mm ID, 0.5-µm film of bonded dimethylsilicone gum (polydimethylsiloxane) !
	! CALIBRATION: standard solutions of MTBE in CS ₂ !
	! RANGE: 0.06 to >10 mg per sample [1] !
	! ESTIMATED LOD: 0.02 mg per sample [1] !
	! PRECISION (s _r): 0.033 @ 9 µg to ≈10 mg per sample [1] !

APPLICABILITY: The working range is 0.2 to >35 ppm (0.75 to >125 mg/m³) for an 80-L air sample. This method is designed for the determination of MTBE in gasoline and may be used for the determination of other components of gasoline.

INTERFERENCES: 2,3-Dimethylbutane may interfere if initial chromatographic temperatures are higher than 0 °C.

OTHER METHODS: This is a new method [1].

REAGENTS:

1. Methyl tert-butyl ether*, reagent grade.
2. Carbon disulfide*, reagent grade.
3. Calibration stock solution, 7.41 mg/mL. Dilute 40 μ L methyl tert-butyl ether to 4.00 mL with carbon disulfide.
4. Helium, prepurified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.
7. Liquid nitrogen or carbon dioxide for subambient cooling of GC oven.

EQUIPMENT:

1. Sampler: Two glass tubes in tandem, each 8 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing activated coconut shell charcoal held by plugs of silated glass wool (front tube = 400 mg, back tube = 200 mg).
2. Personal sampling pump, 0.1 to 0.2 L/min with flexible connecting tubing.
3. Gas chromatograph with sub-ambient cooling, flame ionization detector (page 1615-1).
4. Vials, 5-mL, 2-mL with PTFE-lined crimp caps.
5. Pipettes, TD, 4-, 2- and 1-mL.
6. Syringes, 1-mL, 250-, 100-, 25-, and 10- μ L.

*see SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Methyl tert-butyl ether and carbon disulfide are extremely flammable (flash points -28 °C and -30 °C respectively). Carbon disulfide is also toxic. Work with these compounds in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.1 to 0.2 L/min for a sample size of 2 to 96 L.
4. Separate the tubes, cap, and pack securely for shipment. Chilling of the samples is necessary if they are not expected to be analyzed within five days.

SAMPLE PREPARATION:

5. Add 2.0 mL carbon disulfide to 5-mL vials. Loosely cap vials.
6. Place front and back sorbent sections in separate vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least seven working standards.
 - a. Prepare standards in capped vials by mixing various volumes (i.e., 5 to 230 μ L) of calibration stock solution with carbon disulfide to a total volume of 4.00 mL to obtain concentrations in the range of 0.010 to 5 mg/mL.
 - b. Analyze together with samples and blanks (steps 11 and 12).
9. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each level plus three media blanks.
 - a. Use the 400-mg charcoal tube for DE determination. Hold charcoal in the tube by silanized glass wool.
 - b. Prepare three DE stock solutions by mixing 4, 40, and 160 μ L of methyl tert-butyl ether and making up a total volume to 4.00 mL with carbon disulfide to produce corresponding concentrations of 0.741, 7.41 and 29.62 μ g/ μ L.
 - c. Inject 24 μ L of the 0.741 μ g/ μ L stock solution, 7 and 19 μ L of the 7.41 μ g/ μ L solution, 7, 11, and 14 μ L of the 29.62 μ g/ μ L stock solution onto the tubes near the glass wool plug and draw clean air through the tubes at 0.1 L/min for 1 to 2 minutes.
 - d. Seal tube with plastic caps. Allow to stand overnight.
 - e. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - f. Prepare a graph of DE vs. mg of MTBE recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure the calibration curve and DE are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1615-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.

NOTE: 1. If the sample peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS₂, reanalyze, and apply the appropriate dilution factor in the calculations.

2. These conditions are recommended for the determination of MTBE in gasoline. An initial temperature lower than 0 °C will produce better peak resolution but longer analysis time.

12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of MTBE found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If W_b > W_f/10, report breakthrough and possible sample loss.

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

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

EVALUATION OF METHOD:

A calibration curve in the concentration range 0.74 to 111 mg/mL MTBE in carbon disulfide indicated a linear correlation with a coefficient of 0.9998 and s_p of 3.3% [1]. Other calibration curves at lower concentrations, covering the recovery/stability range, i.e. 9.3 to 426 µg/mL MTBE in CS₂, indicated linear correlation coefficients >0.998. The LOD and LOQ values varied between 18 to 22 µg/mL and 36 to 73 µg/mL, respectively.

A six-level, 31-day storage stability study, conducted at -7 °C, in the range 17.8 to 415 µg MTBE in gasoline spiked on 400 mg charcoal tubes, indicated recoveries of 99.0 ± 4.3% for the first day, 93.2 ± 2.0% for the 17th day, 91.9 ± 7.1% after 23-day storage and 89.0 ± 5.2% after 31-day storage. A five-day room-temperature stability study at 415 µg MTBE in gasoline spiked in 400 mg charcoal tubes indicated a 100.0 ± 4.6% recovery.

Four charcoal tubes spiked with 415 µg MTBE in gasoline had air drawn for six hours at 100 mL/min and then were stored at -7 °C for five days indicating 103.6 ± 9.0% recovery. No sample loss occurred due to breakthrough at the 415-µg per sample MTBE level.

Charcoal tubes which were spiked with 10 mg MTBE in gasoline and which had 6 to 78 L of air drawn through them did not indicate any breakthrough of MTBE. Light hydrocarbons i.e. n-butane, and isopentane, which are not retained by the charcoal, did break through.

REFERENCES:

- [1] Palassis, J. Method Development Efforts for MTBE, NIOSH/DPSE, Measurement Research Support Branch, Cincinnati, Ohio, 1989; paper presented at the Annual Meeting of Federation of Analytical Chemistry and Spectroscopic Societies (FACSS), Chicago, IL (October 4, 1989).

METHOD WRITTEN BY: John Palassis, NIOSH/DPSE

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{OCH}_3$	METHYL CELLOSOLVE ACETATE
2ND EDITION METHOD #: S39	DATE ISSUED: 12/06/74
M.W.: 118.13	CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: liquid; d 1.005 g/mL @ 20 °C;
OSHA: TWA 25 ppm (skin)	BP 145 °C; flash pt. 49 °C;
NIOSH: no REL	VP 0.26 kPa (2 mm Hg) @ 20 °C;
ACGIH: TWA 5 ppm (skin)	
(1 ppm = 4.82 mg/m ³ @ NTP)	

SYNONYMS: 2-methoxyethyl acetate; ethylene glycol monomethyl ether acetate; CAS #110-49-6

SAMPLER: coconut shell charcoal tube, 100 mg/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: ≤ 20 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: OSHA Method 53 [1]

MEASUREMENT CALIBRATION: standards solutions of methyl cellosolve acetate in carbon disulfide in the range 10 to 4500 μg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 10 μg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: samples should be refrigerated upon receipt by the laboratory to minimize hydrolysis [1]

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] OSHA Analytical Methods Manual, Method 53, U.S. Dept. of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory, Salt Lake City, UT. (1985).

Methyl Cellosolve Acetate

Analyte:	Methyl Cellosolve Acetate	Method No.: S39
Matrix:	Air	Range: 51-214 mg/cu m
OSHA Standard:	25 ppm (120 mg/cu m)	Precision (CV _T): 0.0675
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 12/6/74

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 51-214 mg/cu m at an atmospheric temperature and pressure of 23°C and 762 mm. Hg, using a 20 liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 12-360 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7.2 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 10 mg of analyte when a test atmosphere containing 214 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 11-214 mg/cu m was 0.0675. This value corresponds to an 8.1 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 0.5% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10 ft x 1/8 in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
7.2 Methyl Cellosolve Acetate, reagent grade
7.3 Undecane, internal standard
7.4 Purified helium
7.5 Prepurified hydrogen.
7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 A maximum sample size of 20 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 30 ml/min (60 psig) Helium carrier gas flow
 - 2. 35 ml/min (25 psig) Hydrogen gas flow to detector
 - 3. 400 ml/min (60 psig) Air flow to detector
 - 4. 225°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 20 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{C}_6\text{H}_{10}\text{OH}$

METHYLCYCLOHEXANOL

2ND EDITION METHOD #: S374

DATE ISSUED: 01/20/78

M.W.: 114.19

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.92 g/mL @ 20 °C;

BP 155-180 °C;

VP 0.2 kPa (1.5 mm Hg) @ 20 °C

OSHA: TWA 50 ppm

NIOSH: TWA 50 ppm

ACGIH: TWA 50 ppm

(1 ppm = 4.66 mg/m³ @ NTP)

SYNONYMS: hexahydromethylphenol; hexahydroresol; CAS #25639-42-3

SAMPLER: coconut shell charcoal tube, 100/50 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: 12 L/min

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of methycyclohexanol in methylene chloride
in the range 0.1 to 20 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.1 mg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: methycyclohexanol is usually present as mixtures of its isomers, most commonly
a 50:50 mixture of meta- and para- isomers

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Pannwitz, K. H. Diffusion Coefficients Related to Passive Air Monitoring, Dräger Rev., 52,
1-8 (1984).

Methylcyclohexanol*

Analyte:	Methylcyclohexanol	Method No.: S374
Matrix:	Air	Range: 215-920 mg/cu m in a 12-L sample
OSHA Standard:	100 ppm (470 mg/cu m)	Precision ($\overline{CV}_T$): 0.063
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 1/20/78

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing activated coconut charcoal to trap methylcyclohexanol (Reference 11.1).
- 1.2 Methylcyclohexanol is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 215-920 mg/cu m at an atmospheric temperature of 25.5°C and atmospheric pressure of 761 mm Hg, using a 12-liter sample. This sample size is based on the capacity of the charcoal to collect vapors of methylcyclohexanol in air. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of methylcyclohexanol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture. A breakthrough test was conducted at a concentration of 942 mg/cu m and 85% relative humidity. Breakthrough occurred in 116 minutes at an average sampling rate of 0.190 liter/minute. This corresponds to a breakthrough capacity of 20.8 mg and volume of 22.4 liters.

* 50:50 mixture of the meta and para isomers of methylcyclohexanol

3. Interferences

- 3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Any compound that has the same retention time as methylcyclohexanol at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 215-920 mg/cu m was 0.063. This value corresponds to a 30 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.
- 4.2 The Coefficient of Variation is a good measure of the accuracy of the method. Experiments performed in validation studies are described in Reference 11.3. In these experiments the desorption efficiency was greater than 0.919 for a loading of 2.710-11.31 mg on the sorbent. A correction was applied for this recovery. On the average the concentrations obtained at 0.5X, 1X, and 2X the OSHA standard level were 2.9% higher than the "true" concentration for 17 samples collected from dynamically generated test atmospheres. This difference does not represent a bias in the method, but rather a random variation from the experimentally determined "true" concentration. Storage stability studies indicated that the mean concentration of samples analyzed after 7 days compared within 0.2% to the mean concentration of samples analyzed immediately after collection. Thus, there are no known uncorrected sources of bias in the method.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of methylcyclohexanol found on the backup section of the charcoal tube exceeds 25% of that found on the front section, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for using one tube only.

6. Apparatus

- 6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 6.2 Charcoal Tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (12 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon caps.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-mL and other convenient sizes.
- 6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

Whenever possible, reagents should be ACS reagent grade or better.

- 7.1 m-Methylcyclohexanol.
- 7.2 p-Methylcyclohexanol.
- 7.3 Methylene chloride.

7.4 Methylcyclohexanol Stock Standard Solution. Prepare a standard solution of a 50:50 mixture of the m- and p-isomers of methylcyclohexanol.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

8.2.2 The smaller section of charcoal is used as a backup and should be positioned nearer the sampling pump.

8.2.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.2.5 A sample size of 12 liters is recommended. Sample at a known flow rate of 0.01-0.2 liter/minute. Record the sampling time flow rate, and type of sampling pump used.

8.2.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.7 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.2.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank. A minimum of 18 extra charcoal tubes should be shipped for desorption efficiency determinations.

8.2.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-mL stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another sample container vial. These two sections are analyzed separately.

8.3.2 Desorption of Samples. Prior to analysis, 1.0 mL of methylene chloride is pipetted into each sample container. Desorption should be done for 20 minutes. Tests indicated that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. All work with methylene chloride should be performed in a hood.

8.3.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

- 60 mL/min (60 psig) nitrogen carrier gas flow
- 50 mL/min (24 psig) hydrogen gas flow to detector
- 500 mL/min (50 psig) air flow to detector
- 230°C injector temperature
- 230°C detector manifold temperature
- 140°C column temperature

A single peak for the meta and para isomers of methylcyclohexanol will be observed. A retention time of 5-6 minutes is to be expected for a mixture of the meta and para isomers of methylcyclohexanol under these conditions and using the column recommended in Section 6.4.

The method was validated for a mixture of the meta and para isomers of methylcyclohexanol. However, the response characteristics of the flame ionization detector and desorption efficiencies of the ortho isomer were found to be similar to the mixture of the meta and para isomers. Ortho-methylcyclohexanol elutes before the meta/para isomers and may appear as a shoulder peak in front of the meta/para peak. If this occurs, it may be necessary to alter chromatographic conditions to either merge the two peaks or separate them; this will be dependent on the concentration of the ortho isomer.

8.3.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.3.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.4.2 Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of a 50:50 mixture of the meta and para isomers of methylcyclohexanol is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The density of methylcyclohexanol is 0.914 at 20°C. The amount injected is equivalent to that present in a 12-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the methylcyclohexanol onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in

the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of methylcyclohexanol into 1.0 mL of methylene chloride with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)} - \text{Blank (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methylcyclohexanol collected on the charcoal. Plot the desorption efficiency versus weight of methylcyclohexanol found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

- 9.1 From the stock standard solution (Section 7.4), appropriate aliquots are withdrawn and dilutions are made in methylene chloride. Prepare at least 5 working standards to cover the range of 0.56-16.8 mg/mL. This range is based on a 12-liter sample.
- 9.2 Analyze the standards as per Section 8.3.
- 9.3 Prepare a standard calibration curve by plotting concentration of methylcyclohexanol in mg/1.0 mL versus peak area.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/1.0 mL methylene chloride and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.6 The concentration methylcyclohexanol in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (L/mole) at 25°C and 760 mm Hg

M.W. = molecular weight (g/mole) of methylcyclohexanol

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).
- 11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.3 Backup Data Report for Methylcyclohexanol, prepared under NIOSH Contract No. 210-76-0123.

FORMULA: CH₂(C₆H₄NH₂)₂

4,4'-METHYLENEDIANILINE

M.W.: 198.27

METHOD: 5029

ISSUED: 8/15/90

OSHA: 0.01 ppm, 0.1 ppm STEL (proposed) [1]

PROPERTIES: solid; MP 92 °C; BP 399 °C;

NIOSH: potential human carcinogen; lowest
feasible limit recommended [2]

VP 0.2 x 10⁻⁷ kPa

(1.5 x 10⁻⁷ mm Hg) @ 25 °C

ACGIH: 0.1 ppm (skin); Suspected Human Carcinogen [3]
(1 ppm = 8.11 mg/m³ @ NTP)

SYNONYMS: p,p'-diaminodiphenylmethane; MDA; CAS #101-77-9.

SAMPLING	MEASUREMENT
SAMPLER: FILTER (acid-treated glass fiber, 37 mm)	!TECHNIQUE: HPLC, UV AND ELECTROCHEMICAL DETECTION !
FLOW RATE: 1 to 2 L/min.	!ANALYTE: 4,4'-methylenedianiline (MDA) !
VOL-MIN: 10 L @ 0.1 ppm -MAX: 1000 L	!INJECTION VOL: 25 µL !
SHIPMENT: transfer filter to glass vial; extract with 4 mL 0.1 N methanolic KOH before shipping	!COLUMN: C ₁₈ column, 4-µm particle size ! !DETECTOR: UV, 245 nm; electrochemical (ECHD), glassy carbon electrode at +0.75 to +0.85 V vs. Ag/AgCl electrode !
SAMPLE STABILITY: stable at least 60 days at 20 °C [4]	!MOBILE PHASE: 0.1 N sodium acetate in 30% acetonitrile/70% H ₂ O @ 1 mL/min !
FIELD BLANKS: 10% of samples	!CALIBRATION: standard solutions of MDA in 0.1 N methanolic KOH !
MEDIA BLANKS: at least 3 per set	!
ACCURACY	!RANGE: UV: 0.3 to 5 µg per sample [4] !ECHD: 0.025 to 0.5 µg per sample [4] !
RANGE STUDIED: not studied	!ESTIMATED LOD: UV: 0.12 µg per sample ECHD: 0.007 µg per sample [4] !
BIAS: not determined	!
OVERALL PRECISION (s _p): not determined	!PRECISION (s _p): 0.027 @ 0.12 to 1.2 µg per sample [4] !

APPLICABILITY: The working range is 0.025 ppb to 1.2 ppm (0.0002 to 10 mg/m³) for a 100-L air sample, and the method is applicable to STEL measurements. The method is specific for MDA. The use of dual detectors in series gives greater reliability to the analysis, and allows a wide measurement range. The method has been applied to wipe samples.

INTERFERENCES: 4,4'-Diphenylmethane diisocyanate (MDI) will interfere due to its conversion to MDA on the acid-treated glass fiber filter. Other aromatic amines do not interfere.

OTHER METHODS: Methods with acetylation, and the determination of the acetic anhydride derivative of MDA either by HPLC/UV [5] or by GC/EC (OSHA Method 57) [6] have been reported.

REAGENTS:

1. 4,4'-Methylenedianiline (MDA),* reagent grade.
2. Acetonitrile, distilled in glass.
3. Water, deionized.
4. Sodium acetate, reagent grade.
5. HPLC mobile phase: 0.1 N sodium acetate in 30% acetonitrile/70% water.
6. Methanol, distilled in glass.
7. Potassium hydroxide, reagent grade.
8. Calibration stock solution,* 1.0 µg/µL. Dissolve 0.01 g MDA in 10 mL 0.1 N methanolic KOH.
9. Extraction solution: 0.1 N potassium hydroxide in methanol.
10. Sulfuric acid solution: 0.26 N in water. Add, with caution, 1.5 mL concentrated sulfuric acid to deionized water and dilute to 200 mL.

*see SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: filter, acid-treated glass fiber (Gelman AE or equivalent), with a paper O-ring, in a 37-mm polystyrene 3-piece cassette.
NOTE: Prepare filter by adding 0.5 mL 0.26 N sulfuric acid to filter on a glass tray. Heat for 1 hour at 100 °C. Load the filter, backed by a paper O-ring, into a cassette and seal with shrink band to enable open-face sampling.
2. High performance liquid chromatograph (HPLC), with UV detector (245-nm), and an electrochemical detector, glassy carbon electrode operated at +0.75 to +0.85V with reference to silver/silver chloride reference electrode, oxidative mode.
3. Wipe Tabs (Whatman Smear Tabs or equivalent).
4. Sample filter apparatus: 0.45-µm, PTFE.
5. Syringe, 10-mL, disposable.
6. Vials, glass, scintillation, 20-mL, with PTFE-lined caps.
7. Syringes, microliter, readable to 0.1-µL.
8. Pipets, 2-, 4-, and 10- mL.
9. Tweezers.
10. Ultrasonic water bath.
11. Gauze Pad (Johnson Gauze sponges 2x2-12 ply or equivalent).

SPECIAL PRECAUTIONS: 4,4'-Methylenedianiline is a potential human carcinogen [1,2,3]. Avoid contact with acid and base solutions. Handle the acid-treated filters with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front piece and rear plug immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample open-faced at an accurately controlled flow rate between 1 and 2 L/min for a sample volume of 10 to 1000 L.
4. Within 4 hours of completion of sampling, transfer the filter with tweezers to a glass vial. Discard the paper O-ring. Add 4.0 mL 0.1 N methanolic KOH.
NOTE: Wipe Sampling and Skin Pad instructions:
 - a. Identify surfaces to be wiped, usually a 100-cm area.
 - b. Add wetting agent (isopropanol) if needed and wipe in square pattern.
 - c. Place in 20-mL scintillation vial.
 - d. If wetting agent was used, allow the solvent to evaporate.
 - e. Add 0.1 N methanolic KOH to vial (10 mL for gauze pads, 2 mL for smear tabs).
5. Pack securely for shipment. Include appropriate number of blanks in the shipment.

SAMPLE PREPARATION:

6. Agitate the samples for 1 hour in an ultrasonic water bath.
7. Filter the sample solution using a disposable syringe fitted with a 0.45-µm PTFE filter into a clean vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range of interest.
 - a. Make serial dilutions of calibration stock solution as needed to obtain MDA concentrations in the range 0.025 to 1 µg/mL.

- b. Analyze together with samples and blanks (steps 11 through 13).
- c. Prepare a calibration graph (peak area vs. concentration of MDA, μg per sample) for each detector (UV and ECHD).
9. Determine the recovery at least once for each lot of filters used for sampling in the range of interest. Prepare six filters at each of three levels plus three media blanks.
 - a. Add known amounts of MDA in methanol to the filters, using a microliter syringe.
 - b. Cover filters. Allow to stand overnight for solvent evaporation.
 - c. Extract with 4.0 mL extracting solution, prepare samples (steps 6 and 7) and analyze (steps 11 through 13) together with standards.
 - d. Determine recovery (R). Construct a graph of R vs. μg MDA recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set liquid chromatograph to manufacturer's recommendations and parameters given on page 5029-1.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak areas for UV and ECHD responses.

CALCULATIONS:

14. Determine the mass, μg (corrected for recovery) of MDA found on the sample filter (W) and in the average blank filter (B).
15. Calculate concentration (C) of MDA in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

A calibration curve for the UV absorption detector was constructed from 8 standards over the range 0.03 $\mu\text{g/mL}$ to 1.22 $\mu\text{g/mL}$ [4]. The curve was linear over this region and the LOD was determined to be 0.03 $\mu\text{g/mL}$. A calibration curve for the ECHD over the range 0.001 $\mu\text{g/mL}$ to 0.12 $\mu\text{g/mL}$ was linear and the LOD was determined to be 0.002 $\mu\text{g/mL}$. Test samples were prepared by spiking acid-impregnated filters with known amounts of MDA from a solution in methanol. Samples were prepared in triplicate at levels between 0.009 μg per filter and 3.7 μg per filter. (see Table 1 for results):

- a. To evaluate extraction efficiency, filters were analyzed immediately.
- b. To assess storage stability, spiked filters were stored in glass scintillation vials for 1 month prior to analysis.
- c. To investigate the stability of MDA on the filter during sampling, spiked filters were attached to a sampling pump and 1000 L of laboratory air was drawn through them at 2.5 L/min before analysis.

Table 1: Average Percent Recovery (n=3) of MDA from Filter Media

Spiked Amount (μg)	Extraction Efficiency (S.D.)	Storage Stability (S.D.)	Sampling Stability (S.D.)
3.71	94.5 (0.8)	94.4 (1.0)	94.4 (1.0)
1.80	91.3 (0.2)	91.1 (0.4)	90.8 (1.7)
0.93	85.9 (0.8)	86.4 (0.9)	85.5 (0.4)
0.37	84.8 (0.9)	86.0 (0.7)	84.9 (1.0)
0.09	82.0 (2.7)	82.0 (3.8)	77.0 (3.5)
0.037	80.0 (4.1)	83.0 (4.1)	77.0 (3.1)

^a-stored in glass scintillation vial for 1 month.

Nine spiked filters were prepared independently and submitted for analysis as a single blind test. Recoveries from 80 to 95% in the range 0.012 to 1.2 µg MDA per filter.

During method ruggedization, recoveries were observed to drop significantly during shipment in cassettes. The reason has not been determined but stability has been achieved by field extraction of the filter with methanolic KOH. Solutions and extracted filters were prepared, shipped, stored for 60 days, and analyzed. The data are shown in Table 2.

Table 2: Stability of Extracted Filter Solutions

Spiked Amount (µg)	N	% Recovery (S.D.)
9.9	4	92.1 (0.017)
5.1	4	90.4 (0.042)
1.0	4	100.0 (0.050)
0.0	2	NA (NA)

WIPE SAMPLING— This analytical method was used to analyze environmental samples collected on gauze pads and smear tabs. MDA was spiked onto acid-treated gauze pads, plain gauze pads, and smear tabs at 9.2, 0.92 and 0.092 µg per sample. Sets of each level were extracted immediately after allowing the spiking solution to evaporate, one day after spiking, one week after spiking, and one month after spiking. The extraction solution consisted of 10 mL 0.1 N methanolic KOH for the gauze pads and 2 mL for the smear tabs. The best recovery was obtained when the media was extracted immediately after the methanol evaporated. The same-day samples were reanalyzed at various times to determine if MDA would react with the medium when in solution. Recoveries are given in Table 3.

Table 3: Recoveries of MDA from Gauze Pads and Smear Tabs

Sample & Loading	Average Recovered after			
	0 day	1 day	7 days	30 days
Acid-treated Gauze Pad				
9.3 µg	96	89	87	86
0.93 µg	98	90	86	85
0.09 µg	97	85	85	87
Untreated Gauze Pad				
9.3 µg	95	73	70	53
0.93 µg	98	70	63	46
0.09 µg	93	62	60	55
Smear Tab				
9.3 µg	93	64	53	51
0.93 µg	87	62	48	46
0.09 µg	85	56	44	42
Solutions				
9.3 µg	98	97	98	96
0.93 µg	95	96	95	97
0.09 µg	98	97	94	98

MDA was extracted at greater than 90% extraction efficiency from all the media tested. The extraction efficiency did not decrease when the analyte was isolated from the media by extraction or media elimination. However, upon evaporation of the solvent from the spikes, the MDA begins to react with the media and loss of MDA begins immediately. This is shown by the decrease in recovery and the appearance of a yellow discoloration of the white medium. Although the recovery stabilizes, the addition of sulfuric acid to the pads does not prevent the loss of about 7% of the analyte during the first day. Addition of the 0.1 N methanolic KOH serves as an efficient stabilizer when added to the sample with no recovery loss. The improved recovery following field extraction, the imprecise mode of treated media preparation, and safety considerations of using acid-treated media for wipe samples were factors in using field extraction for surface and dermal samples.

REFERENCES:

- [1] Federal Register 29, Part 2, CFR Parts 1910 and 1926 (May 12, 1989).
- [2] NIOSH Current Intelligence Bulletin #47, 4,4'-Methylenedianiline (MDA), U. S. Dept. of Health and Human Services (NIOSH) Publication No. 86-115 (1986).
- [3] Threshold Limit Values and Biological Exposure Indices for 1988-1989, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1988).
- [4] Neumeister, C. E. Method Development for 4,4'-Methylenedianiline, Sequence #4752, NIOSH/MRSB, Cincinnati, OH., NIOSH (unpublished, November 3, 1986).
- [5] Anderson, C. C. and E. C. Gunderson, Methods Validation Study of High Performance Liquid Chromatographic Technique for Determining the MPDA and MDA Content of Air samples, SRI International, Menlo Park, CA (1986).
- [6] Elskamp, C. J. Method 57 (4,4'-Methylenedianiline), Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (1986).

METHOD WRITTEN BY: Charles Neumeister, NIOSH/DPSE.

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SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_6H_5NHCH_3$

MONOMETHYLANILINE

2ND EDITION METHOD #: S153

DATE ISSUED: 07/04/75

M.W.: 107.16

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.989 g/mL @ 20 °C;
BP 196 °C; VP 0.13 kPa (1mm Hg)
@ 36 °C

OSHA: No PEL

NIOSH: No REL

ACGIH: TWA 0.5 ppm (skin)

(1 ppm = 4.38 mg/m³ @ NTP)

SYNONYMS: N-methylbenzenamine; CAS #100-61-8

SAMPLER: bubbler, 0.05 M sulfuric acid

FLOW RATE: ≤1 L/min

RECOMMENDED VOLUME: 100 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: use of a nitrogen-specific detector instead of a flame ionization detector will greatly increase sensitivity. A DB-5 (95% dimethyl-(5%)-diphenyl-polysiloxane coated) fused silica capillary column has been used to analyze for various aromatic amines.

MEASUREMENT CALIBRATION: standard solutions of monomethylaniline in basic sulfuric acid in the range 10 to 400 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: NIOSH method 2002 (3rd ed.) for aromatic amines [1] may be used to eliminate the use of bubblers for sampling but has not specifically evaluated for methylaniline; this bubbler method is more appropriate for area sampling

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH Manual of Analytical Methods, 3rd Ed., Method 2002 (Amines, Aromatic) 1st supplement, 1985, DHHS Publ. (NIOSH) 84-100.

[2] Dmitriev, M.I. Gas Chromatographic Determination of Aromatic Amines in the Air, Gig. Sanit., iss., 1, 57-59 (1985).

8/15/90

NIOSH Manual of Analytical Methods

Monomethyl Aniline

Analyte:	Monomethyl Aniline	Method No.: S153
Matrix:	Air	Range: 4.38-17.52 mg/cu m
OSHA Standard:	2 ppm (9 mg/cu m)-skin	Precision (CV_T): 0.089
Procedure:	Bubbler collection in dilute sulfuric acid, GC analysis of the collected samples after basification with sodium hydroxide	Validation Date: 7/4/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a midjet bubbler containing 10 ml of 0.05 M sulfuric acid to trap the organic vapors present.
- 1.2 The resulting solution is made alkaline with 4 M sodium hydroxide.
- 1.3 An aliquot of sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 4.38-17.52 mg/cu m at an atmospheric temperature and pressure of 22°C and 762 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 1-30 mg/cu m.

3. Interferences

- 3.1 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

- 3.2 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 4.38-17.52 mg/cu m was 0.089. This value corresponds to a 0.8 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.9% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration.

A collection efficiency of 1.00 was determined for the collecting medium. Therefore, no recovery correction should be applied to the final result in Section 10.3.

5. Advantages and Disadvantages of the Method

- 5.1 The samples collected in bubblers are analyzed by means of a quick, instrumental method.
- 5.2 A major disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the adsorbing solution during sampling may occur which will result in loss of the sample.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:
 - 6.1.1 A glass midget bubbler containing the collection medium (Section 7.2).
 - 6.1.2 A pump suitable for sampling at least 1 liter per minute for 100 minutes. The sampling pump is protected from splasher or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
 - 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
 - 6.1.4 Thermometer.

- 6.1.5 Manometer.
- 6.1.6 Stopwatch.
- 6.2 Gas chromatograph equipped with a hydrogen flame ionization detector.
- 6.3 Column (2-ft long X 1/8-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 103. An Ascarite precolumn may be used if necessary to prevent contamination of the column packing with salt.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.
- 6.6 Volumetric flasks: convenient sizes for making solutions.
- 6.7 Pipets: 10-ml or other convenient sizes.
- 7. Reagents
 - 7.1 Monomethyl Aniline (N-Methylaniline), reagent grade.
 - 7.2 Collection medium, 0.05 M sulfuric acid.
 - 7.3 Sodium hydroxide, 4 M (160 g of sodium hydroxide in distilled water, diluted to a final volume of 1 liter).
 - 7.4 Purified nitrogen.
 - 7.5 Purified hydrogen.
 - 7.6 Filtered compressed air.
 - 7.7 Hydrion pH paper.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples.

- 8.3.1 Pour 10 ml of the collection medium (Section 7.2) into each midget bubbler, and mark the liquid level.
- 8.3.2 Connect the midget bubbler with a 5-cm glass splashover tube (6-mm I.D. and 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.
- 8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, the time and/or the volume as accurately as possible. Record the atmospheric pressure and temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute or less. A sample size of 100 liters is recommended.
- 8.3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.05 M sulfuric acid. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1 ml of 0.05 M sulfuric acid, adding the wash to the bubbler. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Add 1 ml of 4 M sodium hydroxide to the sample and mix the solution thoroughly. The pH of the resulting solution should be greater than 10 as indicated with pH paper. The total volume of the solution should be 12 ml and should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 245°C injector temperature
5. 275°C manifold temperature (detector)
6. 170°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable means of area measurement, and preliminary results are read from a standard curve prepared as discussed below in Section 9.

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of monomethyl aniline in benzene (219 mg/ml) into 11 ml of 0.05 M sulfuric acid in a bubbler. The amount introduced is equivalent to that present in a 100-liter air sample. The standards are made alkaline with 1.0 ml of 4 M sodium hydroxide. The solution should be checked with pH paper to make sure that its pH is greater than 10. A parallel blank is prepared in the same manner, except that no analyte is added. The standards and blank are analyzed in exactly the same manner as the samples in Section 8.4.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/sample. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting mg/sample versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/sample and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in sample bubbler}$$

$$\text{mg blank} = \text{mg found in blank bubbler}$$

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

- P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Di Corcia, Antonio and Roberto Samperi, "Gas Chromatographic Determination at the Parts-per-Million Level of Aliphatic Amines in Aqueous Solution," Anal. Chem., 46, No. 8, July 1974, 977-981.
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: CH_3NHNH_2

MONOMETHYLHYDRAZINE

2ND EDITION METHOD #: S149

DATE ISSUED: 07/04/75

M.W.: 46.07

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.874 g/mL @ 25 °C;

BP 87.5 °C;

OSHA: C 0.2 ppm (skin)

VP 6.6 kPa (49.6 mm Hg) @ 25 °C;

NIOSH: carcinogen; C 0.04 ppm

vapor density (air=1) 1.59;

ACGIH: C 0.2 ppm (skin); Susp. Human Carcinogen

flash point -8.3 °C (closed cup)

(1 ppm = 1.88 mg/m³ @ NTP)

SYNONYMS: CAS #60-34-4

SAMPLER: glass midget bubbler containing 15 mL of 0.1 M hydrochloric acid

FLOW RATE: 1.5 L/min

RECOMMENDED VOLUME: 20 L

MEASUREMENT TECHNIQUE: visible spectrophotometry, 730 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION:

standard solutions of monomethyl hydrazine sulfate in 0.1 M hydrochloric acid in the range 1 µg to 100 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.7 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: other hydrazines may interfere

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH Criteria for a Recommended Standard....Occupational Exposure to Hydrazines, DHEW (NIOSH) Publ. No. 78-122 (1978).
- [2] 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.
- [3] Leasure, C.S. and Eiceman, G.A., Anal. Chem., **57** (9), 1890-1894 (1985).
- [4] Mozayani, A. et al. J. Chromatogr. Biomed. Appl., **67**, 4 (1987).

Monomethyl Hydrazine

Analyte:	Monomethyl Hydrazine	Method No.: S149
Matrix:	Air	Range: 0.169-0.78 mg/cu m
OSHA Standard:	0.2 ppm (0.35 mg/cu m) - Ceiling	Precision ($\overline{CV}_T$): 0.106
Procedure:	Bubbler collection, colorimetric	Validation Date: 7/4/75

1. Principle of the Method (Reference 11.1)

- 1.1 Monomethyl hydrazine is collected in a midjet bubbler containing 0.1 M hydrochloric acid.
- 1.2 The resulting solution is reacted with phosphomolybdic acid to form a bluish green colored complex.
- 1.3 The strong absorption maximum at 730 nm is used as a quantitative measure of monomethyl hydrazine.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.169-0.78 mg/cu m, at an atmospheric temperature and pressure of 23°C and 760 mm Hg. The probable range of the method is 0.035-1.05 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted with hydrochloric acid prior to color development to extend the upper limit of the range.
- 2.2 A concentration of 0.035 mg/cu m of monomethyl hydrazine can be determined in a 20-liter air sample based on a 0.025 absorbance using a 5-cm cell.

3. Interferences

Potential interferences result from agents that can reduce the phosphomolybdic acid to form the blue oxide and hence, give an elevated reading--including stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide. Interferences from oxidation of the monomethyl hydrazine giving a diminished reading may occur with halogens and oxygen (especially in presence of Cu (I) ions). Other hydrazine derivatives will also interfere (elevating the reading) and hydrogen dioxide will possibly reoxidize the blue oxide giving a lower reading (References 11.2, 11.3, 11.4, and 11.5).

S149-1

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.169-0.78 mg/cu m was 0.106. This value corresponds to a 0.037 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.6.
- 4.2 A collection efficiency of 0.965, standard deviation of 0.022, (essentially 1.0) was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no bias is introduced in the sample collection step. There is also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The samples, collected in bubblers, are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 Glass bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.
- 5.4 Monomethyl hydrazine is slowly air-oxidized and is difficult to maintain known purity. Therefore, all analytical work is done using a stable salt such as the sulfate of monomethyl hydrazine.

6. Apparatus

- 6.1 Sampling Equipment. The sampling method for the bubbler collection method consists of the following components:
- 6.1.1 A glass, midget bubbler with a stem which has a fritted glass end and containing 15 ml of 0.1 M hydrochloric acid (Section 7.1). The fritted end should have porosity approximately equal to that of Corning EC (170-220 micron maximum pore diameter).
- 6.1.2 A pump suitable for sampling: at least 1.5 liter per minute for 15 minutes. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.
- 6.2 Spectrophotometer. This instrument should be capable of measuring the developed color at 730 nm.
- 6.3 Matched glass cells or cuvettes, 5-cm path length.
- 6.4 Assorted laboratory glassware -- pipets, volumetric flasks, large test tubes, and graduated cylinders of appropriate capacities.
- 7. Reagents

All reagents must be ACS reagent grade or better.

 - 7.1 Collection Medium. 0.1 M hydrochloric acid. Fill a 1000-ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated hydrochloric acid, mix, and bring volume to the 1000-ml mark.
 - 7.2 Phosphomolybdic acid solution (PMA). Dissolve 15 grams PMA in 500 ml distilled water, allow to stand one day, and filter before use through a fluted paper filter.
 - 7.3 Methylhydrazine sulfate.
 - 7.4 Methylhydrazine sulfate, standard solution. Weigh accurately 0.1000 gram methylhydrazine sulfate in a 100-ml volumetric flask and fill to the mark with 0.1 M hydrochloric acid.
- 8. Procedure
 - 8.1 Cleaning of equipment. No specialized cleaning of glassware is required.
 - 8.2 Calibration of personal pump. Personal sampling pump should be calibrated using integrating volume meter (Section 6.1.3) or other means.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Pour 15 ml of the 0.1 M hydrochloric acid (Section 7.1) into each bubbler.

- 8.3.2 Connect a bubbler with a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.
 - 8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.5 liter per minute for 15 minutes.
 - 8.3.4 After sampling, the bubbler stems are lifted out of the bubbler bottom and rinsed with approximately 1 ml 0.1 M hydrochloric acid. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
 - 8.3.5 Care should be taken to minimize spillage or loss by evaporation at all times.
 - 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
 - 8.3.7 Blank. With each batch of ten samples, submit one bubbler from the same lot of bubblers which was used for sample collection and which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.4 Analysis of Samples
- 8.4.1 The sample in each bubbler is analyzed separately.
 - 8.4.2 Transfer the solution to a 25-ml volumetric flask.
 - 8.4.3 Rinse the bubbler with 1 ml 0.1 M hydrochloric acid and add rinse to the volumetric flask.
 - 8.4.4 Add 7.5 ml phosphomolybdic acid solution to the volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.
 - 8.4.5 Bring solution to the 25-ml mark with 0.1 M hydrochloric acid.
 - 8.4.6 Transfer solution to a large test tube and heat in a water bath at 87°C for 50 minutes. Cool solution under running tap water.
 - 8.4.7 Read at 730 nm within 30 minutes in the spectrophotometer against a blank prepared from the 0.1 M hydrochloric acid in the same fashion as the samples.

9. Calculation and Standards

- 9.1 To five 25-ml volumetric flasks, add 15 ml 0.1 M hydrochloric acid using a graduated cylinder.
- 9.2 Carefully pipet 10, 25, 50, and 100 microliters of the standard solution into the flasks (Section 7.4). Process one flask as a blank.
- 9.3 Add to this mixture 7.5 ml of phosphomolybdic acid solution (Section 7.2) using a 10-ml graduated cylinder.
- 9.4 Bring the solution to the 25-ml mark with 0.1 M hydrochloric acid.
- 9.5 Transfer the solution to a large test tube and heat it in a water bath at 87°C for 50 minutes. Cool the solution under running tap water.
- 9.6 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.
- 9.7 Read the blank in the sample cell, then read the samples at 730 nm.
- 9.8 Construct a calibration curve by plotting absorbance against milligrams of monomethyl hydrazine in the color developed solution. Since the calibration curve is made using aliquots of methylhydrazine sulfate, the weight of monomethyl hydrazine must be calculated.

$$\text{mg, methyl hydrazine} = \text{mg, methylhydrazine sulfate} \times \frac{46.07}{144} \times \frac{\text{ml standard}}{100 \text{ ml}}$$

where:

46.07 = molecular weight of methyl hydrazine

144 = molecular weight of methylhydrazine sulfate

10. Calculations

- 10.1 Subtract the absorbance of the blank from the absorbance of each sample.
- 10.2 Determine from the calibration curve (Section 9.8) the mg of monomethyl hydrazine present in each sample.

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg methyl hydrazine (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

M.W. = molecular weight (g/mole) of analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Leo Feinsilver, Joseph Perregrino, and Courtney Smith, Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," Industrial Hygiene Journal, 20, February 1959, 26-31.
- 11.2 Comprehensive Treatise on Inorganic and Theoretical Chemistry, J. W. Mellor (Longmans, N.Y.), 1948, Vols. VII and XI.
- 11.3 Inorganic Chemistry, Heslop and Robinson (Elsevier, N.Y.), 1967.
- 11.4 Advanced Inorganic Chemistry, Cotton and Wilkinson (Interscience, N.Y.), 1966.
- 11.5 Inorganic Chemistry, T. Moeller (Wiley & Sons, N.Y.). 1963.
- 11.6 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: NO

NITRIC OXIDE

2ND EDITION METHOD #: S321

DATE ISSUED: 08/05/77

M.W.: 30.01

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: gas; BP -152 °C; MP -164 °C;

VP 3458 kPa (26000 mm Hg) @ 20 °C;

vapor density (air=1) 1.0

OSHA: TWA 25 ppm

NIOSH: TWA 25 ppm

ACGIH: TWA 25 ppm

(1 ppm = 1.23 mg/m³ @ NTP)

SYNONYMS: nitrogen monoxide; CAS #10102-43-9

SAMPLER: multi-stage solid sorbent tubes; impregnated molecular sieves

FLOW RATE: 25 mL/min

RECOMMENDED VOLUME: 1.5 L

MEASUREMENT TECHNIQUE: visible spectrophotometry, 540 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of sodium nitrite in water in the
range 0.3 to 18 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.3 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH analytical sequence #5821-J [1]

APPLICABILITY: this method is capable of collecting and measuring both nitrogen dioxide
and nitric oxide

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH/DPSE Analytical Sequence No. 5821-J, Measurement Research Support Branch, NIOSH,
(unpublished, 1987).

[2] 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.

[3] Maffiolo, G. and Gourdon, F. Determination of Ambient Nitrogen Oxides, Tech. Mod.,
30(11-12), 29-30 (1988).

[4] Maeda, Y. et al. Determination of Nitrogen Oxides in Air, Chem. Express, 4(7), 455 (1989).

8/15/90

NIOSH Manual of Analytical Methods

Nitric Oxide

Analyte:	Nitrite ion, NO_2^-	Method No.: S321
Matrix:	Air	Range: 11.1 - 48 ppm
OSHA Standard:	25 ppm (30 mg/cu m)	Precision ($\overline{CV}_T$): 0.062
Procedure:	Oxidation to nitrogen dioxide, collection on triethanolamine-coated molecular sieve, desorption with triethanolamine, spectrophotometric analysis	Validation Date: 8/5/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a sampling tube containing in series: 400 mg triethanolamine-impregnated molecular sieve; 1.2 g Draeger oxidizer; 400 mg triethanolamine-impregnated molecular sieve. The first section removes ambient nitrogen dioxide. The Draeger oxidizer transforms nitric oxide to nitrogen dioxide and the last section adsorbs the nitrogen dioxide.
- 1.2 The last triethanolamine-impregnated molecular sieve section in each tube is transferred to a flask, and the nitrogen dioxide is desorbed and hydrolyzed in an aqueous triethanolamine solution to yield nitrite ion. An aliquot is treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)-ethylene-diamine dihydrochloride and the reacted nitrite ion is measured spectrophotometrically.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 11.14-47.7 ppm at an atmospheric temperature of 19°C and atmospheric pressure of 764 mm Hg using a 1.5-liter sample volume. This sample volume is based on the adsorptive capacity of the triethanolamine-impregnated molecular sieve to collect nitric oxide vapors at high relative humidity. This method is capable of measuring much smaller amounts, since the collection and desorption efficiency has been shown to be adequate at levels of approximately 0.5 ppm NO_2 and 9 ppm NO (Reference ii.1).
- 2.2 The upper limit of the sampling and analytical method is dependent on the oxidation efficiency of the Draeger oxidizer

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and adsorptive capacity of the triethanolamine-impregnated molecular sieve section. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. After sampling 108 minutes at 20.94 mL/minute from an atmosphere containing 46.1 ppm NO at 84% relative humidity, 3.8% breakthrough occurred. The recommended sampling volume is thus less than two-thirds the 5% breakthrough capacity. It is expected that the sampling tube will not be suitable at concentrations much in excess of 2X the OSHA standard. Of course, other oxidizable compounds in the air may also reduce the collection efficiency of the sampling tubes.

- 2.3 The detection limit under the prescribed sampling conditions is approximately 0.19 ppm NO.

3. Interferences

- 3.1 Nitrogen dioxide is an interference in this method at some undetermined concentration in excess of 50 ppm. This is due to the unknown capacity of nitrogen dioxide on the first triethanolamine-impregnated molecular sieve section of the sampling tube. Since this is far in excess of the recommended OSHA standard of 1 ppm, such an occurrence is probably not common in the workplace.
- 3.2 Interference due to collection of nitric oxide on the first section of triethanolamine-impregnated molecular sieve is observed to correspond to less than 1% of the NO at 2X the OSHA standard.
- 3.3 Any compound which is collected on the second triethanolamine-impregnated molecular sieve section and which reacts with the colorimetric reagents may act as a positive or negative interference. If such an interference exists, its impact must be determined by independent analysis.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 11.14-47.7 ppm was 0.0621. This value corresponds to a 1.552 ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.
- 4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.4% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the

"found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Another possibility is that the stoichiometric factor for conversion of nitrogen dioxide (gas) to nitrite ion (0.63) is not correct. Several authors have reported values from 0.5-0.9. The value determined by Blacker (Reference 11.4) under similar experimental conditions is 0.63. The analytical data described in Reference 11.3 corroborates this value and, therefore, it has been used for method validation. Storage stability studies conducted on samples collected from an atmosphere containing 19.9 ppm NO indicate that collected samples are stable at least 7 days. For these reasons, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages

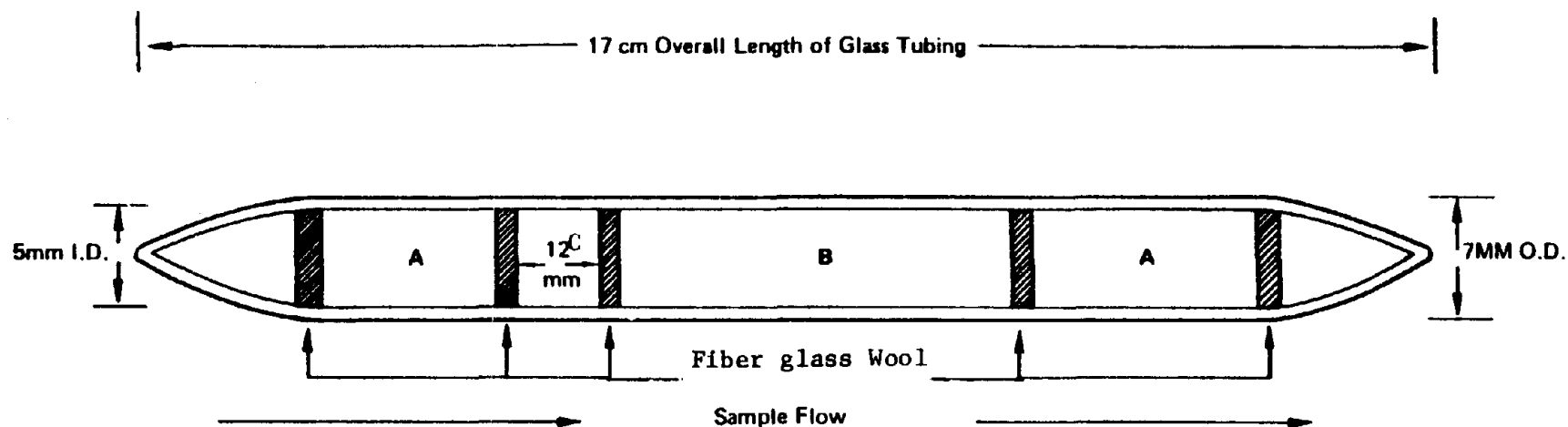
- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal due to the analytical specificity.
- 5.2 The method utilizes a readily available visible spectrophotometer.
- 5.3 If the concentration of nitrogen dioxide present in the environment sampled exceeds the proposed OSHA standard (1 ppm), its concentration may be determined with the same sampling tube as used for nitric oxide analysis.
- 5.4 If the nitric oxide concentration exceeds 2X the OSHA standard, the collection device will not quantitatively collect all of the analyte present.
- 5.5 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated with one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate of 25 milliliters per minute. The pump must be calibrated with a sampling tube in line.
- 6.2 Sampling Tubes. Glass tube with both ends flame-sealed, 17 cm long with 7 mm O.D. and 5 mm I.D., containing the sections listed below and shown schematically in Figure S321-1. The pressure drop across the tube is about 3 cm of H₂O at a flow rate of 25 milliliters per minute.

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A. 400 mg Triethanolamine – Impregnated Type 13 X, 30-40 Mesh Molecular Sieve

B. 1.2 g of Oxidation Material No. 1900277 from Draeger Company of Germany,
supplied by National Mine Service Co.

C. 12 mm glass spacer tube, 4.0 mm O.D., 2.6 mm I.D.

NITRIC OXIDE SAMPLING TUBE

FIGURE S321-1

- 6.2.1 Small plugs of glass wool as shown in Figure S321-1.
- 6.2.2 400-mg triethanolamine-impregnated Type 13X, 30-40 mesh molecular sieve.
- 6.2.3 12-mm glass spacer tube with 4.0 mm O.D., and 2.6 mm I.D.
- 6.2.4 1.2 g, oxidizer, No. 1900277, oxidation material produced by Draeger Company. Available from National Mine Service Company, 3001 Koppers Bldg., Pittsburgh, PA 15219.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g glycerol, 50 mL acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

- 6.3 A spectrophotometer capable of measuring absorbance or transmittance at 540 nm.
- 6.4 Two matched 1-cm silica cells.
- 6.5 Volumetric flasks, 50-mL and other convenient sizes.
- 6.6 Beakers, 100-mL.
- 6.7 Pipets, 1, 5 and 10-mL and other convenient sizes to make standard dilutions.
- 6.8 Balance.
- 6.9 Barometer.
- 6.10 Thermometer.
- 6.11 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better. They are the same as described in Reference 11.1.

- 7.1 Liquid Absorber. Prepare by dissolving 15.0 g triethanolamine in approximately 500 mL distilled water, adding 0.5 mL n-butanol, and diluting to 1 liter.
- 7.2 Hydrogen Peroxide Solution 0.02% (V/V). Prepare by diluting 0.2 mL, 30% hydrogen peroxide to 250 mL with distilled water.
- 7.3 Sulfanilamide Solution. Prepare by dissolving 10 g sulfanilamide in 400 mL distilled water, adding 25 mL concentrated phosphoric acid and diluting to 500 mL.
- 7.4 NEDA Solution. Prepare by dissolving 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride in distilled water and diluting to 500 mL.
- 7.5 Stock Nitrite Solution, 100 ppm NO_2^- . Prepare by dissolving 0.1500 g sodium nitrite in 1 liter of water.
- 7.6 Working Nitrite Solution, 2 ppm NO_2^- . Prepare by diluting 2 mL of the stock nitrite solution to 100 mL with absorbing solution.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be initially soaked in a mild detergent to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water, in that order, and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the two ends of the sampling tube to provide an opening of at least one half of the internal diameter of the tube (5 mm).

- 8.3.2 The tube should be oriented so that the inner glass tube (12 mm) is farthest from the pump.
- 8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.3.5 A sample size of 1.5 liters is recommended. Sample at a flow rate of exactly 0.025 liter per minute for 60 minutes. The flow rate should be known with accuracy of at least $\pm 5\%$. No other flow rate is suitable.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.7 The exposed tube should be labeled appropriately and capped with supplied plastic caps.
- 8.3.8 With each batch of five or fewer samples, submit one sampling tube which has been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.
- 8.3.9 Capped sampling tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, the broken ends of each tube are widened to facilitate removal of the sorbent. The glass wool is removed carefully and discarded, making sure that no sorbent is lost in the process. The triethanolamine-impregnated molecular sieve in back (farthest from the 12-mm inner glass tube) is transferred to a 50-mL volumetric flask. If it is desired to quantify the NO_2 concentration (see restriction noted in Section 5.3) as well as the NO concentration, the triethanolamine-impregnated molecular sieve in front may be transferred to a separate 50-mL volumetric flask. These two sections may be analyzed separately.
- 8.4.2 Extraction of the Sample. Prior to analysis, liquid absorber is added to the flask to bring the volume to 50 mL. The flask is shaken vigorously for about 30 seconds and the solids allowed to settle.

A blank is prepared similarly with a TEA/molecular sieve section from an unexposed sampling tube.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 540 nm and set the zero and 100% transmittance scale using a 1-cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Pipet 10 mL of the extracted sample into a 50 mL volumetric flask.
2. Add 1.0 mL hydrogen peroxide solution, 10.0 mL sulfanilamide solution, and 1.4 mL NEDA solution with thorough mixing after each addition.
3. Allow ten minutes for complete color development.
4. Transfer some of the sample to a 1-cm absorption cell.
5. Measure the absorbance or transmittance at 540 nm using a reagent blank to set zero absorbance.

9. Calibration and Standards

- 9.1 Using freshly prepared working nitrite solution, prepare at least five calibration standards in absorbing solution to cover a nitrite concentration range of 1 to 18 μg nitrite per 10 mL.
- 9.2 Prepare these standards fresh daily by appropriate dilution of the working nitrite solution using absorbing solution for all dilutions. A reagent blank containing no nitrite should also be prepared.
- 9.3 Proceed as in Section 8.4.4.
- 9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the reagent blank versus the concentration of each standard in $\mu\text{g NO}_2^-$ per 10 mL on linear graph paper.

10. Calculations

- 10.1 Correction for the sample blank (obtained by extraction and analysis of the sampling tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{sample blank}}$$

- 10.2 Read the amount of nitrite ion, in $\mu\text{g NO}_2^-$ per 10 mL, corresponding to the Abs_{corr} from the standard curve (Section 9.4).
- 10.3 Multiply the amount of nitrite ion per 10 mL by the factor shown below to obtain the $\mu\text{L NO}_2$ (gas) per 50 mL (total sample) at 25°C and 760 mm Hg.

$$\mu\text{L NO}_2(\text{gas}) \text{ in sample} = \mu\text{g NO}_2^-/10 \text{ mL} \times \frac{5}{1.88 \times 0.63}$$

where:

1 $\mu\text{L NO}_2(\text{gas}) = 1.88 \mu\text{g NO}_2(\text{gas})$ at 25°C and 760 mm Hg, and

1 $\mu\text{g NO}_2(\text{gas}) = 0.63 \mu\text{g NO}_2^- \equiv$ "stoichiometric factor"

- 10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

- 10.5 The concentration of analyte in the air sampled can be expressed in ppm (at standard conditions of 25°C and 760 mm Hg).

$$\text{ppm NO} = \frac{\mu\text{L NO (gas) (see Section 10.3)}}{\text{Air volume sampled (liters)} \times \frac{P}{760} \times \frac{298}{T}}$$

Another method of expressing concentration is mg/cu m

$$\text{mg/cu m} = \text{ppm} \times \frac{30.01}{24.45}$$

where:

P = Pressure (mm Hg) of air sampled

T = Temperature (°C) of air sampled

760 = Standard Pressure (mm Hg)

298 = Standard Temperature (°C)

24.45 = Molar volume (liter/mole) of air at 25°C
and 760 mm Hg

30.01 = Molecular weight of nitric oxide

11. References

- 11.1 M.A. Willey, C. McCammon, Jr., and L. Doemeny, Am. Ind. Hyg. Assoc. J. (38), 358 (1977).
- 11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D. C., Order No. 017-033-00231-2.
- 11.3 S321 Backup Data Report for Nitric Oxide, prepared under NIOSH Contract No. 210-76-0123.
- 11.4 J.H. Blacker, Am. Ind. Hyg. Assoc. J. (34), 390 (1973).

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{H}_2\text{NC}_6\text{H}_4\text{NO}_2$

p-NITROANILINE

2ND EDITION METHOD #: S7

DATE ISSUED: 07/07/78

M.W.: 138.14

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: crystals; sp. gr. 1.424

@ 20 °C; MP 146 °C; BP 332 °C;

VP <<0.1 kPa (<<1mm Hg);

OSHA: TWA $3\text{mg}/\text{m}^3$ (skin)

NIOSH: TWA $3\text{mg}/\text{m}^3$ (skin)

ACGIH: TWA $3\text{mg}/\text{m}^3$ (skin)

SYNONYMS: 4-nitrobenzenamine; CAS #100-01-6

SAMPLER: filter, 0.8- μm mixed cellulose ester membrane

FLOW RATE: 1.5 L/min.

RECOMMENDED VOLUME: ≥ 90 L

MEASUREMENT TECHNIQUE: liquid chromatography, UV detector, 375 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of p-nitroaniline in isopropanol in the range 0.05 to 2 mg per sample.

ESTIMATED LIMIT OF DETECTION (LOD): 0.05 mg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: this method is not applicable for sampling environments where high concentration of p-nitroaniline vapor may be present

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Gas Chromatography/Mass Spectrometric Method for Determination of Semivolatile Organics, U.S. EPA test method #SW-846 (1986)

p-Nitroaniline

Analyte:	p-Nitroaniline	Method No.:	S7
Matrix:	Air	Range:	3.9 - 12.9 mg/cu m
OSHA Standard:	6 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, extraction with isopropanol, HPLC	Validation Date:	7/7/78

1. Synopsis

A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the p-nitroaniline aerosol present. This method is not applicable for sampling environments where significant p-nitroaniline vapor may be present. The filter is transferred to a sample jar and extracted in 5 mL of isopropanol. An aliquot of the sample is injected into a high performance liquid chromatograph equipped with a variable wavelength UV detector set at 375 nm.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was validated over the range of 3.90-12.88 mg/cu m at an atmospheric temperature and pressure of 25°C and 762.5 mm Hg, using a 90-liter sample.
- 2.2 The method may be extended to higher values by further dilution of the sample solution. The detection limit of the analytical method is estimated to be at least 10 µg per mL.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any other compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data based on a single set of conditions cannot be considered as proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.90-12.88 mg/cu m was 0.0544. This value corresponds to a 0.326 mg/cu m standard

deviation at the OSHA standard level. Statistical information may be found in Reference 11.1.

- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average of 95% of the time over the validation range. The concentrations obtained at 0.5, 1 and 2 times the OSHA standard were 1.5% lower than the dynamically generated test concentrations. The analytical method recovery was determined to be 96.6% for a collector loading of 0.2780 mg. In storage stability studies the mean of samples analyzed after seven days was within 2% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 2.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
- 6.1.1 Filter. The filter unit consists of a 37-mm diameter, 0.8 micrometer pore size, mixed cellulose ester membrane filter and a 37-mm diameter cellulose backup pad.
 - 6.1.2 Filter Holder. The filter is placed in a two-piece filter holder held together by tape or a shrinkable band.
 - 6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate is needed. The pump must be calibrated with a representative filter unit in the line.
 - 6.1.4 Thermometer.
 - 6.1.5 Barometer.
 - 6.1.6 Stopwatch.
- 6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 375 nm.

- 6.3 Column (25-cm x 4.6-mm x 6.4-mm stainless steel) packed with Partisil 10 or equivalent.
- 6.4 A syringe or fixed volume sample loop for HPLC injection. A 20- μ L sample volume was used for these studies.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Microliter syringes in convenient sizes for making standard solutions.
- 6.7 Volumetric flasks in convenient sizes for making standard solutions.
- 6.8 Squat form ointment jars with Teflon film gaskets and screw caps.
- 6.9 A 5-mL pipette.
- 6.10 Tweezers.
- 7. Reagents

Whenever possible reagents used should be ACS reagent grade or better.

 - 7.1 p-Nitroaniline, 99%.
 - 7.2 2-Propanol, distilled in glass.
 - 7.3 Hexane, distilled in glass.
 - 7.4 p-Nitroaniline stock solution, 10.8 mg/mL. Dissolve 0.108 g p-nitroaniline in 10 mL isopropanol. This solution should be agitated in an ultrasonic cleaner to aid in dissolution.
 - 7.5 HPLC mobile phase, 40% isopropanol in hexane.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter unit in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

- 8.3.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the edge of the filter is sealed. The cellulose membrane filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.
- 8.3.2 Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.
- 8.3.4 A sample size of at least 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and readjusted as necessary. If the rotameter cannot be readjusted, terminate sampling.
- 8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.
- 8.3.8 Carefully record sample identity and all relevant sample data.
- 8.3.9 Obtain a blank sample by handling one filter in the same manner as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples or partial batch of ten samples.
- 8.3.10 A bulk sample of the suspected material should be submitted to the laboratory in a glass container lined with a Teflon cap.

- 8.3.11 The filter holders should be shipped in a suitable container designed to prevent damage in transit. Never transport the bulk sample in the same container as the sample or blank filters.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the cellulose membrane filter from the holder with the aid of appropriate tweezers and transfer to the 2-oz. ointment jar.
2. Add 5 mL of isopropanol to the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

8.4.2 Analysis by High Pressure Liquid Chromatograph. The mobile phase is 40% isopropanol in hexane. The typical operating conditions for the liquid chromatograph are:

1. 1.0 mL/min solvent flow rate
2. Ambient column temperature
3. 500 psi system pressure
4. 375 nm UV detection wavelength

8.4.3 Injection. A 20- μ L sample aliquot is recommended for this analysis. The sample may be injected either by using an appropriate syringe or by filling a fixed volume sample loop, provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

- 8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determinations should cover the concentration range of interest.

- 8.5.2 Procedure for Determining Recovery. A known amount of p-nitroaniline, equivalent to that present in a 90-liter sample at the selected level, is added to a cellulose membrane filter and air-dried. A stock solution containing 10.8 milligrams of p-nitroaniline per milliliter of isopropanol is prepared. Add 25, 50 and 100-microliter aliquots of the solution to the MCEF and air-dry to produce samples equivalent to 90-liter collections at 0.5, 1 and 2 times the OSHA standard. Six filters at each of the three levels are prepared and allowed to stand overnight. A parallel blank filter is also prepared except no sample is added to it. All filters are then extracted and analyzed as described in Section 8.3.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered} - \text{Filter Blank (mg)}}{\text{Weight (mg) Added}}$$

9. Calibration and Standardization

A series of standards, varying in the concentration range corresponding to approximately 0.1 to 3 times the OSHA standard for the samples under study, is prepared and analyzed under the same HPLC conditions and during the same time period as the unknown samples.

- 9.1 From the stock solution listed in Section 7.4, prepare at least six standards to cover the concentration range of 0.054-1.62 mg/5 mL. This is done by adding from 5 to 150-microliter aliquots of the stock solution to 5 mL isopropanol in ointment jars. Analysis is done as described in Section 8.4.

- 9.2 The series of standards is analyzed under the same HPLC conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in mg/5 mL, because samples are extracted in this amount of isopropanol. Curves are established by plotting concentrations in mg/5 mL versus peak area.

10. Calculations

- 10.1 Read the concentration in mg/5 mL corresponding to the sample peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/5 mL and the volume of the sample injected is identical to the volume of standards injected.

- 10.2 Corrections for the sample blank (Section 8.3.9) must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in sample blank filter

- 10.3 Divide the weight of analyte found on each filter by the recovery (Section 8.5) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Weight found}}{\text{Recovery}}$$

- 10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

- 10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)}}{\text{Air Volume Sampled (cu m)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.
- 11.2 Backup Data Report for p-Nitroaniline, S7, prepared under NIOSH Contract No. 210-76-0123, 7/7/78.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: (C ₆ H ₅) ₂ O	2ND EDITION METHOD #: S72	PHENYL ETHER
M.W.: 170.21		DATE ISSUED: 02/14/75 CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: crystals or liquid;
OSHA: TWA 1 ppm	d 1.072-1.075 g/mL @ 20 °C;
NIOSH: TWA 1 ppm	MP 27 °C; BP 259 °C;
ACGIH: TWA 1 ppm; STEL 2 ppm	VP <0.13 kPa (<1 mm Hg) @ 20 °C

SYNONYMS: 1,1'-oxybisbenzene; diphenyl oxide; diphenyl ether; CAS #101-84-8

SAMPLER: charcoal, 100 mg/50 mg

FLOW RATE: ≤0.2 L/min

RECOMMENDED VOLUME: ≤10 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of phenyl ether in carbon disulfide in the range 7 to 130 µg per sample.

ESTIMATED LIMIT OF DETECTION (LOD): 7 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402

Phenyl Ether

Analyte:	Phenyl Ether (vapor)	Method No.: S72
Matrix:	Air	Range: 3-13 mg/cu m
OSHA Standard:	1 ppm (7 mg/cu m)	Precision ($\overline{CV}_T$): 0.070
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 3-13 mg/cu m at an atmospheric temperature and pressure of 24°C and 766 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.70-21 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.2 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of phenyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 0.6 mg of phenyl ether when a test atmosphere

containing 13.1 mg/cu m of phenyl ether in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3-13 mg/cu m was 0.070. This value corresponds to a 0.49 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 Collection efficiency of the collecting medium was found to be 1.00 ± 0.01 , so that no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which desorption efficiency corrections were made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Phenyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

- 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 230°C injector temperature
 5. 265°C manifold temperature (detector)
 6. 215°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of phenyl ether containing 17.3 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(C_6H_5)_2O$	PHENYL ETHER-BIPHENYL MIXTURE
& $C_6H_5C_6H_5$	2ND EDITION METHOD #: S73
M.W.: 166 (average)	DATE ISSUED: 02/14/75
	CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: liquid; d 1.06 g/mL @ 25 °C;
	BP 257 °C;
OSHA: TWA 1 ppm	VP 0.01 kPa (0.08 mm Hg) @ 25 °C;
NIOSH: TWA 1 ppm	vapor density (air=1) 5.7 (average);
ACGIH: no TLV	flash pt. (open cup) 124 °C
(1ppm = 6.79 mg/m ³ @ NTP)	

SYNONYMS: Dowtherm A; diphenyl oxide-diphenyl mixture; CAS # none

SAMPLER: silica gel tube, 150/75 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: ≤10 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: capillary column may be used for better sensitivity

MEASUREMENT CALIBRATION: standard solutions of phenyl ether-biphenyl mixture in benzene in the range 0.004 to 21 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 4 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.



Phenyl Ether - Biphenyl Mixture
(vapor)

Analyte:	Phenyl Ether-Biphenyl Mixture	Method No.: S73
Matrix:	Air	Range: 3.86-15.7 mg/cu m
OSHA Standard:	1 ppm (7 mg/cu m)	Precision ($\overline{CV}_T$): 0.089
Procedure:	Adsorption on silica gel, desorption with benzene, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.
- 1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with benzene.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The areas of the resulting peaks are determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 3.86-15.7 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.7-21 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.2 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 0.7 mg of analyte when a test atmosphere containing

15.7 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since benzene is used rather than carbon disulfide to desorb the analyte from the silica gel, it is not possible to measure benzene in the sample with this desorbing solvent. If it is suspected that benzene is present, a separate sample should be collected for benzene analysis.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.86-15.7 mg/cu m was 0.089. This value corresponds to a 0.62 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 Collection efficiency of the collecting medium was found to be 1.00 ± 0.01 , so that no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which desorption efficiency corrections were made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% OV-17 on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality benzene.

7.2 Biphenyl, reagent grade.

7.3 Phenyl Ether, reagent grade.

7.4 Phenyl Ether-Biphenyl Mixture: Ten grams of phenyl ether-biphenyl mixture is prepared by dissolving 2.65 grams solid biphenyl in 7.35 grams melted phenyl ether. (Liquid eutectic)

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 Purified nitrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of benzene is pipetted into each sample container. (All work with benzene should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. It is necessary to be able to measure the phenyl ether and biphenyl separately. Using the following operating conditions, biphenyl and phenyl ether are observed as separate chromatographic peaks.
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 200°C injector temperature
 - 5. 250°C manifold temperature (detector)
 - 6. 140°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks for both components are measured separately by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from standard curves prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compounds that are removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of the phenyl ether-biphenyl mixture (Section 7.4) containing 17.5 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (using 2 microliters, 4 microliters, and 8 microliters of hexane solution for the 0.5X, 1X, and 2X OSHA levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of benzene with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The weight (mg) added for each component is calculated from the amount of solution added and the weight percent of that component in the solution. For instance, addition of an 8-microliter aliquot of the hexane solution of 17.5 mg/ml to 0.5 ml benzene results in a standard containing 0.102 mg phenyl ether/0.5 ml benzene and 0.037 mg biphenyl/0.5 ml benzene.

The desorption efficiencies (D.E.) for phenyl ether and biphenyl are determined separately. For each compound, the desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found for the two components separately. These curves are used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml benzene, because samples are desorbed in this amount of benzene. The mixture of phenyl ether-biphenyl described in Section 7.4 is used for the standards. The density of the mixture (1.06 g/ml at 25°C), as given in Reference 11.4, is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. A curve for each component is established by plotting concentration in mg/0.5 ml for that component versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the

sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

The concentration in mg/cu m in air is determined for phenyl ether and biphenyl separately. The concentration of the mixture is the sum of these two concentrations.

10.1 Read the weight, in mg, corresponding to the peak area for each component from the appropriate standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 For each component, add the weights found in the front and backup sections to get the total weight of that component in the sample.

10.4 For each component, read the desorption efficiency from the curve (See Section 8.5.2) for the amount of that component found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of each component in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

The concentration of the mixture in air is the sum of the concentrations of the two components:

$$\text{mg/cu m (mixture)} = \text{mg/cu m (phenyl ether)} + \text{mg/cu m (biphenyl)}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.
- 11.4 Hake, C.L. and Rowe, V.K., "Phenyl Ether-Biphenyl Eutectic Mixture (Dowtherm A)," Industrial Hygiene & Toxicology, Volume II, 1701, (1962).

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_6H_5OCH_2CH(O)CH_2$

2ND EDITION METHOD #: S74

PHENYL GLYCIDYL ETHER

DATE ISSUED: 02/14/75

M.W.: 150.18

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 1 ppm

NIOSH: C 1 ppm

ACGIH: TWA 1 ppm

(1 ppm = 6.14 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.109 g/mL @ 20 °C;

BP 245 °C; FP > 110 °C;

VP 0.0013 kPa (0.01 mm Hg) @ 25 °C;

vapor density (air=1) 4.37

SYNONYMS: 1,2-epoxy-3-phenoxypropane; phenoxy-propane oxide; CAS #122-60-1

SAMPLER: charcoal tube, 100 mg/50 mg

FLOW RATE: ≤1 L/min

RECOMMENDED VOLUME: ≤50 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: solutions of phenyl glycidyl ether in carbon disulfide in the range 0.1 to 6 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method was not evaluated at current standards/recommended levels.

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] Levin, J.O. et al., Solid Sorbent Sampling and Chromatographic Determination of Glycidyl Ethers in Air, J. Chromatogr., 454, 121-128 (1988).

Phenyl Glycidyl Ether

Analyte:	Phenyl Glycidyl Ether	Method No.: S74
Matrix:	Air	Range: 31-121 mg/cu m
OSHA Standard:	10 ppm (60 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 31-121 mg/cu m at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 50 liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 6-180 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of phenyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 25 mg of phenyl glycidyl ether when a

test atmosphere containing 112 mg/cu m of phenyl glycidyl ether in air was sampled at 0.93 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 31-121 mg/cu m was 0.057. This value corresponds to a 3.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the values obtained using the overall sampling and analytical method were 8.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.2)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Phenyl Glycidyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 50 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 1. 50 ml/min (60 psig) nitrogen carrier gas flow
 - 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 - 3. 500 ml/min (50 psig) air flow to detector
 - 4. 230°C injector temperature
 - 5. 265°C manifold temperature (detector)
 - 6. 90°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 50 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_6H_5NHNH_2$

PHENYLHYDRAZINE

2ND EDITION METHOD #: S160

DATE ISSUED: 08/01/75

M.W.: 108.14

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; MP 24 °C; BP 243.5 °C;
d 1.098 g/mL @ 20 °C;
VP 5 Pa (0.04 mm Hg) @ 25 °C;
flash point 88 °C (closed cup)

OSHA: TWA 5 ppm; STEL 10 ppm (skin)

NIOSH: carcinogen; C (120 min) 0.14 ppm

ACGIH: TWA 5 ppm; STEL 10 ppm; Susp. Human carcinogen
(1 ppm = 4.42 mg/m³ @ NTP)

SYNONYMS: hydrazinobenzene; CAS #100-63-0

SAMPLER: glass midget bubbler containing 15 mL of 0.1 M hydrochloric acid

FLOW RATE: ≤ 1 L/min

RECOMMENDED VOLUME: 100 L

MEASUREMENT TECHNIQUE: visible spectrophotometry, 730 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of phenylhydrazine hydrochloride in 0.1 M
hydrochloric acid in the range 1 mg to 90 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.5 mg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: other hydrazines will interfere in the analysis

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] NIOSH Criteria for a Recommended Standard....Occupational Exposure to Hydrazines, DHEW (NIOSH) Publ. No. 78-122 (1978).
- [2] 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.
- [3] Murty, N.K. et al. Determination of Phenyl Hydrazine, Talanta, 31 (6), 466 (1984).
- [4] Hassan, T., Spectrophotometric Determination of Phenyl Hydrazine, Anal. Letters, 21 (4), 633-640 (1988).

Phenylhydrazine

Analyte:	Phenylhydrazine	Method No.:	S160
Matrix:	Air	Range:	10.37-44.8 mg/cu m
OSHA Standard:	5 ppm (22 mg/cu m)--skin	Precision ($\overline{CV}_T$):	0.060
Procedure:	Bubbler collection, complexation, colorimetric	Validation Date:	8/1/75

1. Principle of the Method (Reference 11.1)

- 1.1 Phenylhydrazine is collected in a standard midget bubbler containing 0.1 N hydrochloric acid.
- 1.2 The resulting solution is reacted with phosphomolybdic acid to form a bluish green colored complex.
- 1.3 The strong absorption maximum at 730 nm is used as a quantitative measure of phenylhydrazine.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 10.37-44.8 mg/cu m, at an atmospheric temperature and pressure of 22°C and 761 mm Hg. The probable range of the method is 5-45 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where the absorbance is greater than the limits of the standard curve, the samples can be diluted with hydrochloric acid prior to color development to extend the upper limit of the range.
- 2.2 A concentration of 5 mg/cu m of phenylhydrazine can be determined in a 100-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1 cm cell. Greater sensitivity could be obtained by use of a longer path length cell.

3. Interferences

- 3.1 Any hydrazine derivative will potentially interfere with this method. Other reducing agents such as ferrous salts may also interfere.
- 3.2 Aldehydes and ketones in the air may interfere, because of the potential formation of phenylhydrazones in the acid medium in the bubbler.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 10.37-44.8 mg/cu m was 0.060. This value corresponds to a 1.32 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 A collection efficiency of 1.00 ± 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The samples, collected in bubblers, are analyzed by means of a quick, instrumental method.
- 5.2 Phenylhydrazine is slowly air-oxidized and is difficult to maintain known purity. Therefore, all analytical work is done using phenylhydrazine hydrochloride.

6. Apparatus

- 6.1 Sampling Equipment. The sampling method for the bubbler collection method consists of the following components:
- 6.1.1 A glass, standard midget bubbler with a stem which has a fritted glass end and containing 0.1 N HCl (Section 7.2). The fritted end should have porosity approximately equal to that of Corning EC (170-220 μ maximum pore diameter).
- 6.1.2 A pump suitable for delivering at least 1 liter per minute for 100 minutes. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.1.3 An integrating volume meter such as a dry gas or wet test meter.
- 6.1.4 Thermometer.
- 6.1.5 Manometer.
- 6.1.6 Stopwatch.

- 6.2 Spectrophotometer. This instrument should be capable of measuring the developed color at 730 nm.
- 6.3 Matched glass cells or cuvettes, 1-cm path length.
- 6.4 Assorted laboratory glassware -- pipets, volumetric flasks, and graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

- 7.1 Distilled water.
- 7.2 Collection Medium. 0.1 N HCl. Fill a 1000 ml volumetric flask with approximately 300 ml distilled water, add 8.6 ml concentrated HCl, mix and bring volume to the 1000 ml mark.
- 7.3 Phosphomolybdic acid solution (PMA). Dissolve 15 grams PMA in 500 ml distilled water, allow to stand one day and filter before use through a fluted paper filter.
- 7.4 Phenylhydrazine hydrochloride.
- 7.5 Phenylhydrazine hydrochloride, standard solution. Weigh accurately 0.1000 g phenylhydrazine hydrochloride in a 100-ml volumetric flask and fill to the mark with 0.1 N HCl.

8. Procedure

- 8.1 Cleaning of equipment. No specialized cleaning of glassware is required.
- 8.2 Calibration of personal pump. Personal sampling pump should be calibrated using integrating volume meter (Section 6.1.3) or other means.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Pour 15 ml of the 0.1 N HCl (Section 7.2) into each bubbler.
 - 8.3.2 Connect a bubbler with a 5-cm (6-mm I.D. and 8-mm O.D.) glass tube containing the glass wool plug, then to the personal sampling pump using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.
 - 8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute. A sample size of 100 liters is recommended.

- 8.3.4 After sampling the bubbler stems are lifted out of the bubbler bottom and rinsed with approximately 5 ml distilled water. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.
- 8.3.5 Care should be taken to minimize spillage or loss by evaporation at all times.
- 8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.
- 8.3.7 A "blank" bubbler should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

- 8.4.1 The sample in each bubbler is analyzed separately.
- 8.4.2 Transfer the solution to a 50-ml volumetric flask.
- 8.4.3 Rinse bubbler twice with 5 ml distilled water each and add rinses to volumetric flask.
- 8.4.4 Add 10 ml phosphomolybdic acid solution to volumetric flask. This may be carefully measured in a 10-ml graduated cylinder.
- 8.4.5 Dilute to the 50-ml mark with distilled water.
- 8.4.6 Pipet a 3-ml aliquot into a 10-ml volumetric flask and dilute to 10 ml with distilled water.
- 8.4.7 Read at 730 nm in the spectrophotometer against a blank prepared from the 0.1 N HCl in the same fashion as the samples.

9. Calibration and Standards

9.1 Preparation of the Calibration Curve.

- 9.1.1 To six 50-ml volumetric flasks, add 15 ml 0.1 N HCl using a 25-ml graduated cylinder.
- 9.1.2 Carefully pipet 1, 2, 3, 6, and 9 ml of the standard solution into the flasks (Section 7.5). Process one flask as a blank.

- 9.1.3 Add to this mixture 10 ml of phosphomolybdic acid solution (Section 7.3) using a 10-ml graduated cylinder.
- 9.1.4 Continue as described in Section 8.4.5.
- 9.1.5 Adjust the baseline of the spectrophotometer to zero by reading distilled water in both cells.
- 9.1.6 Read the blank in the sample cell, then read the samples at 730 nm.
- 9.1.7 Construct a calibration curve by plotting absorbance against equivalent milligrams of phenylhydrazine in the color developed solution. Since the calibration curve is made using aliquots of phenylhydrazine hydrochloride, the equivalent weight of phenylhydrazine must be calculated.

$$\begin{array}{lcl} \text{equivalent mg} & \text{mg phenyl-} & \\ \text{of phenyl-} & = & \\ \text{hydrazine} & \text{hydrazine} \cdot \text{HCl} & \\ & \text{weighed out} & \\ & \text{in standard} & \end{array} \times \frac{108.14}{144.6} \times \frac{\text{ml standard}}{100 \text{ ml}}$$

where:

108.14 = molecular weight of phenylhydrazine

144.6 = molecular weight of phenylhydrazine·HCl

10. Calculations

- 10.1 Subtract the absorbance of the blank from the absorbance of each sample.
- 10.2 Determine from the calibration curve (Section 9.1.7) the mg of phenylhydrazine present in each sample.
- 10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg phenylhydrazine (Section 10.2)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

M.W. = molecular weight (g/mole) of analyte

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Leo Feinsilver, Joseph Perregrino, and Courtney Smith, Jr.,
"Estimation of Hydrazine and Three of Its Methyl Derivatives,"
Industrial Hygiene Journal, 20, February 1959, 26-31.
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No.
CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: PH_3

PHOSPHINE

2ND EDITION METHOD #: S332

DATE ISSUED: 03/17/78

M.W.: 34.00

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: gas; d 1.185 g/mL; BP -87.8°C ;
vapor density (air=1) 1.17;
VP $>101\text{ kPa}$ ($>760\text{ mm Hg}$) @ 20°C ;
spontaneously flammable in air if
 P_2H_4 is present

OSHA: TWA 0.3 ppm; STEL 1 ppm

NIOSH: TWA 0.3 ppm; STEL 1 ppm

ACGIH: TWA 0.3 ppm; STEL 1 ppm

(1 ppm = 1.39 mg/m^3 @ NTP)

SYNONYMS: hydrogen phosphide; phosphorus hydride; CAS #7803-51-2

SAMPLER: silica gel coated with mercuric cyanide tube, 300 mg/150 mg

FLOW RATE: 0.01 to 0.2 L/min

RECOMMENDED VOLUME: 16 L

MEASUREMENT TECHNIQUE: UV-VIS spectrophotometry, 625 nm

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of potassium dihydrogen phosphate (KH_2PO_4)
(1.00 mL = $49.94\text{ }\mu\text{g PH}_3$) in the range 0.3 to $10\text{ }\mu\text{g}$
phosphine

ESTIMATED LIMIT OF DETECTION (LOD): $0.3\text{ }\mu\text{g}$ per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: the colorimetric determination of phosphate is subject to interference by any species that also forms a molybdate complex under these conditions; possible interfering species include PCl_3 and PCl_5 vapors and organic phosphorous compounds; the sampler is presently not commercially available, except as a custom fabricated sampler; caution should be exercised when preparing the sampling media as the mercuric cyanide solution is toxic; OSHA method ID-180 [2] employing potassium hydroxide-impregnated beaded carbon media may be used as an alternative method

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-180). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X

Phosphine

Analyte:	Phosphate	Method No.: S332
Matrix:	Air	Range: 0.195-0.877 mg/cu m
OSHA Standard:	0.3 ppm (0.4 mg/cu m)	Precision ($\overline{CV}_T$): 0.091
Procedure:	Collection on coated silica gel, permanganate, extraction, colorimetry.	Validation Date: 3/17/78

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing mercuric cyanide impregnated silica gel to trap the phosphine. The phosphorus is extracted and oxidized to phosphate using a hot, acidic permanganate solution.
- 1.2 The extracted sample is analyzed for phosphate by formation of the phosphomolybdate complex, extraction into a mixture of isobutanol and toluene and reduction using stannous chloride. The absorbance of the reduced phosphomolybdate complex is measured at 625 nm.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was validated over the range of 0.195-0.877 mg/cu m at an atmospheric temperature and pressure of 19.0°C and 765.3 mm Hg, respectively, using a 16-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used. The upper limit of the range of the method depends on the adsorptive capacity of the mercuric cyanide treated silica 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/cu m of phosphine was sampled at a flow rate of 0.2 liter per minute, breakthrough was determined to occur at a sampling volume of 20.75 liters (capacity = 19.86 μ g PH₃). To minimize the probability of overloading the sampling tube, the sample size recommended is less than two-thirds the 5% breakthrough capacity at >80% RH at twice the OSHA standard.
- 2.2 Sampling at 0.2 liter per minute for 80 minutes will yield a 16-liter sample with 6.4 μ g of PH₃ collected at the OSHA standard level. The sensitivity of the method obtained from the slope of the absorbance vs μ g of phosphine calibration curve is 0.0524 absorbance units per μ g of PH₃.

- 2.3 The detection limit of the method determined from twice the standard deviation for the absorbance of six blank treated silica gel tubes corresponds to 0.19 $\mu\text{g PH}_3$ (or 0.0119 mg/cu m for a 16-liter sample).

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including the suspected identities, should be transmitted with the sample.
- 3.2 The colorimetric determination of phosphate is subject to interference by any species which also forms a molybdate complex which is extractable into the isobutanol-toluene mix and absorbs at similar wavelengths.
- 3.3 Any phosphorus compound which is retained by the mercuric cyanide-coated silica gel tube and oxidized to phosphate by hot aqueous permanganate solution will be a major interference. Possible interfering species include PCl_3 and PCl_5 vapors and organic phosphorus compounds. Particulate H_3PO_4 , P_4O_{10} and P_4S_{10} are also possible interferents unless a prefilter is used in conjunction with the sorbent tube. Although a prefilter has not been tested with the method, its use is recommended.
- 3.4 If the possibility of interferences do exist, modification of the analytical procedure must be made to circumvent the problems or an alternative procedure should be used.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{\text{CV}}_T$) for the total sampling method in the range 0.195-0.877 mg/cu m was 0.0908. This value corresponds to a standard deviation of 0.0363 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical procedure was 0.2% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. Also, collected samples, stored for at least seven days, are stable, thus no recovery corrections should be applied to the final result.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable and involves no liquids.
- 5.2 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for only one tube.
- 5.3 The analytical method requires measurement of the absorbance of the phosphomolybdate complex one minute after reduction with stannous chloride. This may present an inconvenience since the samples need to be handled individually.
- 5.4 A disadvantage of the method is that the amount of sample which can be collected is limited by the number of micrograms of phosphine that the tube will hold before overloading. When the amount of phosphine found on the backup section exceeds 25% of that on the front, the probability of sample loss exists.

6. Apparatus

- 6.1 Personal Sampling Pump. A calibrated personal pump whose flow rate can be determined within $\pm 5\%$ of the recommended flow rate. The pump must be calibrated with a representative tube in the line.
- 6.2 Treated Silica Gel Tube. Glass tube with both ends flame sealed 12-cm long with a 6-mm O.D. and a 4-mm I.D. containing two sections of treated silica gel (45/60 mesh, SKC, Inc.). The absorbing section contains 300-mg of the treated silica gel and the backup 150-mg. A small wad of silylated glass wool is also placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in the front of the adsorbing section and at the end of the backup section. The pressure drop across the tube must be less than 2 inches of mercury at a flow rate of 0.2 liter per minute.

The silica gel is coated according to the following procedure:

- 6.2.1 Dry one hundred grams of silica gel at 90°C for 2 hours.
- 6.2.2 Prepare a 2% w/v mercuric cyanide solution in water (2 g $\text{Hg}(\text{CN})_2$ in 100 mL H_2O).
- 6.2.3 Add the dried silica gel to the mercuric cyanide solution and let set for 15 minutes with occasional stirring.
- 6.2.4 Drain the excess mercuric cyanide solution and dry the remaining silica gel at 90°C for 3 hours.

6.2.5 Cool the silica gel to room temperature in a covered beaker.

6.2.6 Expose the silica gel to a humid atmosphere (>80% RH) for 24 hours.

6.3 A spectrophotometer capable of measuring absorbance or transmittance at 625 nm.

6.4 Two matched 5-cm silica cells with tight fitting caps.

6.5 Separatory funnel, 125-mL.

6.6 Beakers, 50-mL.

6.7 Volumetric flasks, 10, 25, 100 and 1000-mL.

6.8 Pipets, 0.2, 10 and 25-mL and other convenient sizes to make standard dilutions.

6.9 Graduated cylinders, 10-mL.

6.10 Water bath (maintained at 65-70°C).

6.11 Syringes, 0.5 and 1.0-mL.

6.12 Balance.

6.13 Barometer.

6.14 Thermometer.

6.15 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better.

7.1 Water, distilled or deionized.

7.2 Potassium dihydrogen phosphate, anhydrous, KH_2PO_4 .

7.3 Sulfuric acid, concentrated.

7.4 Ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

7.5 Ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$.

7.6 Potassium permanganate, KMnO_4 .

7.7 Stannous chloride, SnCl_2 .

- 7.8 Glycerol.
 - 7.9 Toluene.
 - 7.10 Isobutanol.
 - 7.11 Methanol.
 - 7.12 Standard phosphate solution. Prepare by dissolving 200 mg of KH_2PO_4 in 1 L of distilled water. (1.00 mL = 49.94 μg PH_3).
 - 7.13 Molybdate solution. Prepare by dissolving 49.4 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 112 mL of concentrated H_2SO_4 in water to a total volume of 1 L.
 - 7.14 Toluene-isobutanol solvent. Mix equal volumes of toluene and isobutyl alcohol.
 - 7.15 Alcoholic sulfuric acid solution. Add 50 mL of concentrated H_2SO_4 to 950 mL of methyl alcohol.
 - 7.16 Ferrous solution. Prepare by dissolving 7.9 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and 1 mL of concentrated H_2SO_4 in water with a total volume of 100 mL.
 - 7.17 Stannous chloride reagent. Prepare by dissolving 0.4 g of SnCl_2 in 50 mL of glycerol (heat to dissolve).
 - 7.18 Acidic permanganate reagent. Prepare by dissolving 0.316 g of KMnO_4 and 6 mL of concentrated H_2SO_4 in a total volume of 1 L H_2O .
8. Procedure
- 8.1 Cleaning of Equipment
 - 8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.
 - 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water in that order and then dried.
 - 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

- 8.3.1 Immediately before sampling, break the two ends of the silica gel tubes to provide an opening of at least one half of the internal diameter of the tube (2-mm).
- 8.3.2 The treated silica gel tubes should be placed in a vertical direction during sampling to minimize channeling through the sorbent bed.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.3.4 A sample size of 16 liters is recommended. Sample at a known flow rate between 0.2 and 0.01 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.6 The treated silica gel tubes should be labeled appropriately and capped with supplied plastic caps. Under no circumstances should rubber caps be used.
- 8.3.7 With each batch or partial batch of 10 samples, submit one treated silica gel tube which had been handled in the same manner as the sample tubes (break, seal, transport) except that no air is sampled through this tube. This tube should be labeled as blank.
- 8.3.8 Capped treated silica gel tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis each treated silica gel tube is scored with a file and broken open. The glass wool is removed with care and discarded making sure that no silica gel is lost in the process. The silica gel in the front section is transferred to a 50-mL beaker. The separating section of glass wool is removed and discarded. The backup section of silica gel is transferred to another container. These two sections are analyzed separately.
- 8.4.2 Extraction of the Samples. Prior to analysis, 10 mL of the acidic permanganate reagent is pipetted into each

beaker containing the silica gel. The extraction is carried out for 90 minutes at 65-70°C in a water bath. After extraction the acidic permanganate solution is drained into a 10-mL volumetric leaving the silica gel. The volumetric is made to volume with distilled water. The silica gel is washed twice with 3 mL portions of distilled water and the contents drained into another 10 mL volumetric containing 1 mL of ferrous solution. The flask is made up to volume with distilled water and mixed thoroughly.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. 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.

8.4.4 Analytical Procedure

1. Add the contents of both 10-mL volumetric flasks (extract and washings) to a 125-mL separatory funnel.
2. Add 7.5 mL of molybdate reagent and 25 mL of toluene-isobutanol solvent. Shake for 60 seconds. Allow 60 seconds for the aqueous and nonaqueous layers to separate and discard the lower (aqueous layer).
3. Pipet 10 mL of the nonaqueous layer into a 25-mL volumetric containing 10 mL of the alcoholic sulfuric acid solution.

At this stage steps 4 through 6 must be performed within 1 minute.

4. Add 0.5 mL (25 drops) of stannous chloride reagent and make to volume using alcoholic sulfuric acid solution. Mix thoroughly.
5. Transfer the sample into 5-cm cells and stopper immediately.
6. Measure the absorbance or transmittance at 625 nm using water as a blank.

9. Calibration and Standardizations

- 9.1 Add 10 mL of acidic permanganate solution, 1 mL of ferrous reagent to the separatory funnel.
- 9.2 Add 20 to 400 μ L of the standard phosphorus solution to cover the range of 1 to 10 μ g of PH_3 . Add 8 to 9 mL of H_2O to make the total volume of the permanganate solution, ferrous solution, phosphorus solution and water to 20 mL. Prepare at least six calibration standards. A blank containing no phosphorus should also be analyzed.
- 9.3 Proceed as in Sections 8.4.4.2 to 8.4.4.6.
- 9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the blank versus the amount of each standard in μ g of PH_3 added on linear graph paper.

10. Calculations

- 10.1 Correction for the blank (obtained by extraction and analysis of the treated silica gel tube marked "blank") must be made for each sample

$$A_C = A_S - A_B$$

A similar procedure is followed for the backup tube.

- 10.2 The amount of phosphine present in the front tube, corrected for the blank, is found by reading the amount corresponding to A_C from the standard curve. The amount of phosphine found in the backup tube is similarly determined.
- 10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.
- 10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P₁ = pressure during calibration of sampling pump
(mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air samples (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Total mg (Section 10.3)}}{\text{Air Volume Sampled (L)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{34.00} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

34.00 = molecular weight of phosphine

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.
- 11.2 Backup Data Report for Phosphine, S332, prepared under NIOSH Contract No. 210-76-0123, 3/17/78.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(\text{CH}_3\text{O})_2\text{P}(=\text{S})\text{OC}_6\text{H}_2\text{Cl}_3$

RONNEL

2ND EDITION METHOD #: S299

DATE ISSUED: 08/03/79

M.W.: 321.55

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; sp. gr. 1.48; MP 41 °C;
VP 0.1 Pa (<0.001 mm Hg) @ 25 °C

OSHA: TWA 10 mg/m³

NIOSH: TWA 10 mg/m³

ACGIH: TWA 10 mg/m³

SYNONYMS: dimethyl trichlorophenyl phosphate; CAS #299-84-3

SAMPLER: filter, 0.8-µm mixed cellulose ester membrane followed by Chromosorb 102 sorbent tube

FLOW RATE: 1.0 L/min

RECOMMENDED VOLUME: 120 L

MEASUREMENT TECHNIQUE: gas chromatography, FPD in phosphorus mode

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: glass capillary column with stationary phase with polarity similar to the analyte may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of ronnel in toluene in the range 0.2 to 3.6 mg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.2 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: may be adapted to determination of other phosphates with appropriate changes in the chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] MacLeod, K.E. and Lewis, R.G. Portable Sampler for Pesticides and Semivolatile Industrial Organics in Air, Anal. Chem., **54** (2), 310-315 (1982).
- [3] Stan, H.J. Application of Capillary GC/MS to Pesticides Residue Analysis, J. Chromatogr., **467** (1), 85-98 (1989).

8/15/90

NIOSH Manual of Analytical Methods

Ronnel

Analyte:	Ronnel	Method No.:	S299
Matrix:	Air	Range:	2.82-17.1 mg/cu m
OSHA Standard:	10 mg/cu m	Precision ($\overline{CV}_T$):	0.080
Procedure:	Filter/sorbent collection, extraction with toluene, GC/FPD	Validation Date:	8/3/79

1. Synopsis

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter followed by a Chromosorb 102 sorbent tube to trap the particulate and vapors present.
- 1.2 The filter and sorbent are transferred to a jar or other suitable container and ronnel is extracted with toluene.
- 1.3 An aliquot of the sample is injected into a gas chromatograph equipped with a phosphorus flame photometric detector.
- 1.4 The area of resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The method was tested over the range of 2.815-17.11 mg/cu m at an atmospheric temperature and pressure of 27°C and 761.7 mm Hg, using a 120-liter sample. The method may be capable of measuring smaller amounts if the analytical recovery is adequate. Analytical recovery must be determined over the range used.
- 2.2 The upper limit of the method depends upon the adsorptive capacity of the Chromosorb 102. This capacity may vary with the concentration of ronnel in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. Five percent breakthrough was not observed for up to 210 minutes at a sampling rate of 1.0 liter per minute and relative humidity of 85% and temperature of 24°C. The breakthrough test was conducted at an average concentration of 26.99 mg/cu m.
- 2.3 The detection limit of the analytical method was not rigorously determined but is estimated to be at least 0.2 µg/sample.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 Volatile phosphorus-containing compounds are the only major possible interferences due to the selectivity of the detector. Any such compound having the same retention time as the analyte will interfere. Retention time data based on a single set of conditions cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.815-17.11 mg/cu m was 0.080. This value corresponds to a 0.80 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure are found in Reference 11.2.
- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1 and 2 times the OSHA standard were identical to the dynamically generated concentrations ($n = 18$). The analytical recovery was determined to be 99.7% for a collector loading of 0.588 mg. In storage stability studies, the mean of samples analyzed after seven days was within 6.4% of the mean of samples analyzed the day after collection. Experiments performed in these studies are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal and most of those which do occur may be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.
- 5.2 The amount of sample that can be taken is limited by the number of micrograms that the tube will hold before overloading. When the amount of ronnel found on the backup section exceeds 25% of that found on the front section, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling train. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one device only.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of mixed vapor/particulate samples has the following components:
 - 6.1.1 Filter. The filter unit consists of a mixed cellulose ester membrane filter, 0.80 micrometer pore size and 37-mm diameter, supported by a stainless-steel screen (Mine Safety Appliances Co., catalog number 456224), and a 37-mm, two-piece filter holder held together by tape or a shrinkable band.
 - 6.1.2 Personal Sampling Pump. A calibrated personal sampling pump is needed whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a representative sampling train in the line.
 - 6.1.3 Chromosorb 102 Tubes. The tubes are constructed of glass tubing with both ends unsealed. The tubes are approximately 10-cm long with a 10-mm O.D. and an 8-mm I.D. The front section contains 100 mg of 20/40 mesh Chromosorb 102 and the backup section contains 50 mg. Chromosorb 102 is held in place in the tube with 3-mm plugs of silanized glass wool. A 3-mm plug also separates the two sections. To facilitate handling of the Chromosorb 102 resin, the tubes should be acetone rinsed and dried. This reduces the problem of the resin adhering to the walls of the tube.
 - 6.1.4 Thermometer.
 - 6.1.5 Barometer.
 - 6.1.6 Stopwatch.
- 6.2 Connection of Filter Holder and Sorbent Tube. The Chromosorb 102 tube is connected to the outlet of the two-piece filter holder using a modified Luer-lock to 1/4-in I.D., tubing adapter (Millipore Corp., catalog number XX30025 64) and 1/4-in I.D., Tygon tubing.
- 6.3 Gas chromatograph equipped with a phosphorus specific flame photometric detector.
- 6.4 Column (6-ft x 2-mm I.D., glass) Superpak 20M (Analabs, Inc.).
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Microliter syringes in convenient sizes for making standard solutions.

- 6.7 Volumetric flasks in convenient sizes for making standard solutions.
- 6.8 Squat form ointment jars with Teflon film gaskets and screw caps for desorption of samples.
- 6.9 A 15-mL pipette.
- 6.10 Tweezers.

7. Reagents

Whenever possible reagents used should be ACS reagent grade or better.

- 7.1 Ronnel.
- 7.2 Toluene.
- 7.3 Hydrogen, prepurified.
- 7.4 Air, filtered, compressed.
- 7.5 Nitrogen, dried.
- 7.6 Helium, dried.
- 7.7 Ronnel, 24 mg/mL stock solution. Prepare by adding 24 milligrams of ronnel to a tared 2-mL septum capped vial. Add 1 mL of toluene to dissolve the ronnel.
- 7.8 Pre-cleaned Resin. Chromosorb 102, 20/40 mesh (Johns Manville Corp. or Analabs, Inc.) is purified by extraction in a Soxhlet extractor using 1:1 methanol acetone solution for two hours. The resin is then dried at 115°C in a vacuum oven for one hour.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling train in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the center ring seals the edge of the filter. The mixed cellulose ester membrane

filter is held in place by a stainless steel screen and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter.

- 8.3.2 Remove the filter holder plugs and sorbent tube caps and assemble the sampling train. Attach the outlet of the sorbent tube to the personal sampling pump tubing. Clip the sampler to the worker's lapel.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.
- 8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes.
- 8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.
- 8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 After sampling, remove the sorbent tube and Luer-lock adapter from the outlet of the filter holder and connect to the inlet side. Cap the open end of the sorbent tube and plug the outlet of the filter holder with the plugs supplied. Under no circumstances should rubber caps be used.
- 8.3.8 Carefully record sample identity and all relevant sample data.
- 8.3.9 With each batch of samples, submit one sampling train which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.
- 8.3.10 The sampling train should be shipped in a suitable container designed to prevent damage in transit.
- 8.3.11 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match

air samples for identification purposes. This sample should not be transported in the same container as the sample.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the filter from the holder with the aid of appropriate tweezers and transfer to a 2-oz ointment jar.
2. Add the front glass wool plug from the sorbent tube and the front section of Chromosorb 102 to the same container as the filter.
3. Add 15 mL of toluene to the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.
4. The backup Chromosorb 102 section is added to a different container and analyzed separately.
5. If the internal standard method is used, add the internal standard solution in place of toluene.

8.4.3 Analysis by Gas Chromatography. The typical operating conditions for the gas chromatograph are:

1. 20 mL/min (45 psig) helium carrier gas flow.
2. 35 mL/min (60 psig) hydrogen flow to detector.
3. 200 mL/min (60 psig) air flow to detector
4. 230°C injector temperature.
5. 250°C detector temperature.
6. 185°C column temperature.

A retention time of 4 minutes is expected for ronnel.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

- 8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determination should cover the concentration range of interest.
- 8.5.2 Procedure for Determining Recovery. A known amount of ronnel, equivalent to that present in a 120-liter sample at the selected level, is added to a mixed cellulose ester membrane filter and Chromosorb 102 in a 2-oz. ointment jar. A stock solution containing 240 milligrams of ronnel per milliliter of toluene is prepared. Add 2.5, 5.0 and 10.0 microliter aliquots of the solution to the filter and sorbent to produce samples equivalent to 120-liter collections at 0.5, 1 and 2 times the OSHA standard. Six samples at each of the three levels are prepared and allowed to stand overnight. A parallel blank sample is also prepared except that no sample is added to it. All samples are then extracted and analyzed as described in Section 8.4.

The sample recovery equals the average weight in mg recovered divided by the weight in mg added, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered} - \text{Blank (mg)}}{\text{Weight (mg) Added}}$$

9. Calibration and Standardization

A series of standards, varying in the concentration range corresponding to approximately 0.1 to 3 times the OSHA standard for the samples under study, is prepared and analyzed under the same GC conditions. The standards should be interspersed throughout the set of samples.

- 9.1 From the stock solution listed in Section 7.7, prepare at least six standards to cover the concentration range of 0.12-3.6 mg/15 mL. This is done by adding from 5-150 microliter aliquots of the stock solution to 15 mL of toluene in ointment jars or other suitable containers. Analysis is done as described in Section 8.4.
- 9.2 The series of standards is analyzed under the same GC conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in mg/15 mL, because samples are extracted in this amount of solvent. Curves are established by plotting concentrations in mg/15 mL versus peak area.

- 9.3 For the internal standard use toluene containing a predetermined concentration of internal standard to desorb the samples. The concentration of internal standard used should be such that it falls within the linear range of detector response.

10. Calculations

- 10.1 Read the concentration in mg/15 mL corresponding to the sample peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/15 mL and the volume of the sample injected is identical to the volume of standards injected.

- 10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\begin{aligned}\text{mg sample} &= \text{mg found in sample} \\ \text{mg blank} &= \text{mg found in blank}\end{aligned}$$

- 10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected mg sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

- 10.4 For personal sampling pumps with rotameters only, the following corrections should be made:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump
(mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

- 10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ liters per cu m}}{\text{Volume of Air Sampled in Liters}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.
- 11.2 Backup Data Report for Ronnel, NIOSH Method No. S299, prepared under NIOSH Contract No. 210-76-0123, August 3, 1979.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: SO_2F_2

SULFURYL FLUORIDE

2ND EDITION METHOD #: S245

DATE ISSUED: 06/08/79

M.W.: 102.06

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 5 ppm; STEL 10 ppm

NIOSH: TWA 5 ppm; STEL 10 ppm

ACGIH: TWA 5 ppm; STEL 10 ppm

(1 ppm = 4.17 mg/m³ @ NTP)

PROPERTIES: gas; sp. gr. 1.36 (liquid);

BP -55 °C;

VP >101 kPa (760 mm Hg) @ 20 °C;

vapor density (air=1) 3.5

SYNONYMS: Vikane™ ; CAS #2699-79-8

SAMPLER: gas sampling bag, 5-L capacity

FLOW RATE: 0.05 to 0.10 L/min

RECOMMENDED VOLUME: 3 L

MEASUREMENT TECHNIQUE: gas chromatography, FPD

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: an analytical method developed by Dow Chemical Co. [1]
may be used for better specificity and sensitivity

MEASUREMENT CALIBRATION: standard solutions of sulfonyl fluoride in the range
6 to 188 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): not determined; 29 µg per sample as per [1]

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH analytical sequence #6896 [2]

APPLICABILITY: unknown

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Bouyoucos, S.A., Melcher, R.G., and James R. Vaccaro. Collection and Determination of Sulfonyl Fluoride in Air by Ion Chromatography. Am. Ind. Hyg. Assoc. J., 44, 57-61 (1983).

[2] NIOSH/DPSE Analytical Sequence #6896, Measurement Research Support Branch, NIOSH (unpublished, 1988).

[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

8/15/90

NIOSH Manual of Analytical Methods

Sulfuryl Fluoride

Analyte:	Sulfuryl Fluoride	Method No.:	S245
Matrix:	Air	Range:	2.54 - 10.29 ppm
OSHA Standard:	5 ppm (21 mg/cu m)	Precision ($\overline{CV}_T$):	0.025
Procedure:	Collection in gas sampling bag, GC with flame photometric detection	Validation Date:	6/8/79

1. Synopsis

- 1.1 An air sample is pumped into a gas sampling bag with a personal sampling pump.
- 1.2 The sulfuryl fluoride content of the sample is determined by gas chromatography using flame photometric detection in the sulfur mode.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 2.54-10.29 ppm at an atmospheric temperature of 20°C and atmospheric pressure of 760 mm Hg using a 3-liter sample volume.
- 2.2 Under the instrumental conditions used in the validation study, a 2-mL injection of a 3 ppm sulfuryl fluoride standard resulted in a peak whose height was 64% of full scale on a 1-millivolt recorder. The amplifier of the gas chromatograph was set on range 10^4 and attenuation 1.
- 2.3 The limit of detection is estimated at less than 0.8 ng sulfuryl fluoride. Using a 2.5 mL gas sampling loop, this corresponds to a level of approximately 0.1 ppm.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any sulfur compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.54-10.29 ppm was 0.025. This value corresponds to a standard deviation of 0.1 ppm at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure can be found in Reference 11.2.
- 4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ of the "true value" on the average 95% of the time over the validation range. The average of the concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit were 2.0% lower than the dynamically generated test concentrations ($n=18$). In storage stability studies, the mean of samples analyzed after 7 days was within 0.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

- 5.1 The sampling device is portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples in bags are analyzed by means of a quick instrumental method.
- 5.2 One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.
- 5.3 It is difficult to ship the samples by air.

6. Apparatus

- 6.1 Personal Sampling Pump. A personal sampling pump capable of filling a gas sampling bag at approximately 0.05 liter/minute is required. Each personal pump should be calibrated to within $\pm 5\%$. Although sample volume is not used to determine sample concentration, the pump should be calibrated to make certain that the collected sample represents a time-weighted average concentration and to avoid over filling of the bags; i.e., a maximum sampling time can be determined based on the flow rate and sample volume which is less than 80% of the volume of the bag.

The personal sampling pump must be fitted with an outlet port so it is capable of filling a bag. To ensure a leak-free apparatus, adjust the pump so that it delivers at the proper flow rate, and attach the pump outlet to a water manometer with a short piece of flexible tubing. Turn the pump on and observe the water level difference; it should push at least 30 cm of water. If it does not, the pump is incapable of filling the sampling bag and cannot be used.

- 6.2 Gas Sampling Bag. Five-liter capacity, five-layer sampling bags (Calibrated Instruments, Inc., 731 Saw Mill River Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and

storage for at least 7 days. This bag is fitted with a metal valve and hose bib. The valves used in validation studies were found to leak when in the open position. It is necessary to wrap the valve stem connection with Teflon tape or Parafilm to ensure a leak-free connection. For the preparation of calibration standards in the laboratory, Saran or Tedlar bags can be used.

- 6.3 Gas chromatograph, equipped with a flame photometric detector in the sulfur mode and 2-mL gas sampling loop.
- 6.4 Column (0.5-m X 2-mm I.D. glass) packed with 60/80 mesh Carbosieve S (Supelco, Inc.).
- 6.5 Area Integrator. An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Gas-tight Syringes. Convenient sizes for preparing standards.
- 6.7 Regulator for compressed air which is capable of metering gas at approximately 1 liter/minute. The gas line from the regulator should be equipped with a septum-tee for standards preparation.
- 6.8 Water manometer.
- 6.9 Thermometer.
- 6.10 Stopwatch

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 Sulfuryl fluoride, 100%.
- 7.2 Helium, purified.
- 7.3 Air, filtered, compressed.
- 7.4 Hydrogen, prepurified, compressed.
- 7.5 Oxygen, purified, compressed.

8. Procedure

- 8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the valve and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with air and evacuated. This procedure is repeated at least twice.

Bags should be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Check for any discernable leaks and any volume changes or slackening of the bag, especially along seams and in the valve stem, for at least a one-hour period.

8.2 Collection and Shipping of Samples

- 8.2.1 Immediately before sampling, attach a small piece of Teflon tubing to the valve fitting of the five-layer gas sampling bag. Rubber tubing should not be used.
- 8.2.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump. Make sure that all connections are tight and leak-free. The bag valve must be fully opened during sampling.
- 8.2.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required. No tubing is attached to the inlet of the pump.
- 8.2.4 Sample at a flow rate of 0.05 liter/minute or less. Set the flow rate as accurately as possible using the manufacturer's directions. Although the volume of sample collected is not used in determining the concentration, it is necessary to keep the volume to 80% or less of the bag's capacity. Observe the bag frequently to ensure that it is filling properly.
- 8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation. Also record sampling time, flow rate, and type of sampling pump used.
- 8.2.7 The gas sampling bag should be labeled appropriately and sealed tightly.
- 8.2.8 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of being punctured during shipping. Do not ship the bags by air, unless they are stored in a pressurized cabin.

8.3 Analysis of Samples

- 8.3.1 GC Conditions. The typical operating conditions for the gas chromatograph are:

- 45 mL/min helium carrier gas flow
- 150 mL/min hydrogen flow to detector
- 40 mL/min air flow to detector
- 20 mL/min oxygen flow to detector
- 110°C column temperature
- 225°C detector temperature

8.3.2 GC Analysis. Attach the gas sampling bag to the sample loop of the gas chromatograph with a short piece of flexible tubing. Open the valve of the bag and fill the loop by using a vacuum pump or manually applying pressure to the sample bag. Allow the loop to attain atmospheric pressure, and inject the sample. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. A retention time of approximately 4 minutes is to be expected using the above conditions.

8.3.3 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve as discussed in Section 9.

9. Calibration and Standardization

A series of standards, varying in concentration over the range of 0.5-15 ppm is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ppm versus peak area. A logarithmic plot may be used to obtain a linear curve for this detector.

9.1 Completely evacuate and flush several times with air a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Using a calibrated source of air equipped with a septum-tee, meter 3-4 liters of air into the bag. Inject appropriate aliquots of sulfuryl fluoride via a gas tight syringe through the septum. Knead the bag to ensure adequate mixing. Prepare at least 5 working standards to cover the range of 0.5-15 ppm. Analyze these standards as in 8.3.

9.2 The concentration of the bag in ppm equals the volume of sulfuryl fluoride in mL divided by the amount of air in L x 10³.

$$\text{ppm} = \frac{\text{Volume of sulfuryl fluoride (mL)}}{\text{volume of air (L)}} \times 10^3$$

10. Calculations

10.1 Read the concentration in ppm, corresponding to each peak area from the standard curve.

10.2 Another method of expressing concentration is mg/cu m.

$$\text{mg/cu m} = \text{ppm} \times \frac{\text{M.W.}}{24.45} \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

P = pressure (mm Hg) of air sampled
 T = temperature (°C) of air sampled
 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
 M.W. = molecular weight, 102.07 g/mole
 760 = standard pressure (mm Hg)
 298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.
- 11.2 Backup Data Report for Sulfuryl Fluoride, prepared under NIOSH Contract No. 210-76-0123.

S245-6

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(3\text{MgO})(4\text{SiO}_2)(\text{H}_2\text{O})$ TALC, RESPIRABLE
2ND EDITION METHOD #: P&CAM 355 DATE ISSUED: 11/26/81
M.W.: 379.29 CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS: PROPERTIES: solid (powder);
MP 900 to 1000 °C;
sp. gr. 2.5 to 2.8 [1]
OSHA: TWA 2 mg/m³ (respirable)*
NIOSH: TWA 2 mg/m³ (respirable)*
ACGIH: TWA 2 mg/m³ (respirable)*
*for talc which contains no asbestos

SYNONYMS: hydrous magnesium silicate; soapstone; steatite; CAS #14807-96-6

SAMPLER: 10-mm nylon cyclone and 5-µm PVC filter

FLOW RATE: 1.7 L/min

RECOMMENDED VOLUME: 200 L

MEASUREMENT TECHNIQUE: X-ray diffraction

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: qualitative scan should be performed to detect possible
interferences

MEASUREMENT CALIBRATION: standard talc deposited on PVC filters, the matrix absorption
correction of method 7500 (silica) [2] should be used

ESTIMATED LIMIT OF DETECTION (LOD): 10 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: the working range is 0.15 to 10 mg/m³ for a 200-L air sample

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] NIOSH Manual of Analytical Methods, 3rd Ed., Method No. 7500 (Revision #1), Available from Government Printing Office, Washington D.C. (1989).
- [3] Foner, H.A., Adan, N. The Characterization of Papers by X-ray Diffraction Measurement of Cellulose Crystallinity and Determination of Mineral Composition. J. Forensic Sci. Soc., 23, 313-321 (1983).

RESPIRABLE TALC

Methods Research Branch

Analytical Method

Analyte:	Respirable Talc	Method No.:	P&CAM 355
Matrix:	Air	Range:	200 - 4000 $\mu\text{g}/\text{m}^3$
Procedure:	Filter collection, low temperature ashing, Re-deposition on Ag filter, XRD	Precision:	$\overline{\text{ZRSD}}_1 = 5.3$ (analytical) $\overline{\text{ZRSD}}_T = 34$ (sampling and analytical)
Date Issued:	November 26, 1981	Classification:	E (proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a 0.45- μm polyvinyl chloride filter.
- 1.2 The filter and sample are radio-frequency ashed; the residue is suspended in 2-propanol and co-deposited with $\alpha\text{-Al}_2\text{O}_3$ on a silver membrane filter.
- 1.3 The samples are analyzed by X-ray diffraction.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The method was evaluated over the range 50 to 4000 $\mu\text{g}/\text{m}^3$, corresponding to 10 to 800 $\mu\text{g}/\text{filter}$ for a 200-L air sample collected at 20 °C and 750 torr.
- 2.2 The instrumental sensitivity is 0.0053 $\mu\text{g}/\text{count}$ for the 002 peak and 0.0083 $\mu\text{g}/\text{count}$ for the 006 peak.
- 2.3 The detection limit is approximately 12 $\mu\text{g}/\text{filter}$ for the 002 peak and 10 $\mu\text{g}/\text{filter}$ for the 006 peak. The lowest analytically quantifiable level is 50 $\mu\text{g}/\text{filter}$ for the 002 peak and 30 $\mu\text{g}/\text{filter}$ for the 006 peak.

3. Interferences

- 3.1 A preliminary, qualitative scan of the sample is performed and indicates whether interferences are present.
- 3.2 Either the 002 or 006 peak of talc may be used for analysis to assist interfering peaks such as the 310 peak of tremolite (006 peak of talc).

4. Precision and Accuracy

- 4.1 The precision of the analytical method is 5.3% RSD, based on six samples at each of three concentration levels. The total precision of the sampling and analytical method is 34%, based on six samples at each of three concentration levels. The poor precision was caused by the inconsistent synthetic atmosphere generated during testing of the method.
- 4.2 The analytical method recovery was determined to be 1.00 at 160 μg per filter. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples after one day, at the 95% confidence level. Details of the experiment are given in Reference 1.

5. Advantages and Disadvantages

- 5.1 The sampling device is small and portable, and the samples easily collected.
- 5.2 The analytical method requires a skilled operator and expensive equipment.
- 5.3 When no interferences or only avoidable interferences are present, the method is highly specific for talc.
- 5.4 Compared to the alternates of electron or optical microscopy, the method is rapid and very specific.
- 5.5 Occasionally (rarely) talc peaks may be obscured totally by interferences.

6. Apparatus

- 6.1 Sampling equipment, consisting of filter unit (0.45- μm polyvinyl chloride filter with backup pad, 37-mm diameter, in a plastic cassette with 10-mm nylon cyclone) and personal sampling pump capable of sampling at 1.5 - 2 L/min. The pump must be calibrated with a representative filter and cyclone in line, using a soap-bubble flowmeter or wet- or dry-test meter, and its flow rate must be known accurately to within $\pm 5\%$.

- 6.2 Silver membrane filters, 25-mm diameter and 0.45- μ m pore size: Selas Flotronics, Huntingdon Valley, PA 19006.
- 6.3 Vacuum filtration apparatus with modified filtering tower. The bore of the filtering tower should be sized to yield the largest sample surface that can be optimally exposed to the X-ray beam without being shadowed by the sample holder at the low angle ($9.45^\circ 2\theta$) of the 002 talc reflection.
- 6.4 X-ray diffractometer equipped with broad focus copper target X-ray tube, rotating sample holder, secondary beam monochromator, scintillation detector, pulse height analyzer and digital printout capability. The diffractometer parameters should be set to provide high intensity at the expense of resolution. In addition to higher counting rates this will improve statistics by allowing a greater fraction of the talc crystallites to contribute to the peaks.
- 6.5 Micro-pipets with disposable tips (Eppendorf, Oxford or equivalent). Micropipets should be calibrated gravimetrically using 2-propanol. A variety of sizes covering the range from 0.20 mL to 1.00 mL will be required.
- 6.6 Glassware (borosilicate)
 - 6.6.1 Volumetric flasks, class A, 100-mL.
 - 6.6.2 Beakers, 30-mL.
 - 6.6.3 Erlenmeyer flask, wide mouth, tapered stopper, 125-mL.
- 6.7 Ultrasonic Agitator
- 6.8 Low Temperature Asher.
- 6.9 Magnetic Stirrer and Teflon coated stir bars.
- 7. Reagents
 - 7.1 2-propanol.
 - 7.2 Hydrochloric acid, 38% (w/w).
 - 7.3 Ammonium Hydroxide, 30% (w/w).
 - 7.4 Dilute hydrochloric acid, 6 N. Add 50 mL HCl to 40 mL H₂O. Dilute to 100 mL.
 - 7.5 α -Alumina (Alpha Micropolish, Buehler Ltd).
 - 7.6 Talc, TA-99, MMD = 3.45 μ m, MMAD = 5.5 μ m, described in Reference 11.3.

- 7.7 Stock standard talc suspension; suspend 10 mg TA-99 talc in 100 mL 2-propanol in an Erlenmeyer flask containing a magnetic stir bar. Agitate ultrasonically for two minutes followed by two minutes of stirring.
- 7.8 Stock α -Al₂O₃ suspension; suspend 30 mg α -Al₂O₃ in 100 mL 2-propanol as described in Section 7.7.

8. Procedure

8.1 Cleaning of Equipment.

- 8.1.1 Glassware. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, dilute nitric acid (soak 4 hours or longer), and distilled or deionized water.
- 8.1.2 Silver membrane filters. If the qualitative scan described in Section 3 indicates use of the 006 talc peak at 28.59 ° 2 θ , it will be necessary to determine whether the silver filters contain any AgCl whose 111 peak at 27.83 ° 2 θ interferes. If so, the AgCl may be leached from the filters by soaking in concentrated NH₄OH for two hours followed by two rinses in 2-propanol and air drying.

8.2 Collection and Shipping of Samples

- 8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.
- 8.2.2 Attach nylon cyclone to cassette and remove cap. Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette, face down, to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.
- 8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A sample size of 200-L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. (If sampling problems preclude the accurate measurement of air volume, discard the sample.) Record the sampling time, flow rate, and ambient temperature and pressure.
- 8.2.4 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to step 8.2.1.

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring to the cassette.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the filter with tweezers and transfer it to a 30-mL glass beaker.

8.3.2 Ash filter in low temperature asher for 45 minutes.

8.3.3 Add 2 mL 6 N HCl to residue; agitate ultrasonically for 30 seconds and let stand for 3 minutes.

8.3.4 Turn on the magnetic stirrer under the $\alpha\text{-Al}_2\text{O}_3$ suspension and stir for one minute. Turn the stirrer off and immediately withdraw 2 mL of the suspension using a micropipet with disposable tip and transfer to the sample beaker. Agitate ultrasonically for 2 minutes.

8.3.5 Mount silver membrane filter under filtering tower. With vacuum off, add approximately one half inch 2-propanol to the filtering tower. Pour the contents of the sample beaker into the tower with a minimum of splashing and apply vacuum. As the liquid level in the tower permits, rinse the beaker into it with 2-propanol. As the level in the tower approaches the filter, wash down the sides of the tower with 2-propanol from a squeeze bottle being careful not to shoot the stream directly into the liquid. Add no more 2-propanol after the filter surface is exposed.

8.3.6 Let air continue to be pulled through the filter until the sample is dry before releasing the clamp and removing the filter.

8.3.7 Analyze the talc peak selected in Section 3 by step scanning the peak and integrating the counts. Count the background on each side of the peak for one half the time used for peak integration, and add the counts from each side to obtain an average background. The difference between the integrated peak counts and the average background counts is the net peak counts. Matrix correction is recommended (11.2).

9. Calibration and Standardization

9.1 Prepare working standards by pipetting aliquots of the stock standard suspension onto polyvinyl chloride filters. Working standards should contain 0, 20, 50, 100, 200, 400, and 800 μg talc per filter, i.e., 0.20 mL, 0.50 mL, 1.00 mL, 2.00 mL, 4.00 mL, and 8.00 mL stock suspension. Subject all standards to the same procedure as the samples, steps 8.3.3 - 8.3.7.

9.2 Using a least squares linear regression (or higher order fit), generate calibration equations from the net peak counts and prepared

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concentrations ($\mu\text{g talc}$) of the standards.

10. Calculations

- 10.1 From the calibration equations obtained in Section 9, convert the sample net peak counts to $\mu\text{g talc/sample (W)}$.
- 10.2 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000} \left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1} \right)^{1/2}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K).

- 10.3 Calculate the talc concentrations (C) in the air sample ($\mu\text{g}/\text{m}^3$) using the formula:

$$C = \frac{W}{V}$$

11. References

- 11.1 Backup Data Report for Respirable Talc, prepared under NIOSH Contract 210-79-0060.
- 11.2 P&CAM 259, NIOSH Manual of Analytical Methods, Volume 5 (NIOSH Publication 79-141).
- 11.3 Data Summary for Talc (TA-99), prepared under NIOSH Contract 210-75-0043.

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NIOSH Contract No. 210-79-0060
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SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(C_4H_9)_3PO_4$	2ND EDITION METHOD #: S208	TRIBUTYL PHOSPHATE
M.W.: 266.32		DATE ISSUED: 11/21/75
		CURRENT DATE: 8/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:	PROPERTIES: liquid; d 0.98 g/mL @ 20 °C;
OSHA: TWA 2.5 mg/ ³	BP 293 °C; VP very low @ 20 °C,
NIOSH: TWA 2.5 mg/ ³	16.9 kPa (127 mm Hg) @ 177 °C;
ACGIH: TWA 2.5 mg/ ³	flash point 166 °C (closed cup)

SYNONYMS: phosphoric acid tributyl ester; CAS #126-73-8

SAMPLER: filter, 0.8- μ m cellulose ester membrane

FLOW RATE: 1.5 L/min.

RECOMMENDED VOLUME: $\geq$ 100 L

MEASUREMENT TECHNIQUE: gas chromatography, FPD in phosphorus mode

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution

MEASUREMENT CALIBRATION: standard solutions of tributyl phosphate in diethyl ether
in the range 2 to 1000 μ g per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 μ g per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method may be adapted to other phosphates of relatively low volatility with
appropriate changes in chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

- [1] 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.
- [2] Parker, G.B., Analysis of Tributyl Phosphate in Flowing Air Stream, Am. Ind. Hyg. Assoc. J., 41 (3): 220 (1980).
- [3] Kuller, J. et al., Determination of Tributyl Phosphate by Liquid Chromatography, Analysis, 2 (6): 271 (1983).
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Tributyl Phosphate

Analyte:	Tributyl Phosphate	Method No.: S208
Matrix:	Air	Range: 2.7-12.6 mg/cu m
OSHA Standard:	5.0 mg/cu m	Precision ($\overline{CV}_T$): 0.076
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date: 11/21/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.
- 1.2 The filter in the cassette is transferred into a jar and extracted with ether.
- 1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).
- 1.4 The area of the resulting sample peak is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 2.7-12.6 mg/cu m at an atmospheric temperature and pressure of 19°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 1.5-mg sample.
- 2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for tributyl phosphate aerosol was found to be 100% when sampled for 66 minutes at 1.5 liters per minute from a test atmosphere containing 12.6 mg/cu m and at an atmospheric temperature and pressure of 19°C and 761 mm Hg.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

- 3.2 Dibutyl phosphate frequently coexists with tributyl phosphate. However dibutyl phosphate is non-volatile and does not interfere with the gas chromatographic analysis of tributyl phosphate.
- 3.3 It must be emphasized that any phosphorus-containing compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 At higher atmospheric temperatures some distribution between tributyl phosphate particulate and vapor may occur which can yield erroneous values if only the front filter is analyzed. The vapor is absorbed to a limited extent by the cellulose back-up pad. Refer to Section 8 for Sample Collection and Analysis.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.7-12.6 mg/cu m was 0.076. This value corresponds to a standard deviation of 0.38 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference. 11.1.
- 4.2 A collection efficiency of 100% was determined for the collecting medium under special consideration of atmospheric temperature and pressure noted. Thus, no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery from the filters was 100.4%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
 - 6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37-mm, 3-piece cassette filter holder. Front and backup filter units are needed when sampling atmospheres at temperatures above 23°C.

- 6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with the representative filter holders and filters in the line.
- 6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter. The filter is held in the three-piece cassette supported by a cellulose backup pad.
- 6.3 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.
- 6.4 Column (6-ft x 1/8-in stainless steel) packed with 3% OV-101 on 100/120 mesh Supelcoport, or equivalent column capable of achieving the desired resolution.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.
- 6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.
- 6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.
- 6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.
- 7. Reagents
 - 7.1 Anhydrous ether, reagent grade
 - 7.2 Tributyl phosphate, reagent grade
 - 7.3 Purified hydrogen
 - 7.4 Prefiltered, compressed air
 - 7.5 Purified nitrogen
- 8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of personal pumps. Each personal pump must be calibrated with the representative filter cassettes in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and connect the cassette filter to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

Note: If the ambient temperature to be sampled is above 23°C, use two filter cassettes connected in series with a short piece of flexible tubing for sample collection. This arrangement is necessary because some tributyl phosphate vapor may exist at temperatures above 23°C.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassettes.

8.3.4 A sample size of 100 liters is recommended, but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least +5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Separate the front and backup filter cassettes (if two cassettes were used) and seal. Collected sample cassettes should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity including front and backup filter designation, if any, and all relevant sample data.

8.3.9 Blank: With each batch of 10 samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully transfer the cellulose membrane filter and cellulose backup pad with the aid of Millipore filter tweezers to the jar. (Both filter and pad are analyzed.)
2. Pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.
3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.
4. The front filter/pad and backup filter/pad should be analyzed. This applies to sampling at temperatures above 23°C.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 70 ml/min Hydrogen gas flow to detector
3. 150 ml/min air flow to detector
4. 240°C injector temperature
5. 240°C detector temperature
6. 150°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed

from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

- 8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

- 8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.
- 8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within +5%.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) have been dosed accordingly using a solution of tributyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4.

The average recovery value obtained was 100% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in μg recovered from the filter divided by the weight in μg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered}}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and, therefore, it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in μg , corresponding to the total peak area from the standard curve. No volume corrections are needed because the standard curve is based on μg per 10.0 ml ether, and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

10.3 Add the amount found in the front filter/pad and backup filter/pad to determine total weight in the sample. This applies to samples collected at temperatures above 23°C.

- 10.4 Divide the total weight by the recovery to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

- 10.5 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg , a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V = volume of air in liters @ 25°C and 760 mm Hg
 V_s = volume of air sampled
 p = pressure (mm Hg) of air sampled
 T = temperature ($^{\circ}\text{C}$) of air sampled
 760 = standard pressure (mm Hg)
 298 = standard temperature ($^{\circ}\text{K}$)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg}/\text{cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

FORMULA: $\text{CCl}_2\text{FCClF}_2$

1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE

M.W.: 187.38

METHOD: 1020

ISSUED: 8/15/87

REVISION #1 : 8/15/90

OSHA: 1000 ppm; STEL 1250 ppm
NIOSH: 1000 ppm; STEL 1250 ppm [1]
ACGIH: 1000 ppm; STEL 1250 ppm
(1 ppm = 7.66 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.55 g/mL @ 20 °C;
BP 47.6 °C; MP -35 °C;
VP 38 kPa (384 mm Hg; 51% v/v) @ 20 °C;
not combustible

SYNONYMS: Refrigerant 113; Freon TF; CAS #76-13-1.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	! TECHNIQUE: GAS CHROMATOGRAPHY, FID
FLOW RATE: 0.01 to 0.05 L/min	! ANALYTE: 1,1,2-trichloro-1,2,2-trifluoroethane (TTE)
VOL-MIN: 0.1 L @ 1000 ppm -MAX: 3 L	! DESORPTION: 1 mL CS_2 ; stand 30 min
SHIPMENT: refrigerated	! INJECTION VOLUME: 1 μL
SAMPLE STABILITY: not determined	! TEMPERATURE-INJECTOR: 250 °C ! -DETECTOR: 300 °C ! -COLUMN: 1 min @ 32 °C; ! 5 °C to 90 °C
FIELD BLANKS: 10% of samples	! CARRIER GAS: He, 1 to 2 mL/min
	! COLUMN: DB-Wax/Stabilwax fused silica capillary, ! 30m x 0.32 mm ID, split injection 5:1
	! CALIBRATION: standard solutions of analyte ! in CS_2
RANGE STUDIED: 3300 to 14200 mg/m^3 [2] (1.5-L samples)	! RANGE: 0.015 to 14 mg per sample
BIAS: not significant [2]	! ESTIMATED LOD: 0.005 mg per sample [2]
OVERALL PRECISION (s_p): 0.07 [2]	! PRECISION (s_p): 0.02 @ 5.6 to 23 mg per ! sample [3]
APPLICABILITY: The working range is 10 to 17000 mg/m^3 (1.3 to 2300 ppm) for a 1.5-L air sample.	
INTERFERENCES: None identified	
OTHER METHODS: This revises NIOSH methods S129 [4] and 1020 (dated 8/15/87).	

REAGENTS:

1. Carbon disulfide (CS₂), chromatographic quality.*
2. 1,1,2-Trichloro-1,2,2-trifluoroethane (TTE), reagent grade.*
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged, and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1020-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10- to 100-μL, readable to 0.5%.
7. Volumetric flasks, 10-mL.
8. Pipet, TD 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). 1,1,2-Trichloro-1,2,2-trifluoroethane is a narcotic [1]. Work with these compounds only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 3 L.
4. Cap the samplers. Pack securely for shipment in a refrigerated container.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS₂ 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 five working standards.
 - a. Add known amounts of TTE to CS₂ in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain TTE concentrations in the range 0.005 to 14 mg/mL.
 - b. Analyze with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs. mg TTE).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.

- b. Inject a known amount (2 to 20 μL) of TTE or a standard solution of TTE in CS_2 directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. mg TTE 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 1020-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
- NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2 , reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Method S129 was issued on May 9, 1975 [4], and validated with generated atmospheres using calibrated syringe drive and independent verification by gas chromatography [3]. Average recovery was 100.3% (18 samples) in the range 3300 to 14,200 mg/m^3 for 1.5-L samples. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 60 min at 0.046 L/min from an atmosphere containing 14,500 mg/m^3 1,1,2-trichloro-1,2,2-trifluoroethane in dry air. Desorption efficiency for 18 samples of SKC Lot 105 activated coconut charcoal spiked with 5.6 to 23 mg 1,1,2-trichloro-1,2,2-trifluoroethane averaged 1.01 with $s_r = 0.02$.

REFERENCES:

- [1] NIOSH Testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
- [2] Pendergrass, S., Method Development Efforts, NIOSH/DPSE Analytical Sequence Nos. 6937, 6956 and 6916A, Measurement Research Support Branch, Cincinnati, Ohio, NIOSH, (unpublished, 1989).
- [3] Documentation of the NIOSH Validation Tests, S129, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB-274-248 from NTIS, Springfield, VA 22161.
- [4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S129, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: Stephanie Pendergrass, NIOSH/DPSE; S129 originally validated under NIOSH Contract CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $C_9H_4O_5$

TRIMELLITIC ANHYDRIDE

2ND EDITION METHOD #: P&CAM 322

DATE ISSUED: 08/29/80

M.W.: 192.13

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: solid; MP 161 to 163 °C;
VP 0.56×10^{-6} kPa (4×10^{-6} mm Hg)
@ 20 °C

OSHA: TWA 0.04 mg/m^3

NIOSH: TWA 0.04 mg/m^3 ; extremely toxic in workplace

ACGIH: TWA 0.059 mg/m^3

SYNONYMS: 1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid; CAS #552-30-7

SAMPLER: filter, $0.8 \mu\text{m}$ PVC-copolymer

FLOW RATE: 1.5 to 2.0 L/min.

RECOMMENDED VOLUME: 400 L

MEASUREMENT TECHNIQUE: gas chromatography, FID

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of derivatized trimellitic anhydride in a mixture of pyridine, diethyl ether and pentane, in the range 19 to 96 μg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 2 μg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: NIOSH HHE Reports [1]

APPLICABILITY: method may be adapted to other organic anhydrides e.g. maleic, succinic, phthalic, with appropriate changes in chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH Health Hazard Evaluation reports Nos. HETA-82-355-1375 (1982) and HHE-79-7-639, NIOSH, unpublished, 1982.

[2] Rushing, L.G. and Thomson, H.C. Jr. Simultaneous Determination of Trimellitic Anhydride and Its Acid Impurity by GC/FID, J. Anal. Toxicol., **6**(6), 290 (1982).

[3] Geyer, R. et al. Determination of Trimellitic Anhydride by HPLC, Chromatogr. Commn., **9** (5), 308-309 (1986).

8/15/90

NIOSH Manual of Analytical Methods

TRIMELLITIC ANHYDRIDE

Measurement Support Branch

Analytical Method

Analyte:	Trimellitic Anhydride*	Method No:	P&CAM 322
Matrix:	Air	Range :	0.048 - 0.24 mg/m ³
Procedure:	Filter collection, extraction derivatization, GC-FID	Precision:	0.087
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Trimellitic anhydride (TMA) is collected from air on a PVC-copolymer membrane filter. The filter is extracted with methanol and the methanol volume is reduced by evaporation. Boron trifluoride/methanol is added to the extract to derivatize the anhydride. The mixture is heated at 97°C for 20 minutes during which the anhydride is converted to its trimethyl ester. After cooling the boron trifluoride is complexed and precipitated with a pyridine/pentane/ether mixture. An aliquot of the mixture is injected and analyzed by a gas chromatograph equipped with flame ionization detector. The concentration of unknown samples is determined from a calibration curve.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The working range is from 0.048 - 0.24 mg/m³ for a 400-L air sample corresponding to 19.2 - 96/μg sample.
- 2.2 The detection limit was not determined, but it is estimated to be on the order of 2 μg per 5 μL injection at 8 x 10 attenuation using F.I.D.

3. Interferences

- 3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

*1,2,4-Benzenetricarboxylic acid-1,2-anhydride

3.2 Any compound that has the same retention time as the trimethyl ester of trimellitic anhydride at the operating conditions described in this method is an interference. The interference may be eliminated by changing the operating conditions of the chromatograph, e.g. by changing the temperature programming or carrier gas flow-rate.

3.3 This method will not differentiate between trimellitic anhydride and trimellitic acid. Under derivatization both compounds will form the same trimethyl ester (trimethyl trimellitate).

4. Precision and Accuracy

The analytical pooled relative standard deviation (RSD) is 8.7% determined from 15 TMA spiked PVC-copolymer filters over the range of 19.2-96 $\mu\text{g}/\text{filter}$. The average recovery is 103.3%. Calibration standards ($n=21$) exhibited an RSD of 7.6%.

5. Advantages and Disadvantages

5.1 The method offers a one step derivatization procedure in which the anhydride directly converts into its corresponding trimethyl ester.

5.2 The method has a low detection limit, 2 μg .

5.3 Trimellitic anhydride recoveries are quantitative with acceptable precision.

5.4 After derivatization, samples are stable for at least two days. The retention time of the ester is approximately 7.5 minutes.

5.5 The method may be used as a general method for other organic anhydrides and carboxylic acids.

5.6 See Section 3.3.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Polyvinyl chloride-copolymer membrane filters, 0.8 μm in pore size, 37-mm in diameter, Gelman DM-800 or equivalent.

6.1.2 Plastic three piece 37-mm filter holders (cassettes). The filter is supported in the cassette by a cellulose backup pad.

6.1.3 A personal air sampling pump capable of operating at 1.5 to 2.0 liters per minute.

6.1.4 A thermometer, barometer and a stopwatch.

6.2 Analytical Equipment

- 6.2.1 Gas chromatograph equipped with a flame ionization detector (FID) and glass-lined injection port.
- 6.2.2 A stainless-steel column, 9' (274 cm), 2-mm I.D. packed with 60/80 mesh Tenax-GC (Applied Science Labs., Inc., State College, PA.) or equivalent porous polymer packing. No liquid stationary phase is needed.
- 6.2.3 A strip-chart recorder, 1mV full scale.
- 6.2.4 Test tubes, glass 13 x 100-mm size with Telfon lined screw caps. Rubber lined caps produce extraneous peaks.
- 6.2.5 Glass syringe, 10 μ L.
- 6.2.6 Pipettes, 10 μ L, 25 μ L, 50 μ L, variable 50-250 μ L and 0.25-5 mL.
- 6.2.7 Volumetric flask, 250 mL.
- 6.2.8 Beakers, 50 mL and 250 mL.
- 6.2.9 Hot plate, variable heat settings.
- 6.2.10 Watch glasses to fit on 50 mL beakers.
- 6.2.11 Ultrasonic bath.
- 6.2.12 Air evaporator/concentrator (6 syringe manifold block for reducing the methanol volume in the test tubes).
- 6.2.13 High temperature GC injection septa (350°C).
- 6.2.14 Analytical balance, to $\pm$ 0.01 mg.
- 6.2.15 Tweezers, flexible tubing, applicator stick, weighing paper.

7. Reagents

Whenever possible, reagents used should be ACS reagent grade or better.

- 7.1 Methanol.
- 7.2 Pentane.
- 7.3 Diethyl ether.
- 7.4 Boron trifluoride/methanol, 14% w/v mixture (commercially available from GC supplier).
- 7.5 Pyridine.
- 7.6 Pyridine mixture. Prepare a 7:3 pyridine/pentane mixture in a screw-cap tube.

7.7 Trimellitic anhydride (1,2,4-Benzenetricarboxylic anhydride).

7.8 Laboratory compressed-air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PVC-copolymer membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lie flat on the backup pad and the spacer ring does not fit snugly into the bottom of the filter holder, sample leakage will occur around the filter. Remove the cassette plugs. Use a piece of flexible tubing to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 400 liters is recommended. Sample at a flow rate of 1.7 liters per minute for 4 hours. The flow rate should be known with an accuracy of at least $\pm 5\%$. A high volume air sample may also be submitted along with the other personal samples for qualitative GC work.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit at least one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Extraction

Place a field or a spiked filter sample in a 50-mL beaker and add 3 mL methanol. Put a watch-glass on the beaker and place beaker on a hot plate (65°C) for one minute. Remove beaker and place it in the ultrasonic bath for one minute (watch-glass is still on the beaker to prevent sample loss and water contamination of the sample during ultrasonication).

Rinse the bottom of the watch glass with 1 mL methanol and collect the rinse in the beaker. Lift the filter with tweezers above the methanol level and rinse both sides of the filter slowly with two 3-mL aliquots of methanol, collecting the rinse in the same beaker. Roll and squeeze the filter with tweezers against the inside wall of the beaker to remove methanol retained by the filter, then discard the filter.

Place the beaker on the hot plate (55°C) and reduce the methanol level to less than 5 mL. Transfer the methanol extract to a test tube. Rinse the beaker two or three times with small amounts of methanol and combine the rinsings in the test tube. Evaporate the methanol in the test tube to near dryness (about 10 µL) by blowing warm air over the surface with the use of the evaporator block. For comparison, 10 µL methanol may be added to an empty test tube to observe the amount of 10 µL. The sample is now ready for derivatization.

8.4.2 Derivatization

To each sample or standard tube that contains an anhydride sample, add 125 µL BF₃/methanol. Screw the cap tightly and place the tube in a water bath (97°C) for 20 minutes. Remove tube and let it cool to room temperature. Add the following solvents to the tube: 50 µL diethyl ether, 50 µL pentane, and 50 µL of the pyridine mixture. Between solvent additions screw the cap on each tube to prevent evaporation of the solvents. Shake tube mildly between additions. (With the pyridine addition a white precipitate forms, which is a complex of BF₃·pyridine.) After a few minutes the white material precipitates and the sample is ready for analysis. No centrifuging is necessary.

8.4.3 Gas Chromatographic Conditions

Column: See Section 6.2.2

Column Temperature

Program: 250°C for 2 minutes, then 16°/min
to 310°C, hold for 4 min. at 310°C

Injection Temperature: 315°C
 Detector Temperature: 325°C
 Helium Flow Rate: 35 mL/min
 Hydrogen Flow Rate: 53 mL/min
 Air Flow Rate: 550 mL/min
 Detector: FID, Attenuation 16 x 10 and 32 x 10
 Injection Volume: 5 µL
 Retention Time: 7.5 minutes

8.5 Filter Recovery Determination

- 8.5.1 Spiking Solution. Prepare a stock solution of 0.01 M trimellitic anhydride (1.92 µg / µL) by dissolving 0.4803 g TMA in a 250 mL volumetric flask containing methanol and making up the remaining volume with methanol.
- 8.5.2 Spike six PVC-copolymer filters for each level using pipettes. Use 10, 25, and 50 µL volumes of the spiking solution to get 19.2, 48, and 96 µg TMA on each filter respectively. When each filter is dry, follow Section 8.4 to analyze the sample.
- 8.5.3 Percent recovery (R, extraction efficiency) is determined as follows:

$$R = \frac{W_r}{W_s} \times 100$$

where: W_r = micrograms recovered

W_s = micrograms spiked

Convert peak area to micrograms from the equation of the calibration curve.

9. Calibration and Standardization

- 9.1 Using the 0.01 M TMA solution from 8.5.1, prepare 6 calibration standards per level by pipetting 10, 25, and 50 µL into test tubes. This is equivalent to 19.2, 48, and 96 µg TMA per each level. Be sure to screw the caps on the tubes between additions. Follow Section 8.4.2 to derivatize the standards.

- 9.2 Since the total volume in each tube after extraction is different- 285, 300, and 325 μ L for 19.2, 48, and 96 μ g level respectively - a correction for the areas must be made. Use the factors of 1.053 and 1.14 to multiply the areas of the standards at the 48 and 96 μ g levels respectively.
- 9.3 Prepare a plot of the corrected areas of the standards versus concentration of TMA. Do statistical analysis of "least squares" to determine the equation of the calibration curve.
- 9.4 Suggestion: It was found, after the method was completed, that since no sample loss occurred even when the sample was completely evaporated, that one may eliminate the correction factors and the evaporation of field samples to 10 μ L by completely evaporating to dryness standards and field samples and carrying out the normal procedure from there on.

10. Calculations

- 10.1 The concentration of unknown TMA samples can be determined graphically from the plot of peak areas of the standards versus concentration.
- 10.2 The concentration of unknown TMA samples may also be determined from the equation of line obtained from "least squares" statistical analysis

$$C = \frac{A - Y}{M}$$

where: C = concentration of TMA in μ g/sample

A = peak area of the sample

Y = line intercept value (from least squares)

M = line slope value (from least squares).

- 10.3 For personal pumps with rotameters only, the following correction for air volumes sampled should be made:

$$\text{Corrected volume} = F \times T \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{\frac{1}{2}}$$

where: F = sample flow rate

T = sampling time

P_1 = pressure during calibration of sampling pump in mm Hg

P_2 = pressure of air sampled in mm Hg

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.4 The concentration of trimellitic anhydride in air (C_A) can be expressed in mg/m^3

$$C_A = \frac{W}{V}$$

where: W = weight of field sample in μg

V = volume of air sampled in liters

11. References

- 11.1 Snell, F.D., and L.S. Ettre, Encyclopedia of Industrial Chemical Analysis, 17, 171, (1968).
- 11.2 NIOSH Current Intelligence Bulletin # 21, "Trimellitic Anhydride", Publication No. 78-121.
- 11.3 Biondi, P.A., and M. Cagnasso, Journal of Chromatography, 109, 389 (1975).

John Palassis

Measurement Services Section

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(C_6H_4CH_3)_3PO_4$

TRIORTHOCRESYL PHOSPHATE

2ND EDITION METHOD #: S209

DATE ISSUED: 11/21/75

M.W.: 368.37

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 1.12 g/mL @ 20 °C;

OSHA: TWA 0.1 mg/m³ (skin)

BP 420 °C; VP 0.27 kPa

NIOSH: TWA 0.1 mg/m³ (skin)

(1.7 mm Hg) @ 25 °C,

ACGIH: TWA 0.1 mg/m³ (skin)

1.3 kPa (10 mm Hg) @ 200 °C

SYNONYMS: o-tolyl phosphate; phosphoric acid triorthocresyl ester; CAS #78-30-8

SAMPLER: filter, 0.8-µm cellulose ester membrane

FLOW RATE: 1.5 L/min.

RECOMMENDED VOLUME: ≥100 L

MEASUREMENT TECHNIQUE: gas chromatography, FPD in phosphorus mode

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution

MEASUREMENT CALIBRATION: standard solutions of triorthocresyl phosphate in diethyl ether in the range 0.05 to 24 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.05 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] NIOSH/OSHA Occupational Health Guidelines of 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.

[2] Nomeir, Amin A. et al., High Performance Liquid Chromatographic Analysis of Triorthocresyl Phosphates and Metabolites, Anal. Biochem., 135 (2), 296 (1983).

Triorthocresyl Phosphate

Analyte:	Triorthocresyl Phosphate	Method No.: S209
Matrix:	Air	Range: 0.029-0.170 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$): 0.086
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date: 11/21/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.
- 1.2 The filter in the cassette is transferred into a jar and extracted with ether.
- 1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).
- 1.4 The area of the resulting sample peak is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.029-0.170 mg/cu m at an atmospheric temperature and pressure of 19°C and 761 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.02-0.3 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 30-microgram sample.
- 2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for triorthocresyl phosphate aerosol was found to be 99% when sampled for 66 minutes at 1.5 liters per minute (100 liters) from a test atmosphere containing 0.17 mg/cu m. Similarly, the collection efficiency was found to be 99% for a 150-liter sample at 0.19 mg/cu m.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.2 It must be emphasized that any phosphorus-containing compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.029-0.17 mg/cu m was 0.086. This value corresponds to a standard deviation of 0.009 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 98.8% was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method--the average recovery from the filters was 101.3%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
- 6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37-mm, 3-piece cassette filter holder.
- 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

- 6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter. The filter is held in the three-piece cassette supported by a cellulose backup pad.
- 6.3 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.
- 6.4 Column (6-ft x 1/8-in stainless steel) packed with 3% OV-101 on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.
- 6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.
- 6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.
- 6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

- 7.1 Anhydrous ether, reagent grade
- 7.2 Triorthocresyl phosphate, reagent grade
- 7.3 Purified hydrogen
- 7.4 Prefiltered, compressed air
- 7.5 Purified nitrogen

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and shipping of samples
 - 8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that

the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

- 8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.
- 8.3.4 A sample size of 100 liters is recommended but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least +5%.
- 8.3.5 Turn the pump on and begin sample collection. During the sampling period the pump rotameter should be observed frequently. It is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air; the sampling should be terminated at any evidence of a problem.
- 8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.
- 8.3.8 Carefully record sample identity and all relevant sample data.
- 8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. At least one blank per 10 samples should be submitted.
- 8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.

2. Transfer filter to the jar and pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.
 3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.
- 8.4.2 GC Conditions. Follow instrument manufacturer's recommendation on optimum gas flow rates. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (50 psig) Nitrogen carrier gas flow
 2. 70 ml/min Hydrogen gas flow to detector
 3. 150 ml/min Air flow to detector
 4. 250°C injector temperature
 5. 250°C detector temperature
 6. 220°C column temperature
- 8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

- 8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.
- 8.5.2 Procedure for determining recovery. A known amount of a standard stock solution of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm 5\%$.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) have been dosed accordingly using a solution of triorthocresyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The average recovery value obtained over all levels was 101% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in μg recovered from the filter divided by the weight in μg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered}}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. The triorthocresyl phosphate liquid is viscous and is difficult to measure accurately with a microliter syringe. Thus, it is suggested that a stock solution of triorthocresyl phosphate in ether be prepared by weighing triorthocresyl phosphate and diluting to volume. This stock solution can be used for the preparation of other calibration standards. Prepare calibration standards fresh daily. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC

conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

NOTE: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and therefore it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

10.1 Read the weight, in μg , corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 10.0 ml ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

10.3 Divide the total weight by the recovery to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V = volume of air in liters @ 25°C and 760 mm Hg

V_s = volume of air sampled

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

- 10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $(C_6H_5)_3PO_4$

TRIPHENYL PHOSPHATE

2ND EDITION METHOD #: S210

DATE ISSUED: 11/21/75

M.W.: 326.28

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

OSHA: TWA 3.0 mg/m³

NIOSH: TWA 3.0 mg/m³

ACGIH: TWA 3.0 mg/m³

PROPERTIES: crystals; MP 50 °C; sp. gr. 1.27;

BP 245 °C @ 11 mm Hg;

1.27 @ 60 °C;

VP <0.05 kPa (<0.1 mm Hg)

SYNONYMS: phosphoric acid triphenyl ester; CAS #115-86-6

SAMPLER: filter, 0.8-µm cellulose ester membrane

FLOW RATE: 1.5 L/min.

RECOMMENDED VOLUME: ≥100 L

MEASUREMENT TECHNIQUE: gas chromatography, FPD in phosphorus mode

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: non-polar capillary column may be used for better resolution and sensitivity

MEASUREMENT CALIBRATION: standard solutions of triphenyl phosphate in diethyl ether in the range 10 to 600 µg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 10 µg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: this method may be adapted to other phosphates of relatively low volatility with appropriate changes in chromatographic conditions

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] 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.

[2] Haraguchi et al., Sampling and Analysis of Phosphoric Acid Triesters in Ambient Air, Taiki Osen Gaikkeishi, 20 (6), 407 (1985).

Triphenyl Phosphate

Analyte:	Triphenyl Phosphate	Method No.: S210
Matrix:	Air	Range: 1.25-6.99 mg/cu m
OSHA Standard:	3.0 mg/cu m	Precision ($\overline{CV}_T$): 0.066
Procedure:	Filter collection, extraction with ether, GC/FPD	Validation Date: 11/21/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a cellulose ester membrane filter to trap the organic aerosol present.
- 1.2 The filter in the cassette is transferred into a jar and extracted with ether.
- 1.3 An aliquot of the eluted sample is injected into a gas chromatograph with a flame photometric detector (FPD).
- 1.4 The area of the resulting sample peak is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 1.25-6.99 mg/cu m at an atmospheric temperature and pressure of 24°C and 759 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the probable useful range of this method is 0.5-9 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 900-microgram sample.
- 2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for triphenyl phosphate aerosol was found to be 99% when sampled for 66 minutes at 1.5 liters per minute from a test atmosphere containing 7.0 mg/cu m.

3. Interferences

- 3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

- 3.2 It must be emphasized that any phosphorus-containing compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 1.25-6.99 mg/cu m is 0.066. This value corresponds to a standard deviation of 0.2 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.
- 4.2 A collection efficiency of 99.3% was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery from the filters was 99.1%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
- 6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.
- 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.
- 6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three-piece cassette supported by a cellulose backup pad.
- 6.3 Gas chromatograph equipped with a flame photometric detector and phosphorus-filter.

- 6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum-lined screw caps.
- 6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.
- 6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.
- 6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.
- 7. Reagents
 - 7.1 Anhydrous ether, reagent grade
 - 7.2 Triphenyl phosphate, reagent grade
 - 7.3 Purified hydrogen
 - 7.4 Prefiltered, compressed air
 - 7.5 Purified nitrogen
- 8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and shipping of samples
 - 8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.
 - 8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.
- 8.3.4 A sample size of 100 liters is recommended but a larger sample size can be collected if desired. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of at least +5%.
- 8.3.5 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.
- 8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.
- 8.3.8 Carefully record sample identity and all relevant sample data.
- 8.3.9 Blank: With each batch of 10 samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.
2. Transfer filter to the jar and pipet into the jar 10.0 ml of ether. Seal the jar immediately to minimize evaporation.
3. Allow the samples to stand for at least 30 minutes with occasional agitation. Tests indicate that this period is adequate for complete extraction.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (50 psig) Nitrogen carrier gas flow
2. 20 ml/min Hydrogen gas flow to detector
3. 150 ml/min Air flow to detector
4. 250°C injector temperature
5. 250°C detector temperature
6. 210°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

- 8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within +5%.

For this validation study, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly using a solution of triphenyl phosphate in ether. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 99% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in μg recovered from the filter divided by the weight in μg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered}}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml ether, because samples are desorbed in this amount of ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

NOTE: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FPD response. The FPD response is very sensitive to minor variations in hydrogen flow rate and therefore it is recommended that calibration standards must be carefully interspersed with the samples.

10. Calculations

- 10.1 Read the weight, in μg , corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 10.0 ml ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample} = \mu\text{g found in sample filter}$

$\mu\text{g blank} = \mu\text{g found in blank filter}$

10.3 Divide the total weight by the recovery to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V = volume of air in liters @ 25°C and 760 mm Hg

V^s = volume of air sampled

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m ($\mu\text{g per liter} = \text{mg per cu m}$).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

SECOND EDITION METHOD UPDATE INFORMATION

FORMULA: $\text{CH}_3\text{COOCH}=\text{CH}_2$

VINYL ACETATE

2ND EDITION METHOD #: P&CAM 278

DATE ISSUED: 05/10/78

M.W.: 86.09

CURRENT DATE: 08/15/90

CURRENT STANDARDS/RECOMMENDED LEVELS:

PROPERTIES: liquid; d 0.93 g/mL @ 20 °C;

BP 72.7 °C; VP 11.1 kPa (83 mm Hg)

@ 20 °C; vapor density (air=1) 3.0

OSHA: TWA 10 ppm; STEL 20 ppm

NIOSH: C 4 ppm

ACGIH: TWA 10 ppm

(1 ppm = 3.48 mg/m³ @ NTP)

SYNONYMS: acetic acid ethenyl ester; CAS #108-05-4

SAMPLER: Chromosorb 107 tube, 300 mg/50 mg

FLOW RATE: ≤ 0.1 L/min

RECOMMENDED VOLUME: ≤ 3 L

MEASUREMENT TECHNIQUE: gas chromatography, FID, thermal desorption

FIELD BLANKS OR MEDIA BLANKS: field blanks, 10% of samples

RECOMMENDED MEASUREMENT OPTIONS: none

MEASUREMENT CALIBRATION: standard solutions of vinyl acetate in hexane in the range
0.5 to 330 μg per sample

ESTIMATED LIMIT OF DETECTION (LOD): 0.5 μg per sample

RECENT NIOSH HEALTH HAZARD EVALUATION REFERENCE: none

APPLICABILITY: vinyl acetate is used mostly in adhesive, paints and textile industries;
other substances may interfere with the analysis

OTHER METHODS AND/OR LITERATURE REFERENCES:

[1] Kollar, V. et al., Determination of Vinyl Acetate in Working Atmosphere. Chem. Pap.,
42 (2), 147-160 (1988).

VINYL ACETATE

Measurements Research Branch

Analytical Method

Analyte:	Vinyl Acetate	Method No.	P&CAM 278
Matrix:	Air	Range:	8-210 mg/m ³ in 1.5 liters of air
Procedure:	Adsorption on Chromo- sorb 107, thermal de- sorption, GC-FID	Precision:	8%
Date Issued: May 10, 1978			
Date Revised:		Classification: E (Proposed)	

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing a Chromo-sorb 107 to trap the vinyl acetate present.
- 1.2 The tube is thermally desorbed into a 300 mL chamber.
- 1.3 An aliquot of the desorbed vapor is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 Sample loadings between 2 and 332 µg of vinyl acetate per sampling device are acceptable. Samples have been successfully collected from dynamically generated atmospheres of vinyl acetate over the concentration range of 8.2 to 206 mg/m³. The relative humidity of the sampled air was greater than 80%.

- 2.2 The slope of a typical calibration curve (integrator response versus mass of vinyl acetate per sample tube) was 687 (v.S)/g. The sensitivity of the flame ionization detector was 4.04×10^{-6} C/g of vinyl acetate.
- 2.3 The lowest quantifiable level was determined to be 0.5 μ g of vinyl acetate per 300 mg bed of Chromosorb 107. At this loading the relative standard deviation of replicate samples was better than 10%.

3. Interferences

- 3.1 When two or more substances are known or suspected to be present in the air sampled, such information should be transmitted with the sample, because the substances may interfere with the analysis of vinyl acetate.
- 3.2 Any substance which has the same retention time as vinyl acetate at the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.
- 3.3 If the possibility of interference exists, separation conditions (column packing, temperature, carrier flow, detector, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The pooled relative standard deviation of the sampling and analytical method was 8.1%. This reflects the precision of sampling and analysis of 50 samples of vinyl acetate collected with calibrated personal sampling pumps from humid atmospheres (>80%) over the concentration range of 8 to 200 mg/m^3 . The relative standard deviation of samples collected from atmospheres averaging 8.6 (range 8.2 to 9.0) mg/m^3 was 9.5%, from atmospheres averaging 24.3 (range 18.6 to 39.2) mg/m^3 was 8.0%, and from atmospheres averaging 181 (range 159 to 206) mg/m^3 was 5.9%.
- 4.2 The concentration of the sampled air was independently determined using a gas phase infrared analyzer. The samples were collected from humid air and stored at room temperature. The determination averaged 7% high, 5% high and 4% low when analyzed on days 1, 7

and 14, respectively. Thus the analyte displayed an 0.8% per day storage loss when stored at room temperature. This loss can be attributed to the analyte degrading in the presence of water, because samples spiked with 18 µg of vinyl acetate in hexane gave 98% recovery when stored for 14 days at room temperature.

- 4.3 The breakthrough volume and therefore capacity of Chromosorb 107 for vinyl acetate decreased with increasing relative humidity. Under the most adverse conditions tested, 83% relative humidity, the breakthrough volume was found to be 4.0 L when an atmosphere of vinyl acetate at 1 mg/m³ was sampled at 0.125 L/min.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Many of the interferences can be eliminated by altering chromatographic conditions.
- 5.2 The sampling tubes are analyzed using a quick instrumental method and can be reused after the analysis is completed.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will be imprecise because the pump is usually calibrated for one tube only.
- 5.4 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the sampling device. When the amount of vinyl acetate found on the backup section exceeds 10% of the amount found on the front section, the possibility of sample loss exists. Migration from the front to the backup section is not a problem because the sections are separated and individually capped immediately after sampling.

6. Apparatus

- 6.1 Personal sampling pump capable of accurate performance at 0.1 L/min. The pump must be calibrated with a representative sampling device in line and must be fully charged prior to being used.
- 6.2 Chromosorb 107 sampling tubes. Individual front and backup tubes (Century Systems Corporation "Flare" tubes or equivalent) are used. The front section is a stainless steel tube 7.3 cm long with a 6-mm o.d., a 4-mm i.d., and a 45° flare at one end. The backup section is a chrome plated nickel tube 3 cm long with a 6-mm o.d.,

a 4-mm i.d., a 45° flare at one end and a hose connection at the other end. Each tube has a permanent metal frit in the outlet end of the tube. The front section contains 300 mg of prewashed Chromosorb 107 held in place with a removable metal frit. The backup section contains 50 mg of prewashed Chromosorb 107 held in place with a plug of silylated glass wool. The sampling device is assembled by joining the front and backup section with a nylon nut and fitting. A hollow nylon ferrule is placed between the two sections. The pressure drop across the tubes must be less than 10 inches of water at a flow rate of 0.1 L/min.

The Chromosorb 107 is washed in a Soxhlet extractor for eight hours with water, eight hours with methanol and eight hours with dichloromethane. The sorbent is then dried overnight in a vacuum oven. The tubes are loaded with sorbent and thermally purged for two minutes with helium at 150°C. After cooling in a closed container the ends are capped.

- 6.3 Thermal desorber equipped with thermostatted desorbing oven, 300-ml sample reservoir, and a 2-mL gas sampling loop (Century Systems Corporation Programmed Thermal Desorber or equivalent).
- 6.4 Gas chromatograph equipped with a flame ionization detector and electronic integrator.
- 6.5 GC column (20 ft x 1/8 in.o.d.) made of silanized stainless steel and packed with 10% FFAP on 80/100 mesh Chromosorb W AW.
- 6.6 Vials 1.5-mL, with aluminum serum cups equipped with Teflon lined silicone rubber septa.
- 6.7 Microliter syringes, 10- μ l and convenient sizes for making standards.
- 6.8 Macropipette, 1000- μ l, with disposable plastic tips.
- 6.9 U-tube, glass with at least one hose connection, approximately 75-mL internal volume.
- 6.10 Pump capable of drawing 200 mL/min through a front section of the sampling device.
- 6.11 Gas bag, 10 liter volume for helium purge gas.
- 6.12 Test tubes with close fitting plastic caps.
- 6.13 Ring stand with clamps.

7. Reagents

Whenever possible, reagents used should be ACS Reagent Grade or better.

- 7.1 Vinyl acetate, practical, inhibited with hydroquinone and freshly distilled before use.
- 7.2 Hexane, (UV grade).
- 7.3 Helium, Bureau of Mines Grade A.
- 7.4 Hydrogen, prepurified.
- 7.5 Air, filtered and compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis of vinyl acetate is washed with detergent and rinsed thoroughly with tap water and distilled water.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling remove the plastic caps from the inlet and outlet ends of the sampling tube.
 - 8.2.2 Connect the tube to the sampling pump using a short piece of flexible tubing. The backup section is positioned nearest the pump. The sampling tube is kept vertical during sampling. to prevent channeling through the device.
 - 8.2.3 Air being sampled does not pass through any hose or tubing before entering the sampling device.
 - 8.2.4 The temperature, pressure, and volume of air sampled is measured and reported. The volume sampled should not exceed 3 liters sampled at a flow rate of 0.1 L/min or less. Record either the flow rate and sampling time or the initial and final stroke readings and the volumetric stroke factor.
 - 8.2.5 Immediately after sampling, disassemble the two sections, cap the sections with plastic caps, and label the sections. Do not use rubber caps.
 - 8.2.6 For every ten samples taken, handle one sampling device in the same manner as the samples (uncap, disassemble, cap, label and transport) however do not sample any air through this device. Label this device as a blank.

- 8.2.7 Samples received at the laboratory are logged in and analyzed as soon as possible. Samples stored at room temperature for 14 days exhibit an 11% loss of analyte.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Remove the caps from either a front or a back section. Wipe the outside of the tube with a clean laboratory wiper.

- 8.3.2 Thermal Desorber Conditions. Typical operating conditions for the thermal desorber are:

Desorbing oven temperature	150°C
Desorbing rate, helium gas	70 mL/min
Transfer line temperature	160°C
Pressure equalization time	15 sec.

- 8.3.3 Gas Chromatographic Conditions. Typical operating conditions for the gas chromatograph are:

Helium carrier gas flow rate	33 mL/min
Hydrogen flow to detector	40 mL/min
Air flow to detector	435 mL/min
Injector temperature	160°C
Manifold(detector) temperature	160°C
Oven temperature	60°C

Under these conditions, the capacity ratio for vinyl acetate was 4.4.

- 8.3.4 Thermal Desorption of Samples. Wipe off the tube and insert it in the desorbing oven. Desorb with helium at atmospheric pressure. The helium is stored in the 10-L gas bag. Desorbing with air chars the Chromosorb and renders it unsuitable for reuse.
- 8.3.5 Injection. Inject a 2 mL aliquot of the desorbed vapors into the GC column. Since the desorbed vapors are stored in a reservoir, as many as five replicate injections of each sample can be made.
- 8.3.6 Measurement of Area. Measure the area of the sample peak with an electronic integrator or other suitable technique of area measurement. The results are read from a standard curve as prepared in Section 9.4.
- 8.3.7 Preparation for Next Sample. After satisfactory analysis is obtained, purge the thermal desorber with helium for two minutes.

Remove the tube from the desorbing oven, place it in a test tube and cap the test tube. When the tube is cool, remove it from the test tube and cap it with the plastic cups.

9. Calibration and Standardization

- 9.1 It is convenient to express the concentration in terms of μg of vinyl acetate per sample tube. Standard curves are prepared by loading clean sampling tubes (front sections) with known amounts of vinyl acetate. The density of vinyl acetate ($0.932 \text{ mg}/\mu\text{L}$ at 20°C) is used to convert the volume taken to mass.
- 9.2 Preparation of Standards. Pipet 1.00 mL aliquots of hexane into clean glass vials. Crimp the vials shut with an aluminum serum cap equipped with a Teflon lined silicone rubber septum. Inject either 25 , 10 , 5 or $1 \mu\text{L}$ of freshly distilled vinyl acetate into each vial. These standard solutions are freshly prepared for each analysis.
- 9.3 Loading the Standard. Support a U-tube on a ring stand. Using a short length of tubing attach the outlet end of a clean front section of a sampling tube to a small pump. The inlet end of the clean front section is attached to the side of the U-tube that has the hose connection. Use the solvent flush technique to withdraw a $2 \mu\text{L}$ aliquot of a standard solution. Turn on the pump and inject this $2 \mu\text{L}$ aliquot into the end of the μ tube farthest from the sampling tube. Sweep enough air through the U-tube (2 min at $200 \text{ mL}/\text{min}$ approximately 5 volume changes) to insure that all the vinyl acetate is loaded on the sample tube. Stop the pump, remove the sample tube cap both ends, and label. This tube now contains a known amount of vinyl acetate.
- 9.4 Standardization. Analyze each tube from Section 9.3 as per Section 8.3. The standard curve is obtained by plotting the amount of vinyl acetate loaded on a tube versus the peak area found. If conditions warrant, prepare standards at higher or lower concentrations.

10. Calculations

- 10.1 The sample weight in μg is read from the standard curve.
- 10.2 Blank corrections are not expected. If the analysis shows a blank correction is needed, the correction is:

$$W_F = W_S - W_b$$

where: W_F = corrected amount (μg) on the front section of the charcoal tube

W_S = amount (μg) found on the front section of the charcoal tube

W_b = amount (μg) found on the front section of the blank charcoal tube

A similar procedure is followed for the backup sections.

10.3 The concentration, C , of vinyl acetate in the air sampled is expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$.

$$C = \frac{W_F + W_B}{V}$$

where: W_F = amount of vinyl acetate found on front section in μg

W_B = amount of vinyl acetate found on backup section in μg

V = volume of air sampled in liters

10.4 If desired the results may be expressed in ppm at 25°C (298°K) and 760 torr.

$$C(\text{ppm}) = C(\mu\text{g}/\text{L}) \times \frac{24.45}{86.1} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure of air sampled in torr

T = temperature of air sampled in $^\circ\text{C}$

24.45 = molar volume at 25°C and 760 torr in liters/mol

86.1 = molecular weight of vinyl acetate in g/mol

11. References

- 11.1 D. L. Foerst, Alexander W. Teass and Maria Risholm-Sundman, "A Sampling and Analytical Method for Vinyl Acetate in Air", (manuscript in preparation) Measurements Research Branch, NIOSH, Cincinnati, OH 1978.

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*U.S. Government Printing Office: 1990-748-160/20613