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NIOSH MANUAL OF ANALYTICAL METHODS
THIRD EDITION

THIRD SUPPLEMENT

U.S. National Institute for Occupational Safety and Health

Cincinnati, Ohio

May 1989

THIS THIRD SUPPLEMENT CONTAINING 34 METHODS FOR 69 TOXIC CHEMICAL COMPOUNDS IS ENCLOSED AS AN UPDATE TO THE NIOSH MANUAL OF ANALYTICAL METHODS, 3RD EDITION (1984). THE METHODS FOR THE SUPPLEMENT WERE SELECTED ON THE BASIS OF THEIR USE, INPUT FROM THE CLIENTS AND NIOSH CHEMISTS ON NEED FOR CHANGE AND THE HEALTH IMPLICATIONS OF THE COMPOUNDS. SOME METHODS FOR INCLUSION WERE SELECTED FROM THE SECOND EDITION OF THE MANUAL; SOME WERE REVISED FROM THE THIRD EDITION; AND SOME ARE NEW METHODS.

ANY COMMENTS REGARDING THE SUPPLEMENT OR THE NIOSH MANUAL OF ANALYTICAL METHODS IN GENERAL WOULD BE APPRECIATED BY NIOSH AND SHOULD BE DIRECTED TO:

MANUAL COORDINATOR
NIOSH MANUAL OF ANALYTICAL METHODS
DIVISION OF PHYSICAL SCIENCES
AND ENGINEERING (R-2)
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ERRATA for method 7401 (ALKALINE DUSTS):

CALCULATIONS:

13. Using the normality (N) and volumes of NaOH in the titration of the sample (V_{NaOH-s}) and average blank filter (V_{NaOH-b}), and the volume of air sampled, V(L), calculate the concentration, C (mg/m^3), of alkalinity (as NaOH with equivalent weight = 40.0):

$$C = \frac{V_{NaOH-b} - V_{NaOH-s}) \bullet N \bullet 4 \times 10^4}{V}, \ mg/m^3$$

CLIP THE INFORMATION FROM THIS ERRATA PAGE AND INSERT IN THE CORRESPONDING SPACE ON PAGE 7401-4.

TRANSMITTAL NOTICE

This is the third supplement to the NIOSH Manual of Analytical Methods, 3rd edition (printed February 15, 1984, first supplement dated May 15, 1985, second supplement dated August 15, 1987). The contents of this supplement are dated May 15, 1989 and include the 35 methods on the reverse side of this page.

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

- REMOVE the following pages: v through xii (contents), ACETIC ACID (Method 1603), ACRYLONITRILE (Method 1604), ASBESTOS FIBERS (Method 7402), CHROMIUM, HEXAVALENT (Method 7600), FIBERS (Method 7400), FLUORIDES (Method 7902)[1], FORMALDEHYDE (GC) (Method 2502)[2], FORMALDEHYDE (UV-VIS) (Method 3500), FORMALDEHYDE (POLAROGRAPHY) (Method 3501), KETONES I (Method 1300), MERCURY (Method 6000)[2], SILICA, (CRYSTALLINE, RESPIRABLE) (Method 7500), SULFUR DIOXIDE (Method 6004), and pp. A-11 through A-55 (indexes).

- ADD the enclosed methods alphabetically[3] to your Manual. Add the enclosed Table of Contents[4] and Indexes[5].

- 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 relacements.

- NOTE for many methods in the Manual, new OSHA PELs[6], NIOSH RELs[7], and ACGIH TLVs[8], are in effect.

- NOTE: New guidelines[9] in addition to those cited previously for protecting safety and health of health care workers.

NOTES: (1) This method is withdrawn because of problems [Appl. Ind. Hyg. 3 (11), 302, (1988)].
(2) These methods have been replaced by Methods 2541 (FORMALDEHYDE) and 6009 (MERCURY), respectively (enclosed).
(3) 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.
(4) Current Issue dates have been added for each method. Discard previous versions.
(5) The Index of Second Edition Method Numbers has been made more useful by a cross-reference to 3rd ed. method names.
(6) OSHA PELs. TABLES Z-1-A, Z-2, and Z-3, Fed. Reg. Vol. 54, No. 12, January 19, 1989;
(7) 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.
(8) ACGIH TLVs. American Conference of Governmental Industrial Hygienists. TLVs and Biological Exposure Indices for 1988-89, ACGIH, Cincinnati, Ohio, (1988), or more recent issuance.
(9) "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 May 15, 1989, Supplement to the NIOSH Manual of Analytical Methods, 3rd ed.:

Method No.		Method
2538		ACETALDEHYDE
1603	*	ACETIC ACID
1604	*	ACRYLONITRILE
2539		ALDEHYDES, SCREENING
2010		AMINES, ALIPHATIC
3509		AMINOETHANOL COMPOUNDS II
9002		ASBESTOS (bulk)
7402	*	ASBESTOS FIBERS
2525		1-BUTANETHIOL
5510		CHLORDANE
7600	*	CHROMIUM, HEXAVALENT
7604		CHROMIUM, HEXAVALENT
5030		CYANURIC ACID
2540		DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE
5519		ENDRIN
7400	*	FIBERS
2541		FORMALDEHYDE
3500	*	FORMALDEHYDE
3501	*	FORMALDEHYDE
2505		FURFURYL ALCOHOL
2531		GLUTARALDEHYDE
6010		HYDROGEN CYANIDE
5521		ISOCYANATES
1300	*	KETONES I
6009	*	MERCURY
2537		METHYL METHACRYLATE
2522		NITROSAMINES
5512		PENTACHLOROPHENOL
7609		QUARTZ in coal mine dust
5027		RIBAVIRIN
7500	*	SILICA, (crystalline, respirable)
6004	*	SULFUR DIOXIDE
5516		2,4- & 2,6-TOLUENEDIAMINE
2536		VALERALDEHYDE

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

CONTENTS

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V. A. INDEX OF THIRD EDITION METHOD NUMBERS

3rd ed. Method Number	Substance
0500	NUISANCE DUST, TOTAL
0600	NUISANCE DUST, RESPIRABLE
1000	ALLYL CHLORIDE
1001	METHYL CHLORIDE
1002	CHLOROPRENE
1003	HYDROCARBONS, HALOGENATED:
	Benzyl chloride
	Bromoform
	Carbon tetrachloride
	Chlorobenzene
	Chlorobromomethane
	Chloroform
	o-Dichlorobenzene
	p-Dichlorobenzene
	1,1-Dichloroethane
	1,2-Dichloroethylene
	Ethylene dichloride
	Hexachloroethane
	Methylchloroform
	Tetrachloroethylene
	1,1,2-Trichloroethane
	1,2,3-Trichloropropane
1004	sym-DICHLOROETHYL ETHER
1005	METHYLENE CHLORIDE
1006	TRICHLOROFLUOROMETHANE
1007	VINYL CHLORIDE
1008	ETHYLENE DIBROMIDE
1009	VINYL BROMIDE
1010	EPICHLOROHYDRIN
1011	ETHYL BROMIDE
1012	DIBROMODIFLUOROMETHANE
1013	1,2-DICHLOROPROPANE
1014	METHYL IODIDE
1015	VINYLIDENE CHLORIDE
1016	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE
1017	BROMOTRIFLUOROMETHANE
1018	DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUOROETHANE
1019	1,1,2,2-TETRACHLOROETHANE
1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE
1022	TRICHLOROETHYLENE
1024	1,3-BUTADIENE
1300	KETONE I:
	Acetone
	Cyclohexanone
	Diisobutyl ketone
	2-Hexanone
	Methyl isobutyl ketone
	2-Pentanone
1301	KETONES II:
	Camphor
	Ethyl butyl ketone
	Mesityl oxide
	Methyl (n-amyl) ketone
	5-Methyl-3-heptanone
1400	ALCOHOL I:
	tert-Butyl alcohol
	Ethanol
	Isopropyl alcohol
1401	ALCOHOL II:
	n-Butyl alcohol
	sec-Butyl alcohol
	Isobutyl alcohol
	n-Propyl alcohol
1402	ALCOHOLS III:
	Allyl alcohol
	Cyclohexanol
	Diacetone alcohol
	Isoamyl alcohol
	Methyl isobutyl carbinol
1403	ALCOHOLS IV:
	2-Butoxyethanol
	2-Ethoxyethanol
	Methyl cellosolve
1450	ESTERS I:
	n-Amyl acetate
	sec-Amyl acetate
	n-Butyl acetate
	sec-Butyl acetate
	tert-Butyl acetate
	2-Ethoxyethyl acetate
	Ethyl acrylate
	Isoamyl acetate
	Isobutyl acetate
	Methyl isoamyl acetate
	n-Propyl acetate
1550	HYDROCARBONS, BP 36 - 126 °C:
	Benzene
	Cyclohexane
	Cyclohexene
	n-Heptane
	n-Hexane
	Methylcyclohexane
	n-Octane
	n-Pentane
	Toluene

3rd Ed. Method Number	Substance
1501	HYDROCARBONS, AROMATIC:
	Benzene
	p-tert-Butyl toluene
	Cumeme
	Ethylbenzene
	α-Methylstyrene
	Napthalene
	Styrene
	Toluene
	Vinyl toluene
	Xylene
1550	NAPHTHAS
	Coal tar naphthas
	Kerosene
	Mineral spirits
	Petroleum ether
	Petroleum naphtha
	Rubber solvent
	Stoddard solvent
1551	TURPENTINE
1600	CARBON DISULFIDE
1601	1,1-DICHLORO-1-NITROETHANE
1602	DIOXANE
1603	ACETIC ACID
1604	ACRYLONITRILE
1606	ACETONITRILE
1607	ETHYLENE OXIDE
1608	GLYCIDOL
1609	TETRAHYDROFURAN
1610	ETHYL ETHER
1611	METHYLAL
1612	PROPYLENE OXIDE
1613	PYRIDINE
1614	ETHYLENE OXIDE
2000	METHANOL
2001	CRESOLS
2002	AMINES, AROMATIC:
	Aniline
	N,N-Dimethylaniline
	N,N-Dimethyl-p-toluidine
	o-Toluidine
	2,4-Xylidine
2003	1,1,2,2-TETRABROMOETHANE
2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE
2005	NITROBENZENES:
	4-Chloronitrobenzene
	Nitrobenzene
	Nitrotoluene
2007	AMINOETHANOL COMPOUNDS:
	2-Aminoethanol
	2-Dibutylaminoethanol
	2-Diethylaminoethanol
2008	CHLOROACETIC ACID
2010	AMINES, ALIPHATIC
	Diethylamine
	Dimethylamine
2500	2-BUTANONE
2501	ACROLEIN
2503	MEVINPHOS (Phosdrin)
2504	TETRAETHYL PYROPHOSPHATE (TEPP)
2505	FURFURYL ALCOHOL
2506	ACETONE CYANOHYDRIN
2507	NITROGLYCERIN/EGDN
2508	ISOPHORONE
2510	1-OCTANETHIOL
2513	ETHYLENE CHLOROHYDRIN
2514	ANISIDINE
2515	DIAZOMETHANE
2516	DICHLOROFLUOROMETHANE
2517	PENTACHLOROETHANE
2518	HEXACHLORO-1,3-CYCLOPENTADIENE
2519	ETHYL CHLORIDE
2520	METHYL BROMIDE
2521	METHYL CYCLOHEXANONE
2522	NITROSAMINES
	N-nitrosodimethylamine
	N-nitrosodiethylamine
	N-nitrosodipropylamine
	N-nitrosodibutylamine
	N-nitrosomorpholine
	N-nitrosopiperidine
	N-nitrosopyrrolidine
2523	1,3-CYCLOPENTADIENE
2524	DIMETHYL SULFATE
2525	1-BUTANETHIOL
2526	NITROETHANE
2527	NITROMETHANE
2528	2-NITROPROPANE
2529	FURFURAL
2530	BIPHENYL
2531	GLUTARALDEHYDE
2533	TETRAETHYL LEAD (as Pb)
2534	TETRAMETHYL LEAD (as Pb)
2535	TOLUENE-2,4-DIISOCYANATE
2536	VALERALDEHYDE
2537	METHYL METHACRYLATE
2538	ACETALDEHYDE (GC)
2539	ALDEHYDES, SCREENING
2540	DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE

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, o-ANISIDINE, and o-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	o-TERPHENYL
5022	ARSENIC, ORGANO-: p-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
5030	CYANURIC ACID
5500	ETHYLENE GLYCOL
5502	ALDRIN and LINDANE
5503	POLYCHLOROBIPHENYLS
5504	ORGANOTIN COMPOUNDS (as Sn) Bibutyltin bis(isooctyl 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	NAPHTHYAMINES α-Naphthylamine β-Naphthylamine 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
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
7102	BERYLLIUM

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)	
7604	CHROMIUM, HEXAVALENT (IC)	
7609	QUARTZ in coal mine dust	
7900	ARSENIC (hydride AAS)	
7901	ARSENIC TRIOXIDE (graphite AAS)	
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
	Cadmiun	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 HIPPURIC 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	CHRYSOTILE 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

TBR = To be revised; the 2nd Ed. method is recommended for use at present.

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method [Number]
P&CAM	102	1	Lead in blood (Dithizone)	LEAD [7082]; 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	NRIU
	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	BIRYLLIUM [7102]; ELEMENTS-ICP [7300]
	124	1	Selenium in urine	NRIU
	125	1	Formaldehyde	FORMALDEHYDE [2541, 3500, 3501]
	126	1	Hydrogen sulfide	NRIU
	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	TOLUENE-2,4-DIISOCYANATE [2535]
	142	1	MDI	NRIU

	2nd Ed. Method Number	Vol. Number	Substance	3rd Ed. Method [Number]
P&CAM	145	1	Mercury in urine	MERCURY IN URINE [8309]
	146	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	152	1	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
	153	1	Ozone	NRIU
	154	1	Ozone	NRIU
	158	1	Parathion	EPN, MALATHION and PARATHION [5012]
	159	1	Oil mist	MINERAL OIL MIST [5026]
	160	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	163	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	165	1	Mercury in urine	NRIU
	167	1	Mercury in blood	NRIU
	168	1	Aniline	AMINES, AROMATIC [2002]
	168	1	o-Toluidine	AMINES, AROMATIC [2002]
	168	1	2,4-Xylidine	AMINES, AROMATIC [2002]
	168	1	Dimethylaniline	AMINES, AROMATIC [2002]
	169	1	Chromic acid	CHROMIUM, HEXAVALENT [7600, 7604]
	173	1,5	Aluminum	ALUMINUM [7013]; ELEMENTS-ICP [7300]
	173	1	Antimony	NRIU
	173	1,5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	173	1,5	Barium	NRIU
	173	1,5	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]
	173	1,5	Bismuth	NRIU
	173	1,5	Cadmium	CADMIUM [7048]; ELEMENTS-ICP [7300]
	173	1,5	Calcium	CALCIUM [7020]; ELEMENTS-ICP [7300]
	173	1,5	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
	173	1,5	Cobalt	COBALT [7027]; ELEMENTS-ICP [7300]
	173	1,5	Copper	COPPER [7029]; ELEMENTS-ICP [7300]
	173	1,5	Indium	NRIU
	173	1,5	Iron	ELEMENTS-ICP [7300]
	173	1,5	Lead	LEAD [7082]; ELEMENTS-ICP [7300]
	173	1,5	Lithium	ELEMENTS-ICP [7300]
	173	1,5	Magnesium	ELEMENTS-ICP [7300]
	173	1,5	Manganese	ELEMENTS-ICP [7300]
	173	1,5	Molybdenum	ELEMENTS-ICP [7300]
	173	1,5	Nickel	ELEMENTS-ICP [7300]
	173	1,5	Palladium	NRIU
	173	1,5	Potassium	NRIU
	173	1,5	Rubidium	NRIU
	173	1,5	Silicon	NRIU
	173	1,5	Silver	ELEMENTS-ICP [7300]
	173	1,5	Sodium	ELEMENTS-ICP [7300]
	173	1,5	Strontium	ELEMENTS-ICP [7300]
	173	1,5	Tellurium	ELEMENTS-ICP [7300]
	173	1,5	Thallium	ELEMENTS-ICP [7300]
	173	1,5	Vanadium	ELEMENTS-ICP [7300]
	173	1,5	Zinc	ZINC [7030]; ELEMENTS-ICP [7300]
	175	5	Mercury	NRIU; see MERCURY [6009]
	176	1	Tin	ELEMENTS-ICP [7300]
	177	1	Gallium	NRIU
	178	1	Vinyl chloride	VINYL CHLORIDE [1007]
	179	1	Carbon disulfide	CARBON DISULFIDE [1600]

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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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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)	CHRYSOTILE 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	TBR
	248	1	Hydrazine	HYDRAZINE [3503]
	248	1	Methyl hydrazine	TBR
	248	1	Phenyl hydrazine	TBR
	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	TBR
	256	1	Azelaic acid	AZELAIC ACID [5019]
	257	1	Phosphorus	PHOSPHORUS [7905]
	259	1,5	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
	260	4	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
	261	4	Antimony	NRIU
	262	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]; METALS IN URINE [8310]
	263	4	Hexamethylenetetramine	NRIU
	264	4	Naphthylamines	NAPHTHYLAMINES [5518]
	265	4	Arsine	ARSINE [6001]
	266	4	Vinylidene chloride	VINYLIDENE CHLORIDE [1015]
	267	5	Sulfuric acid	NRNR; see ACIDS, INORGANIC [7903]
	268	5	Sulfur dioxide, sulfates, sulfites	SULFUR DIOXIDE [6004]
	269	4	4-Aminobiphenyl	TBR

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

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P&CAM	326	6	TDI	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	TBR
	335	6	Pentachloroethane	PENTACHLOROETHANE [2517]
	336	6	Tetraethyl pyrophosphate	TETRAETHYL PYROPHOSPHATE-TEPP [2504]
	337	7	p-Chlorophenol	TBR
	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	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	TBR
	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	TBR
	S8	2	Ozone	NRIU

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S10	2	Camphor	KETONES II [1301]
S11	5	Chloroacetaldehyde	TBR
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	o-TERPHENYL [1521]
S28	2	Cyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S29	2	Ethylbenzene	HYDROCARBONS, AROMATIC [1501]
S30	2	Styrene	HYDROCARBONS, AROMATIC [1501]
S31	2	sec-Amyl acetate	ESTERS I [1450]
S32	2	tert-Butyl acetate	ESTERS I [1450]
S33	2	Dibutyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
S35	2	Ethyl acrylate	ESTERS I [1450]
S36	2	Ethyl formate	TBR
S37	2	Methyl isoamyl acetate	ESTERS I [1450]
S38	2	Methyl acrylate	TBR
S39	2	Methyl cellosolve acetate	TBR
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	TBR
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	TBR
S50	2	Isopropyl acetate	TBR
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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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	TBR
S69	2	Dipropylene glycol methyl ether	TBR
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	TBR
S73	2	Phenyl ether-biphenyl mixture	TBR
S74	2	Phenyl glycidyl ether	TBR
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	TBR
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	TBR
S82	2	Cyclohexene	HYDROCARBONS, BP 36-126 °C [1500]
S84	5	Methyl acetylene (propyne)	TBR
S85	6	Methyl acetylene/propadiene	TBR
S86	2	Naphtha, coal tar	NAPHTHAS [1550]
S87	2	Propane	TBR
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	TBR
S93	2	LPG	TBR
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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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	NRIU
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE [1020]
S130	2	Tetrachloronaphthalene	NRIU
S131	2	1,1,1,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE
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	TBR; see AMINES, ALIPHATIC [2010]
S139	3	Diethylamine	AMINES, ALIPHATIC [2010]
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS [2007]; AMINOETHANOL COMPOUNDS II [3509]
S141	4	Diisopropylamine	TBR; see AMINES, ALIPHATIC [2010]
S142	3	Dimethylamine	AMINES, ALIPHATIC [2010]
S143	3	1,1-Dimethyl hydrazine	TBR
S144	3	Ethylamine	AMINES, ALIPHATIC [2010]
S146	3	N-Ethyl morpholine	AMINES, ALIPHATIC [2010]
S147	3	Isopropylamine	TBR; see AMINES, ALIPHATIC [2010]
S148	6	Methylamine	TBR; see AMINES, ALIPHATIC [2010]
S149	3	Methyl hydrazine	TBR
S150	3	Morpholine	AMINES, ALIPHATIC [2010]
S152	3	Triethylamine	TBR; see AMINES, ALIPHATIC [2010]
S153	3	Monomethylaniline	TBR
S155	3	Tetramethylsuccinonitrile	NRIU
S156	3	Acrylonitrile	ACRYLONITRILE [1604]
S158	4	2-Aminopyridine	TBR
S160	3	Phenyl hydrazine	TBR
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	TBR
S167	3	Cresol	CRESOLS [2001]
S168	3	o-Toluidine	AMINES, AROMATIC [2002]
S169	4	Acetic acid	ACETIC ACID [1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE [3506]

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S173	5	Formic acid	TBR
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	TBR
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	TBR
S209	3	Triorthocresyl phosphate	TBR
S210	3	Triphenyl phosphate	TBR
S211	5	1-Chloro-1-nitropropane	TBR
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	TBR
S215	4	Dinitrotoluene	TBR
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	TBR
S227	3	n-Propyl nitrate	TBR
S228	4	Picric acid	TBR
S229	3	Arsine	ARSINE [6001]
S237	3	Hydrazine	HYDRAZINE [3503]
S243	4	Stibine	STIBINE [6008]
S244	5	Sulfur hexafluoride	TBR
S245	6	Sulfuryl fluoride	TBR
S246	3	Hydrogen chloride	ACIDS, INORGANIC [7903]
S248	3	Carbon disulfide	CARBON DISULFIDE [1600]
S249	3	Carbon dioxide	TBR

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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	TBR
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	TBR
S275	3	Aldrin	ALDRIN and LINDANE [5502]
S276	5	ANTU	TBR
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	TBR
S284	6	Endrin	ENDRIN [5519]
S285	3	EPN	EPN, MALATHION, and PARATHION [5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE [1607, 3702]
S287	5	Heptachlor	TBR
S288	4	Hydrogen cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S290	3	Lindane	ALDRIN and LINDANE [5502]
S291	5	Methyl formate	TBR
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]
S293	3	Nicotine	TBR
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	TBR
S300	5	Rotenone	ROTENONE [5007]
S301	5	Sodium fluoroacetate	TBR
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]

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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	TBR
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	TBR
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	TBR
S341	3,7	Lead	LEAD [7082]; ELEMENTS-ICP [7300]
S342	6	Mercury, organo	TBR
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
S345	5	Acetaldehyde	ACETALDEHYDE [3507]
S346	4	Allyl glycidyl ether	TBR
S347	5	Ammonia	AMMONIA [6701]
S348	5	Ammonium sulfamate	TBR
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	TBR
S369	3	Magnesium oxide fume	ELEMENTS-ICP [7300]
S370	3	Malathion	EPN, MALATHION, and PARATHION [5012]
S371	4	Methoxychlor	TBR
S372	3	Methyl bromide	METHYL BROMIDE [2520]
S374	4	Methylcyclohexanol	TBR
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]

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S380	3	Naphtha, petroleum	NAPHTHAS [1550]
S381	4	Sodium hydroxide	ALKALINE DUSTS [7401]
S382	3	Stoddard solvent	NAPHTHAS [1550]
S383	4	Tetraethyl lead	TETRAETHYL LEAD [2533]
S384	4	Tetramethyl lead	TETRAMETHYL LEAD [2534]
S385	3	Titanium dioxide	TBR
S388	4	Vanadium	ELEMENTS-ICP [7300]
S391	3	Vanadium	ELEMENTS-ICP [7300]
CRDT	--	Fibrous glass	CARBON BLACK [5000]; FIBERS [7400]
CRDT	--	Nitrous oxide	NITROUS OXIDE [6600]
CRDT	--	Organotins	ORGANOTIN COMPOUNDS [5504]
SDS29	--	Nuisance dust, respirable	NUISANCE DUST, RESPIRABLE [0600]

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*      Example: The references to method title and number are listed in the following manner:  *
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*                                                                                       *
*      ACETIC ACID, 1603                              (Method title)                    *
*      Ethanoic acid, see ACETIC ACID, 1603           (Synonym)                         *
*      Glacial acetic acid, see ACETIC ACID, 1603     (Synonym)                         *
*      Methane carboxylic acid, see ACETIC ACID, 1603 (Synonym)                         *
*      CAS #64-19-7, see ACETIC ACID, 1603            (Chemical Abstracts Registry Number)  *
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Cumene, see HYDROCARBONS, AROMATIC, 1501
Cummingtonite-grumerite, see FIBERS, 7400; ASBESTOS FIBERS, 7402; ASBESTOS (bulk), 9002
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Cyclohexane-solubles, see COAL TAR PITCH VOLATILES, 5023
Cyclohexanol, see ALCOHOLS III, 1402
Cyclohexanone, see KETONES I, 1300
Cyclohexene, see HYDROCARBONS, BP 36-126 °C, 1500
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Diamine, see HYDRAZINE, 3503
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2,4-Diaminotoluene, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
2,6-Diaminotoluene, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
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1,2,5,6-Dibenzanthracene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; (GC), 5515
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2,6-Dibromo-4-cyanophenyl octanoate, see BROMOXYNIL and BROMOXYNIL OCTANOATE, 5010
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1,2-Dibromoethane, see ETHYLENE DIBROMIDE, 1008
3,5-Dibromo-4-hydroxybenzonitrile, see BROMOXYNIL and BROMOXYNIL OCTANOATE, 5010
2-Dibutylaminoethanol, see AMINOETHANOL COMPOUNDS, 2007
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DIBUTYL PHTHALATE, 5020
Dibutyltin bis(isooctyl mercaptoacetate), see ORGANOTIN COMPOUNDS, 5504
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1,4-Dichlorobenzene, see HYDROCARBONS, HALOGENATED, 1003
o-Dichlorobenzene, see HYDROCARBONS, HALOGENATED, 1003
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3,3'-Dichlorobenzidine, see BENZIDINE and 3,3'-DICHLOROBENZIDINE, 5509
3,3'-Dichloro[1,1'-biphenyl]-4,4'-diamine, see BENZIDINE and 3,3'-DICHLOROBENZIDINE, 5509
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CAS # 62-75-9, see NITROSAMINES, 2522
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CAS # 64-19-7, see ACETIC ACID, 1603
CAS # 66-25-1, see ALDEHYDES, SCREENING, 2539
CAS # 67-56-1, see METHANOL, 2000
CAS # 67-63-0, see ALCOHOLS I, 1400
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CAS # 67-66-3, see HYDROCARBONS, HALOGENATED, 1003
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CAS # 68-12-2, see DIMETHYLFORMAMIDE, 2004
CAS # 71-23-8, see ALCOHOLS II, 1401
CAS # 71-36-3, see ALCOHOLS II, 1401
CAS # 71-43-2, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126 °C, 1500; BENZENE by portable GC, 3700
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CAS # 72-20-8, see ENDRIN, 5519
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CAS # 74-88-4, see METHYL IODIDE, 1014
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CAS # 74-96-4, see ETHYL BROMIDE, 1011
CAS # 74-97-5, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-00-3, see ETHYL CHLORIDE, 2519
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CAS # 75-34-3, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-35-4, see VINYLIDENE CHLORIDE, 1015
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CAS # 75-56-9, see PROPYLENE OXIDE, 1612
CAS # 75-60-5, see ARSENIC, ORGANO-, 5022
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CAS # 75-63-8, see BROMOTRIFLUOROMETHANE, 1017
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CAS # 76-01-7, see PENTACHLOROETHANE, 2517
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CAS # 76-14-2, see DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUOROETHANE, 1018
CAS # 76-22-2, see KETONES II, 1301
CAS # 77-47-4, see HEXACHLORO-1,3-CYCLOPENTADIENE, 2518
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CAS # 78-00-2, see TETRAETHYL LEAD (as Pb), 2533
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CAS # 78-84-2, see ALDEHYDES, SCREENING, 2539
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CAS # 79-34-5, see 1,1,2,2-TETRACHLOROETHANE, 1019
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CAS # 98-83-9, see HYDROCARBONS, AROMATIC, 1501
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CAS # 99-08-1, see NITROBENZENES, 2005
CAS # 99-97-8, see AMINES, AROMATIC, 2002
CAS #100-00-5, see NITROBENZENES, 2005
CAS #100-37-8, see AMINOETHANOL COMPOUNDS, 2007
CAS #100-41-4, see HYDROCARBONS, AROMATIC, 1501
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CAS #8065-48-3, see DEMETON, 5514
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FORMULA: CH_3CHO

M.W.: 44.05

ACETALDEHYDE

METHOD: 2538

ISSUED: 5/15/89

OSHA: 100 ppm; STEL 150
NIOSH: carcinogen; lowest feasible level
ACGIH: 100 ppm; STEL 150 ppm
(1 ppm = 1.80 mg/m^3 @ NTP)

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

SYNONYMS: acetic aldehyde; ethanal; CAS #75-07-0.

SAMPLING

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

FLOW RATE: 0.01 to 0.05 L/min

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

SHIPMENT: routine

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

FIELD BLANKS: 10% of samples

ACCURACY

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

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.12 [2]

MEASUREMENT

!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: oxazolidine derivative of acetaldehyde
!
!DESORPTION: 5 mL toluene, 60 min ultrasonic
!
!INJECTION VOLUME: 1 µL, splitless
!
!TEMPERATURE: -INJECTOR: 250 °C
! -DETECTOR: 300 °C
! -COLUMN: 70 °C 1 min; 6 °C/min
! to 110 °C (hold 2 min)
! 30 °C/min to 260 °C
! (hold 1 min.)
!
!CARRIER GAS: He, 1 mL/min; makeup 29 mL/min
!
!COLUMN: wide-bore, fused-silica capillary,
! 15 m x 0.32 mm; 1-µm DB-1301 film
!
!CALIBRATION: standard solutions of acetaldehyde
! on coated sorbent
!
!RANGE: 4 to 2200 µg per sample [2]
!
!ESTIMATED LOD: 2 µg per sample [1,2]
!
!PRECISION (s_r): 0.090 @ 26 to 107 µg
! per sample [1]
!

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

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

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

REAGENTS:

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

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 11 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing two sections of 40/60 mesh 2-(hydroxymethyl) piperidine coated on XAD-2 and separated by 2-mm glass-wool plug (front = 450 mg; back = 225 mg). Tubes are commercially available (Supelco, Inc. ORBO Cat # 669-98) or may be prepared (see APPENDIX B).
2. Personal sampling pump, 0.01 to 0.05 L/min. with flexible connecting tubing.
3. Gas chromatograph, capillary column, FID, integrator (page 2538-1).
4. Vials, 7-mL, glass, with PTFE-lined screw caps.
5. Ultrasonic bath or mechanical shaker.
6. Pipets, volumetric, 1- and 5-mL with pipet bulb.
7. Flasks, volumetric, 10- and 25-mL.
8. Syringe, 10-µL, readable to 0.1 µL.

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

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

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

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

MEASUREMENT:

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

CALCULATIONS:

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

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

EVALUATION OF METHOD:

This method was originally developed and validated by OSHA [2] over the range 180 to 720 mg/m^3 per sample. A storage study was done by spiking commercially-available tubes with standard solutions of acetaldehyde [1]. Recovery (26.8 and 107 µg/sample) was 100% after 21 days of refrigerated storage. A migration study was also performed at the above concentrations. After 21 days refrigerated storage, no acetaldehyde was detected on the back sections of the samples. Additional evaluation information is available [2]. Field samples of acetaldehyde were also successfully analyzed by utilizing this method [1].

REFERENCES:

[1] Williams, Karen J. Analytical Report for Acetaldehyde Samples, NIOSH (MRSB) Sequence #6384, Unpubl. NIOSH (1988).
[2] "OSHA Analytical Methods Manual," U. S. Dept. of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory, Salt Lake City, UT, Method #68 (1988).
[3] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Allyl Compounds, Aldehydes, Epoxides and Peroxides, International Agency for Research on Cancer Vol 36:101-132 Lyon, France (1984).

METHOD REVISED BY: Karen J. Williams, NIOSH/DPSE

APPENDIX A: PREPARATION OF CALIBRATION STOCK SOLUTION

Prepare by diluting a known amount of acetaldehyde with toluene:

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

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

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

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

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

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

FORMULA: CH_3COOH; $C_2H_4O_2$

M.W.: 60.05

ACETIC ACID

METHOD: 1603
ISSUED: 2/15/84
REVISION #1: 5/15/89

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

PROPERTIES: liquid; d 1.049 g/mL @ 25 °C;
BP 118 °C; MP 17 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 20 °C;
explosive range 5.4 to 16% v/v in air

SYNONYMS: glacial acetic acid; methane carboxylic acid; ethanoic acid; CAS #64-19-7.

SAMPLING

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

FLOW RATE: 0.01 to 1.0 L/min

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

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

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 12.5 to 50 mg/m^3 [2]
(173-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.058 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acetic acid

DESORPTION: 1 mL formic acid; stand 60 min

INJECTION VOLUME: 5 µL

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

CARRIER GASES: N_2 or He, 60 mL/min

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

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

RANGE: 0.5 to 10 mg per sample

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION (s_r): 0.007 @ 0.3 to 5 mg per sample [1,2]

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

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

OTHER METHODS: This revises Method S169 [1], and Method 1603 (dated 2/15/84).

REAGENTS:

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

*See Special Precautions.

EQUIPMENT:

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

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

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

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

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

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

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

MEASUREMENT:

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

CALCULATIONS:

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

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

EVALUATION OF METHOD:

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

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., V. 4, S169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[2] Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123, available as "Ten NIOSH Analytical Methods," Order No. PB 275-834 from NTIS, Springfield, VA 22161.
[3] User check, UBTL, NIOSH Sequence #4213-K (unpublished, January 31, 1984).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: G. David Foley, Y. T. Gagnon, and K. J. Williams, NIOSH/DPSE; S169 originally validated under NIOSH Contract CDC-210-76-0123.

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FORMULA: CH_2=CHCN

M.W.: 53.06

ACRYLONITRILE

METHOD: 1604
ISSUED: 2/15/84
REVISION #1: 5/15/89

OSHA: 2 ppm; C 10 ppm (skin)
NIOSH: carcinogen; 1 ppm; C10 ppm (skin) [1]
ACGIH: carcinogen; 2 ppm (skin)
(1 ppm = 2.17 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.8004 g/mL @ 25 °C; BP 77.2 °C; VP 11 kPa (83 mm Hg; 11% v/v) @ 20 °C explosive range 3 to 17% v/v in air

SYNONYMS: 2-propenenitrile; vinyl cyanide; CAS #107-13-1.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

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

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2,3]

BLANKS: 10% of samples

ACCURACY

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

BIAS: not significant [2,3]

OVERALL PRECISION (s_r): 0.06 [2,3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: acrylonitrile

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

INJECTION VOLUME: 2 µL

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

CARRIER GAS: N_2 or He, 25 mL/min

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

CALIBRATION: standard solutions of distilled acrylonitrile in hexane

RANGE: 0.015 to 1 mg per sample [2]

ESTIMATED LOD: 0.001 mg per sample [2]

PRECISION (s_r): 0.06 @ 0.016 mg per sample [2]

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

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

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

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REAGENTS:

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

*See Special Precautions.

EQUIPMENT:

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

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a severe fire and explosion hazard (flash point = -30 °C). Acrylonitrile is explosive, flammable, toxic and a suspect carcinogen [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 0.2 L/min for a total sample size of 3.5 to 20 L.
4. Cap the samplers caps and pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.001 to 1 mg acrylonitrile per sample.
   a. Add known amounts of calibration stock solution, or a serial dilution thereof, to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

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

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg acrylonitrile 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 1604-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
    NOTE 2: Under these conditions t_r for acrylonitrile is ca. 8.5 min.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Method S156 [3] was validated at levels of 0.48, 0.95, and 1.91 mg per sample, using samples of acrylonitrile prepared both by sampling standard atmospheres generated by calibrated syringe drive and by spiking standard solutions in hexane on to the charcoal [6].

After the OSHA standard for acrylonitrile was lowered to 2 ppm, the method was evaluated by NIOSH at levels of 8.6 and 16.6 µg per sample (desorption solvent 2% acetone in CS2), using samples from gas bag atmospheres and by spiking the charcoal with standard solutions of acrylonitrile in hexane [2]. At the higher levels (> 16 µg), the recoveries of acrylonitrile averaged 94% and the s_r were 0.06. At the lower level (8.6 µg), the recovery for the two sets of samples prepared from standard atomospheres averaged 79% with a s_r of 0.14. The sample set prepared by spiking charcoal at the lower level had a recovery of 94%. The parity between the recoveries of samples obtained from test atmospheres and from liquid spikes at the lower level suggested a possible problem with accuracy at this level [2]. Samples were found to be stable for at least seven days at room temperature [2,6]. Several breakthrough studies have been reported. At 80% relative humidity, breakthrough occurred after 184 minutes (36.7 L) sampling 8 mg/m^3 at 0.2 L/min [7]. Breakthrough did not occur after sampling dry air at 92 mg/m^3 at 0.2 L/min for 4 hours [6].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Acrylonitrile, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-116 (1978); revised March, 1978 as part of NIOSH testimony at OSHA hearing.

[2] Gagnon, Y. T. and Posner, J. C. Recovery of Acrylonitrile from Charcoal Tubes at Low Levels, Am. Ind. Hyg. Assoc. J., 40, 923-925 (1979).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Ibid, V. 1, P&CAM 202, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[5] Marano, R. S., Levine, S. P. and T. M. Harvey. Trace Determination of Subnanogram amounts of Acrylonitrile in Complex Matrices by Gas Chromatography with a Nitrogen Selective Detector. Anal. Chem., 50, 1948 (1978).

[6] Documentation of the NIOSH Validation Tests, S156, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[7] OSHA Report, Acrylonitrile Method 37, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, UT (May, 1982).

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

FORMULA: Table 1

M.W.: Table 1

ALDEHYDES, SCREENING

NIOSH METHOD: 2539

ISSUED: 5/15/89

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

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

SYNONYMS: Table 1

SAMPLING

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

FLOW RATE: 0.01 to 0.05 L/min

VOLUME: 5 L

SHIPMENT: @ 25 °C or lower

SAMPLE STABILITY: stable $\geq$ 1 week @ 25 °C

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 6 per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID & GC/MS

ANALYTE: oxazolidine prepared from aldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

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

TEMPERATURE-INJECTION: 250 °C

-DETECTOR: 280 °C

-COLUMN: 1 min @ 70 °C; 6 C/min to 110 °C for 2 min; 30 C/min to 260 °C

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

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

CALIBRATION: standard solutions of aldehydes spiked on sorbent

RANGE AND PRECISION: not determined

ESTIMATED LOD: 2 µg aldehyde per sample

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

INTERFERENCES: High-boiling naphtha mixtures, such as kerosene and mineral spirits may have components with retention times similiar to the oxazolidines and may be interferences in the gas chromatographic analysis.

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

REAGENTS:

1. Toluene, chromatographic quality
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas or equivalent). Extract 4 hrs in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Formaldehyde,* 37% (w/v) solution in water.
5. Formaldehyde stock solution, 1 µg/µL (see APPENDIX A).
6. Acetaldehyde*.
7. Acrolein*.
8. Propionaldehyde*.
9. Butyraldehyde*.
10. Isobutyraldehyde*.
11. Crotonaldehyde*.
12. Valeraldehyde*.
13. Isovaleraldehyde*.
14. Hexanal*.
15. Heptanal*.
16. Furfural*.
17. Sulfuric acid, 0.02 N.
18. Sodium hydroxide, 0.01 N.
19. Sodium sulfite, 1.13 M.
20. Water, deionized, then distilled.
21. Hydrogen, prepurified.
22. Air, filtered, compressed.
23. Helium, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

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

SPECIAL PRECAUTIONS: Aldehydes can irritate the mucous membranes and act on the central nervous system [2]. Certain aldehydes are also suspect carcinogens. Work with these compounds only in a well-ventilated hood.

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

9. Prepare qualitative oxazolidine standard samples.
   a. Prepare aldehyde standard stock solutions.
   NOTE: Aldehydes can oxidize to other compounds on exposure to air. This will introduce bias into the method, so use of freshly-opened bottles of aldehydes is recommended.
      (1) Inject an aliquot of formaldehyde stock solution directly onto the sorbent.
      (2) Take special care with acetaldehyde due to its volatility. To prepare acetaldehyde standard solutions, weigh a 10-mL capped volumetric flask containing about 5 mL toluene. With a cooled pipette, transfer about 1 mL of acetaldehyde into the weighed flask, recap and reweigh. Dilute to the mark.
      (3) For the other aldehydes, add measured aliquots (ca. 12 µL) of each to toluene in 10-mL volumetric flasks and dilute to the mark. From the density of each aldehyde, determine the amount of each aldehyde present in each solution (ca. 1 µg/µL).
   b. Inject 10 µL of the standard aldehyde solutions separately onto blank tubes from the same lot as the field samples.
   c. Analyze (steps 4 through 8 and 11 through 13) along with blanks for qualitative identification of derivative peaks by retention times.
10. Determine limit of detection (LOD) for individual aldehydes by GC/FID with standards covering the range 0.5 to 10 µg per sample. Do this once, when first setting up the method to determine approximate sensitivities for the various aldehyde derivatives. Subsequently, analyze only low-level formaldehyde standard samples with each set of samples as an internal check that the analytical system is working.
   a. Weigh 120-mg portions of unused sorbent from media blanks into vials. Keep at least three 120-mg portions of this sorbent for determination of the background levels of each aldehyde.
   b. Add 0.5- to 10-µL aliquots of the individual aldehyde standard solutions to obtain standard samples in the range 0.5 to 10 µg per 120 mg portion of sorbent. Cap vials and allow to stand overnight at room temperature.
   c. Desorb the standard samples of aldehydes (steps 7 and 8) and analyze (steps 11 through 13) along with blanks.
   d. Determine lowest spike to be detected (peak area greater than three times the background or lowest standard observable) to estimate LOD for each aldehyde.
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.

MEASUREMENT:

11. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2539-1. Inject 1-µL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene.
12. Compare retention times of unknown peaks in samples to the retention times for the oxazolindines as determined by the qualitative standard samples. (See Appendix B for sample chromatogram).

a. Analyze samples with GC retention times matching any oxazolidine by GC/MS using the same GC columns and conditions if possible. Alternate columns such as a DB-WAX (formaldehyde, acetaldehyde, propanal) or DB-1 (remaining aldehydes) may also be used for GC/MS confirmation depending on which aldehyde is suspected.

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

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

NOTE 2: The absence of some C_3-C_5 aldehydes, such as propionaldehyde, isobutyraldehyde and crotonaldehyde, does not necessarily mean that these compounds are not present in the air sampled. These compounds are not efficiently trapped by the sorbent, and will readily breakthrough the sampler sorbent beds.

NOTE 3: Higher molecular weight aldehydes, such as isovaleraldehyde, hexanal and heptanal, probably will be more efficiently collected on the sorbent due to their lower vapor pressure. Thus, absence of these compounds in sample results may be indicative of the absence of these compounds in the environment sampled.

13. Report the presence of a particular aldehyde if:

a. There is a detectable peak by GC-FID at the correct retention time for that aldehyde derivative.

b. The correct mass spectrum for the derivative is obtained by GC/MS at the proper retention time.

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[1] Occupational Safety and Health Administration , "OSHA Analytical Method Manual," American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1985).

[2] Kennedy, E. R., P. F. O'Connor, Y. T. Gagnon. Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography. Anal. Chem., 56, 2120-2123 (1984).

[3] Kennedy, E. R., Y. T. Gagnon, J. R. Okenfuss, A. W. Teass. The Determination in Air of Selected Low-molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography. Appl. Ind. Hyg., 3, 274-279 (1988).

METHOD WRITTEN BY: Ardith A. Grote and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

Table 1. General Information

Compound (Synonyms)	Formula	MW	d(g/mL) @ 20 °C	BP(°C)	Exposure Limits (ppm) OSHA	NIOSH	ACGIH	VP(mm Hg) (@ 20 °C)
Formaldehyde (formic aldehyde; formalin; CAS # 50-00-0)	CH_2O	30.03	—	-19.5	1 2 STEL	Carc.[a]; 0.016 0.1 C	1	20 (-88 °C)
Acetaldehyde (acetic aldehyde; ethyl aldehyde; CAS # 75-07-0)	C_2H_4O	44.05	0.788 (@ 16 °C)	21	100 150 STEL	Carc.[a]	100	740
Propionaldehyde (propanal; CAS # 128-38-6)	C_3H_6O	58.08	0.807	49	--	--	--	300
Acrolein (2-propenal; allyl aldehyde; CAS # 107-02-8)	C_3H_4O	56.06	0.839	52.5	0.1 0.3 STEL	0.1 0.3 STEL	0.1	214
Butyraldehyde (butanal; CAS # 123-72-8)	C_4H_8O	72.10	0.802	75	--	--	--	92
Isobutyraldehyde (2-methylpropanal dimethylacetaldehyde; CAS # 78-84-2)	C_4H_8O	72.10	0.794	64	--	--	--	170
Crotonaldehyde (2-butenal; ß-methyl acrolein; CAS # 4170-30-3)	C_4H_6O	70.09	0 853	104	2	2	2	30
Valeraldehyde (pentanal; CAS # 110-62-3)	$C_5H_{10}O$	86.13	0.810	102	50	50	50	50
Isovaleraldehyde (3-methylbutanal; isopentanal; CAS # 590-86-3)	$C_5H_{10}O$	86.13	0.785	92	--	--	--	50
Hexanal (caproaldehyde; CAS # 66-25-1)	$C_6H_{12}O$	100.16	0.834	131	--	--	--	10
Heptanal (enanthal; CAS # 111-71-7)	$C_7H_{14}O$	114.18	0.809 (@ 30 °C)	153	--	--	--	3
Furfural (2-furancarboxaldehyde; CAS # 98-01-1)	$C_5H_4O_2$	96.08	1.16 (@ 25 °C)	162	2 (skin)	--	2	65

[a] - Carcinogen

Table 2. Mass spectral data for aldehyde derivatives of 2-(hydroxymethyl)piperidine (HMP)

	HMP DERIVATIVE		
Aldehyde	Formula	Base Peak m/z	Other Characteristic Ions m/z
Formaldehyde	$C_7H_{13}NO$	97	126, 127*
Acetaldehyde	$C_8H_{15}NO$	126	140, 141*
Propionaldehyde	$C_9H_{17}NO$	126	154, 155*
Acrolein	$C_9H_{15}NO$	126	152, 153*
Butyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Isobutyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Crotonaldehyde	$C_{10}H_{17}NO$	126	166, 167*
Valeraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Isovaleraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Hexanal	$C_{12}H_{23}NO$	126	196, 197*
Heptanal	$C_{13}H_{25}NO$	126	210, 211*
Furfural	$C_{11}H_{15}NO_2$	192	95, 163, 193*

* indicates molecular ion.

APPENDIX A:

SORBENT PREPARATION (optional if commercially prepared tubes are used):

Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for ca. 1 hr. To determine the amount of background for each batch, extract several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for any aldehydes other than formaldehyde and possibly acetaldehyde.

SYNTHESIS OF ALDEHYDE OXAZOLIDINES:

Place a solution of purified 2-hydroxymethylpiperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 20mL portions of toluene to rinse residual 1-(hydroxymethyl)piperidine from the container used for weighing. Add anhydrous magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 10 mmole of aldehyde in 10 mL of toluene to the 2-hydroxymethylpiperidine solution dropwise with stirring over 1 hr. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene and excess aldehyde from the solution at reduced pressure by rotary evaporation.

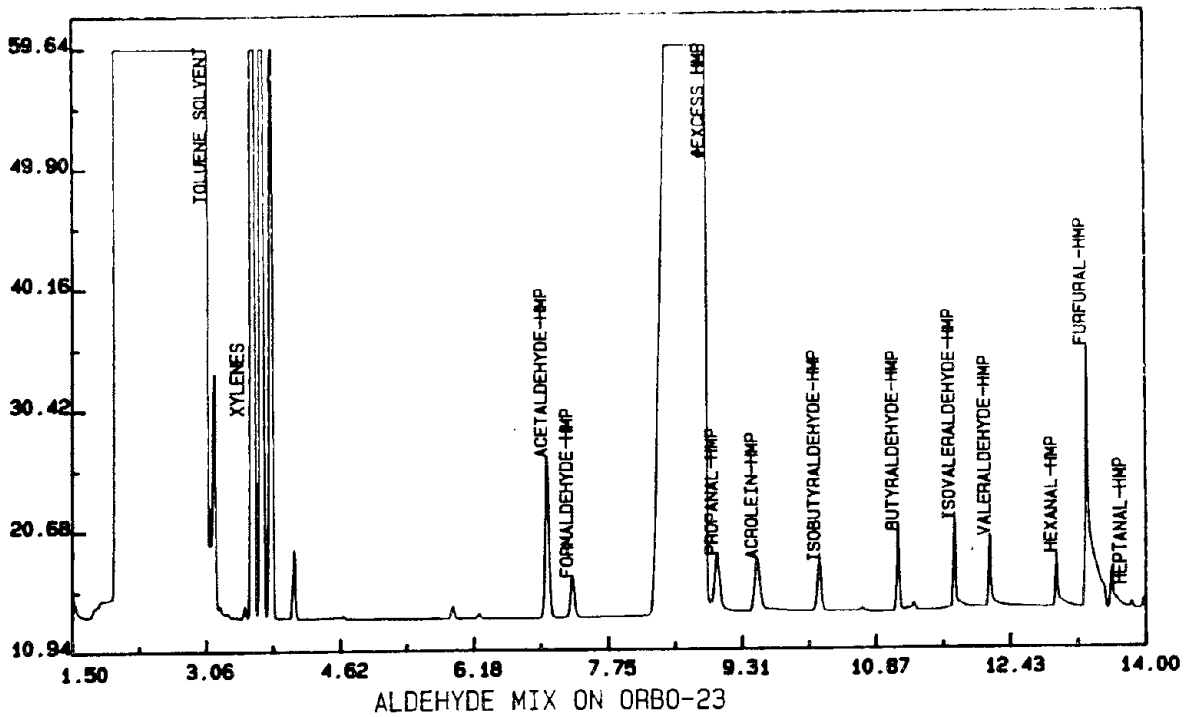
PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL):

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50 mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL stock formaldehyde solution. The pH should be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0 \times (N_a \bullet V_a - N_b \bullet V_b)}{V_s}$$

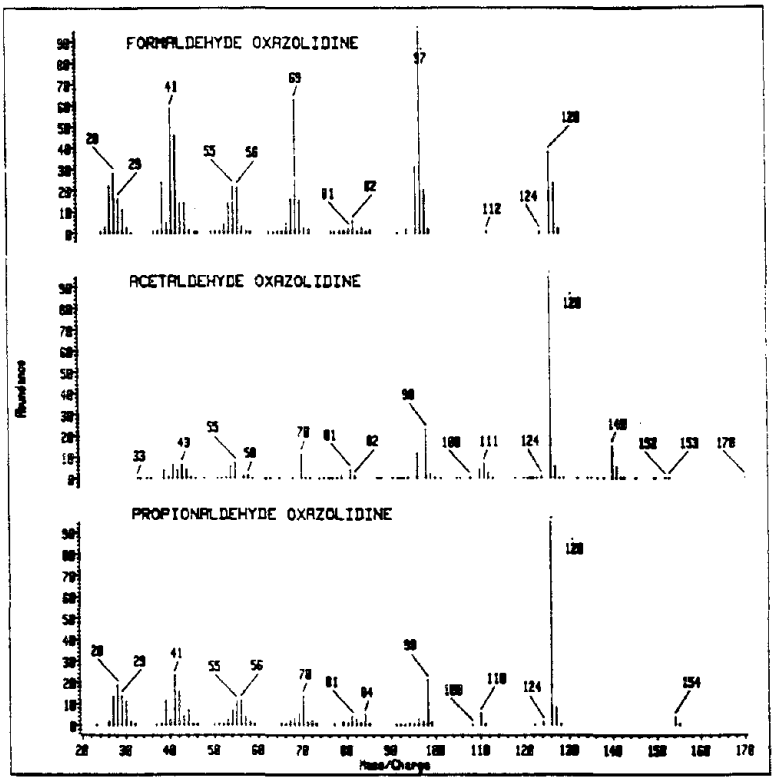
where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_s = volume of formaldehyde stock solution (10.0 mL).

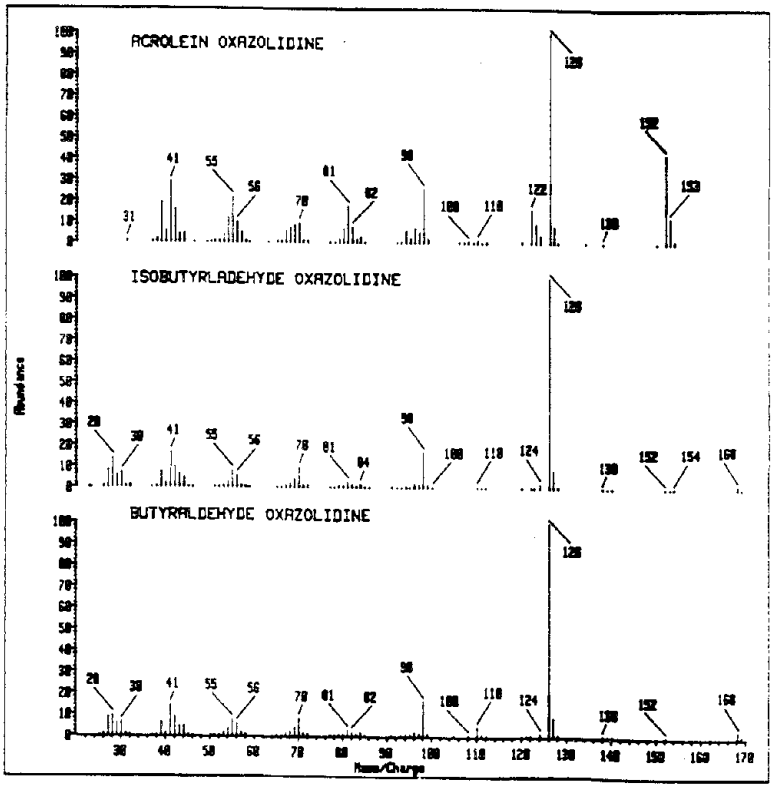
APPENDIX B: Sample chromatogram of aldehyde oxazolidines on DB-1301 column using conditions listed on page 2539-1.



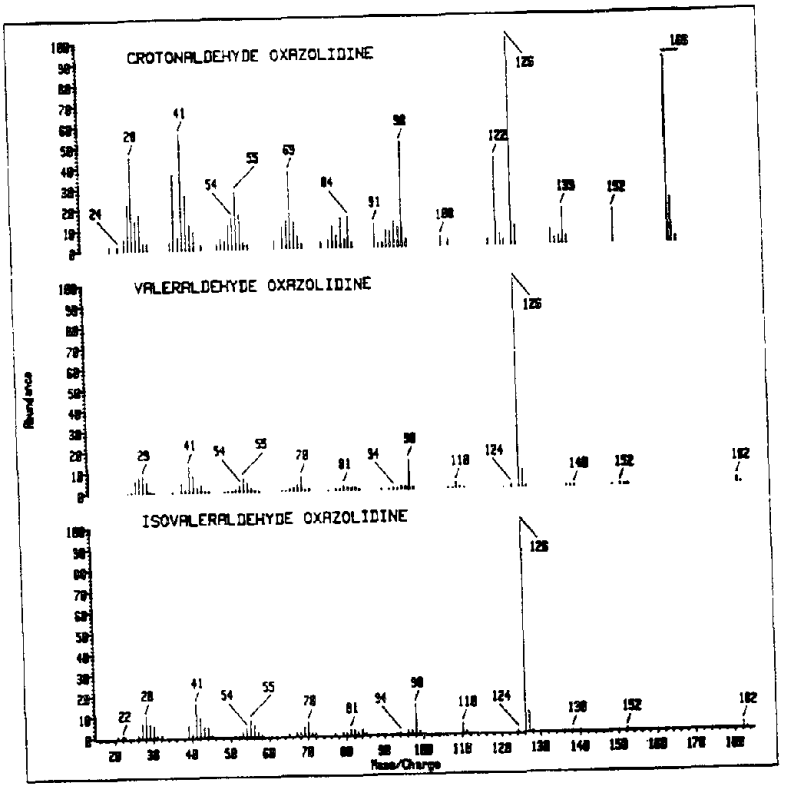
ALDEHYDE MIX ON ORBO-23
15M DB-1301 COLUMN

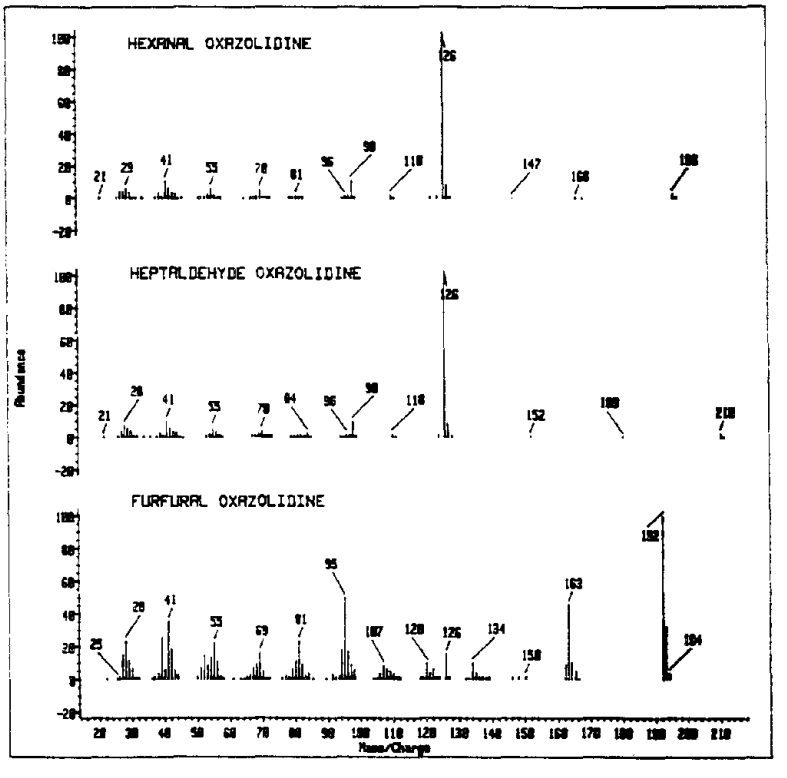
APPENDIX C: Reference mass spectra of oxazolidines of aldehydes individually spiked onto ORBO-23 tubes. GC/MS conditions: HP 5890 gas chromatograph interfaced (direct) to HP 5970 mass-selective detector (70eV); 30-m DB-1 column, 0.25-mm I.D., 1.0-µm film; 70 °C for 1 min, 15 °C/min to 300 °C; interface temperature, 280 °C; injector, 250 °C, 1 µL splitless injection; scan 20-400 amu.





APPENDIX C: (cont'd.)





FORMULA: (1) Diethylamine; $(C_2H_5)_2NH$
(2) Dimethylamine; $(CH_3)_2NH$

M.W.: (1) 73.14; (2) 45.08

AMINES, ALIPHATIC
METHOD: 2010
ISSUED: 5/15/89

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: (1) DEN; diethamine; N-ethylethanamine; CAS #109-89-1
(2) N-methylmethanamine; CAS #124-40-3

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)	TECHNIQUE: GAS CHROMATOGRAPHY, FID
FLOW RATE: 0.01 to 1.0 L/min	ANALYTE: amines listed above
VOL-MIN: 3 L @ OSHA standards (Table 1) -MAX: 30 L	DESORPTION: 1 mL dilute H_2SO_4 in 10% (v/v) aqueous methanol, 3 h ultrasonic
SHIPMENT: routine	INJECTION VOLUME: 1 µL
SAMPLE STABILITY: not determined	COLUMN: 1.8 m x 4-mm ID glass, 4% Carbowax 20M + 0.8% KOH on Carbosieve B (60/80 mesh)
FIELD BLANKS: 10% of samples	CARRIER GAS: nitrogen, 30 mL/min
	CALIBRATION: standard solutions of analyte in dilute sulfuric acid
ACCURACY	RANGE: (1) 0.5 to 11 mg per sample [1] (2) 0.15 to 2.6 mg per sample [1]
RANGE STUDIED: see EVALUATION OF METHOD	ESTIMATED LOD: 0.02 mg per sample
BIAS: not significant	PRECISION (s_r): see EVALUATION OF METHOD
OVERALL PRECISION (s_r): see EVALUATION OF METHOD	

APPLICABILITY: The working ranges for 20-L air samples are 8 to 183 ppm (25 to 550 mg/m^3) for diethylamine and 4 to 71 ppm (7.5 to 130 mg/m^3) for dimethylamine. A nitrogen-specific detector instead of an FID will greatly increase sensitivity. This alternate detector has been used for amines on a 30-m x 0.25-mm x 0.25-µm film DB-5 fused-silica capillary column, with column temperature 60 °C for 1 min, programmed to 300 °C at 10°/min; detector, 300 °C and injector, 250 °C.

INTERFERENCES: This method has been evaluated only in dry air [1]. Silica gel has greatly reduced capacity at high humidity. The methanol peak could interfere in low-level analyses.

OTHER METHODS: This revises and combines Methods S139 and S142 [2]. The methods for other aliphatic amines are similar [3,4,5,6,].

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REAGENTS:

1. Sulfuric acid, 0.1 M, in 10% (v/v) aqueous methanol (90% H_2O + 10% methanol.*
2. Potassium hydroxide (KOH) solution, 0.3 M.*
3. Amines, highest purity available.*
   NOTE: Dimethylamine is commercially available as a 40% aqueous solution (Aldrich co. or equivalent).
4. Calibration stock solution.* Dilute 1 mL of amine to 10 mL with deionized water. Check concentration by titrating with standard sulfuric acid.
5. Hydrogen, prepurified.
6. Nitrogen, purified.
7. Air, compressed and filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube flame-sealed ends, with plastic caps, 7 cm x 6-mm OD x 4-mm ID, containing two sections of 20/40 mesh silica gel (front = 150 mg; back = 75 mg) held in place by urethane foam plugs. Silanized glass wool plug precedes front.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 2010-1). The GC inlet shall have a removable glass liner.
4. Vials, glass, 2-mL, with PTFE-lined caps.
5. Ultrasonic bath.
6. Syringes, 20-µL.
7. Pipets, 0.5-, 1-, 2-, and 10-mL.
8. Volumetric flasks, 10-mL.
9. File.
10. Tweezers.

SPECIAL PRECAUTIONS: The amines are highly flammable and have strong ammoniacal odors. They can cause severe eye damage and can easily be absorbed through the skin [7]. Sulfuric acid is highly corrosive, and potassium hydroxide is caustic. All work with these compounds should be performed in a hood. Use proper protective clothing including gloves, safety glasses, and laboratory coat.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the samples immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1.0 L/min for a total sample size of 3 to 30 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 0.1 M H_2SO_4 in aqueous methanol. Tightly cap the vial.
7. Agitate the vials in ultrasonic water bath for 3 h.
   NOTE: The water in the ultrasonic bath can get hot (ca. 50-60 °C) during the desorption period. Therefore, all vials must be tightly capped to minimize evaporation losses.
8. Neutralize the sample solution as follows: let silica gel particles settle for a few minutes. Transfer a 500-µL aliquot of the supernatant liquid to a clean vial. Add 500 µL 0.3 M KOH. (The pH of the solution should be greater than 10). Analyze the solutions immediately (steps 12 through 14).
   NOTE: It is important that no silica gel is present when adding KOH; otherwise loss of analyte will occur [1].

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards covering the range of interest.
   a. Add aliquots of the calibration stock solutions to 10-mL volumetric flasks and dilute to the mark with 0.1 M sulfuric acid in aqueous methanol.
   b. Neutralize the standards as in step 8.
   c. Analyze with samples and blanks (steps 12 through 14).
   d. Prepare a calibration graph (peak area or peak height vs. mg of amine per sample).
10. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus media blanks.
   a. Measure the amount of silica gel used in the front sorbent section into a vial.
   b. Inject a known amount (1 to 20 µL) of calibration stock solution or a dilution thereof directly onto the silica gel.
   c. Cap vial. Allow to stand overnight.
   d. Desorb and neutralize as in steps 6 through 8.
   e. Analyze together with working standards and blanks (steps 12 through 14).
   f. Prepare a graph of DE vs. mg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2010-1. Use the following conditions as a guide.

Compound	Temperature (°C)		
	Injection	Column	Detector
Diethylamine	160	70	200
Dimethylamine	155	60	200

NOTE: Use a removable glass liner at the inlet to the GC column. Remove the glass liner from the gas chromatograph and clean it with water and acetone rinses at the end of each day. In order to prevent salt buildup the glass GC liner was soaked in a saturated KOH solution and packed with KOH-coated glass wool. [8].

13. Inject sample aliquot manually using solvent flush technique or with autosampler.
14. Measure peak area or peak height.

CALCULATIONS:

15. Read the mass, mg (corrected for DE), of analytes found in sample front (W_f) and back (W_b) sorbent sections and in the media blank front (B_f) and blank back (B_b) sorbent sections corresponding to peak area from the calibration graph.
   NOTE: If $W_b > W_{f/10}$, report breakthrough and possible sample loss.
16. Calculate the concentration of analyte, C (mg/m^3), in the air volume sampled, V (L):

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

EVALUATION OF METHOD:
Precisions, biases, and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard [1,2,3]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere.

	SAMPLING					MEASUREMENT		
Substance	Breakthrough in Dry Air, Vol. (L)	Conc. (mg/m^3)	Range, mg/m^3 (volume)	Overall Precision (s_r)	Average Recovery[b]	Range (mg per Sample)	Precision (s_r)	Avg. DE
Diethylamine	>46[a]	160	36-165	0.07	0.95	1.8-7.1	0.02	0.82
Dimethylamine	>45.6[a]	42.5	7.02-29.5	0.062	0.989	0.4-1.7	0.03	0.92

[a]Breakthrough experiments performed at flow rate of 0.2 L/min.
[b]Recovery as measured by test method ÷ reference method.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S139 and S142, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
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[5] Campbell, Evan E., G. O. Wood, and R. G. Anderson. "Development of Air sampling Techniques," Los Alamos Scientific Laboratory, Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), and LA-6057-PR (September 1975).
[6] Wood, G. O. and R. G. Anderson. "Development of Air Monitoring Techniques Using Solid Sorbents," Los Alamos Scientific Laboratory, Progress Reports LA-6216-PR (February 1976) and LA-6513-PR (September 1976).
[7] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981).
[8] Andre, C. E. and A. R. Mosier. "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," Anal. Chem., 45:1971 (1973).

METHOD WRITTEN BY: Paula Fey O'Connor, NIOSH/DPSE.

Table 1 Exposure Limits and Properties

Compound	Exposure limits, ppm OSHA	NIOSH	ACGIH	mg/m^3/ppm @ NTP	Properties
Diethylamine	10; STEL 25	10; STEL 25	10; STEL 25	2.99	liquid; d 0.708 g/mL @ 20 °C; vapor density (air = 1) 2.5; VP 25.9 kPa (195 mm Hg) @ 20 °C
Dimethylamine	10	10	--	1.84	Gas; vapor density (air = 1) 1.6; VP 173.9 kPa (1307.2 mm Hg) @ 20 °C; explosive limits in air 2.8 to 14% (v/v)

FORMULA: (1) $HOCH_2CH_2NH_2$
(2) $(HOCH_2CH_2)_2NH$
(3) $(HOCH_2CH_2)_3N$

AMINOETHANOL COMPOUNDS II
METHOD: 3509
ISSUED: 5/15/89

M.W.: (1) 61.10; (2) 105.14; (3) 149.19

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS:
(1) 2-aminoethanol; monoethanolamine; MEA; CAS #141-43-5;
(2) 2,2'-iminodiethanol; diethanolamine; DEA; CAS #111-42-2;
(3) 2,2',2"- nitrilotriethanol; triethanolamine; TEA; CAS #102-71-6.

SAMPLING

SAMPLER: Impinger
(15 mL 2mM hexanesulfonic acid)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 5 L
-MAX: 300 L

SHIPMENT: routine

SAMPLE STABILITY: stable at least 3 weeks @ 20 °C [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1] and Table 2

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, ion pairing [2,3]

ANALYTE: MEA, DEA, TEA

INJECTION LOOP VOLUME: 50 µL

ELUENT: 2mM hexanesulfonic acid (HSA), 1 mL/min (2mM HSA/0.5% v/v acetonitrile may also be used to reduce run time)

COLUMNS: Ion-pairing guard and cation separator, Dionex MPIC-NG1, MPIC-NS1 and cation suppressor

CONDUCTIVITY SETTING: 3 µS full scale

RANGE: see EVALUATION OF METHOD [1] and Table 2

ESTIMATED LOD: 7 to 20 µg per sample (Table 2)

PRECISION (s_r): see EVALUATION OF METHOD [1] and Table 2

APPLICABILITY: The working ranges for MEA, DEA, and TEA are 0.08 to 12 ppm (0.2 to 30 mg/m^3), 0.09 to 7 ppm (0.4 to 30 mg/m^3) and 0.1 to 5 ppm (0.6 to 30 mg/m^3), respectively, for a 100-L sample. The method is better suited to area sampling than personal sampling because it uses an impinger for sample collection.

INTERFERENCES: Larger amines such as cocmorpholine, triethylenediamine, 4-ethylmorpholine, 2-oxybis(N,N-dimethyl)ethylamine, n-cetyl-N,N-dimethylamine do not elute under these analytical conditions and do not interfere. Other low molecular weight amines may interfere. Sodium and ammonium ions can interfere with MEA.

OTHER METHODS: This is adapted from the method of Bouyoucos and Melcher [2,3]. There are no other NIOSH methods for DEA or TEA. MEA can be determined by method 2007, using silica gel collection and gas chromatographic analysis.

REAGENTS:

1. Hexanesulfonic acid (HSA), 2mM (diluted from 0.1M solution obtained from Dionex Corp.).
2. Acetonitrile, reagent grade.
3. Ethanolamine*, high purity.
4. Diethanolamine*, high purity.
5. Triethanolamine*, high purity.
6. Water, distilled.
7. Regenerant for IC suppressor. For fiber suppressor use 40mM tetramethylammonium hydroxide (TMAOH) at 2 mL/min. For cation micromembrane suppressor use 2mM TMAOH at 4 mL/min. For packed-bed column suppressor, regenerate with 0.5N NaOH, rinse with distilled water, then convert to borate form by regenerating with 0.5N H_3BO_3 for 10 min., finally rinsing with distilled water.
8. Calibration stock solution, 1 µg/µL. Weigh 0.10 g of each amine into 100-mL volumetric flask and dilute to mark with 2 mM hexanesulfonic acid. Store in a polyethylene bottle.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: midget impinger.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing and glass wool trap.
3. Ion chromatograph, with ion-pairing guard and separator columns, cation suppressor (can be packed-bed column in borate form, fiber supressor or micromembrane suppressor), integrator and strip chart recorder (page 3509-1).
4. Marker, China.
5. Vials, scintillation, plastic, 20 mL, for shipping and storage of samples.
6. Syringes, 10-mL, polypropylene, with luer tip.
7. Filters, luer tip, with membrane filter, 13- or 25-mm, 0.45-µm pore size.
8. Micropipets (or microliter syringes), 1- to 500-µL.
9. Flasks, volumetric, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipet, 15-mL.

SPECIAL PRECAUTIONS: Ethanolamines can cause skin and eye irritation [4]. Usual laboratory safety procedures should be exercised.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the impinger with 15 mL of 2mM HSA. Mark the initial liquid level.
3. Attach impinger to sampling pump with flexible tubing. Insert a glass wool trap between the impinger and sampling pump to prevent splashover.
4. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 5 to 300 L.
5. Fill the sample solution in the impinger to the 15-mL mark with distilled water.
6. Transfer each impinger solution to a vial for shipment. Pack securely to avoid spillage during transit.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards over the range of interest.
   a. Add known aliquots of calibration stock solution to 50-mL volumetric flasks and dilute to the mark with eluent.
   b. Store working standards in tightly-capped polyethylene bottles (glass may introduce sodium ions, a chromatographic interference). Prepare fresh weekly.
   c. Analyze working standards together with samples and blanks (steps 8 through 11).
   d. Prepare a calibration graph for each analyte (peak height vs. mg analyte).

MEASUREMENT:

8. Set the ion chromatograph to manufacturer's recommendations and to conditions given on page 3509-1. When using fiber or micromembrane suppression, if the background level is high, make several injections of acetonitrile through the sample loop to lower the background level.
   NOTE: Filter all samples, eluents, and water flowing through the ion chromatograph to avoid plugging system valves or columns.
9. Transfer a portion of sample solution to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.
10. Inject 50-µL sample aliquot. For manual operation, inject 2 to 3 mL of sample from syringe (through inline filter) to ensure complete rinse of the sample loop.
11. Measure peak height. If sample peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, mg, of analyte in the impinger (W) and in the average media blank (B) from the calibration graph.
13. Calculate the concentration, C, of analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated for DEA with generated air samples and for all three specified amines with liquid spiked samples [5]. Samples for DEA were generated from methanol solution delivered by a syringe pump to an ultrasonic nebulizer producing a mist which was mixed with dry, heated air in the initial mixing chamber to evaporate the methanol. The flow passed into a sampling manifold where it was mixed with humidified air to maintain a relative humidity of 73-78%. The system was monitored by measuring the level of methanol in the sampling manifold with a Miran 1A infrared analyzer. The recovery of DEA calculated from the methanol concentration varied from 70-95% in different generation runs. After studies were complete, the initial mixing chamber was rinsed with 2 mM HSA and was found to contain 52 mg DEA, and a rinse of the sampling chamber contained 23 mg DEA, indicating that DEA was lost in the generator during sample generation, and explaining the variation in recovery vs. that calculated from the methanol concentration. In the first run, four samples were generated to test the generation system. These samples were expected to contain 1305 µg DEA based on monitoring of the methanol concentration. They were found to have 1237 ± 56 µg DEA, giving a recovery of 94.8%. Next, twelve samples at each of two levels were generated for storage studies. All samples were collected at 0.75 L/min and stored at room temperature (20 °C). Finally, six samples including backup impingers were generated for breakthrough studies. The results of the storage and breakthrough studies are given below:

Storage studies:

	2-Day Storage			21-Day Storage			Recovery
	N	Found, µg	RSD	N	Found, µg	RSD	after 21 days
Low level	5	226	4.9	5	215	13.4	95.1%
High level	6	885	3.3	4	865	3.0	97.7%

Breakthrough studies (stored 39 days at 20 °C):

	N	Found, µg	RSD	Breakthrough (average)
Front section	6	4433	7.2	
Back section	6	137	N/A	2.68% (range 1.0-5.4%)
Total	6	4570	8.2	

The method was further evaluated by spiking 2 mM hexanesulfonic acid impinger solutions with all three ethanolamines, at 2, 10, and 20 times the estimated LOQ, using six spikes per analyte at each level, and analyzing them after storage at room temperature (20 °C) either for 2 days or for 21 days. Recovery of all analytes and at all levels tested (42 to 409 µg MEA, 79 to 712 µg DEA, and 117 to 1161 µg TEA) was between 94 and 106% after 3 weeks storage.

REFERENCES:

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METHOD WRITTEN BY: Michele Bolyard and George Williamson, NIOSH/DPSE.

Table 1. Exposure limits and properties.

Compounds	Exposure limits, ppm OSHA	NIOSH	ACGIH	Properties
Monoethanolamine (MEA)	3; STEL 6	3; STEL 6	3; STEL 6	liquid; d 1.02 g/mL @ 20 °C; BP 170 5 °C; VP <0.13 kPa (<1 mm Hg); flash point 152 °C
Diethanolamine (DEA)	3	3	3	crystals or liquid; d 1.088 g/mL @ 30 °C; MP 28 °C; BP 269 °C; VP <0.001 kPa (0.01 mm Hg); flash point 152 °C
Triethanolamine (TEA)	No PEL	No REL	No TLV	liquid; d 1.124 g/mL @ 20 °C; MP 21.2; BP 335 °C (decomp.); VP 0.001 kPa (<0.01 mm Hg); flash point 191 °C

Table 2. Range, LOD, and LOQ.

	Range Studied (mg/sample)	mg/m^3=1ppm @ NTP	LOD (mg/sample)	LOQ (mg/sample)	Measurement precision (s_r)
Monoethanolamine (MEA)	0.04 to 0.4	2.50	0.007	0.02	0.028
Diethanolamine (DEA)	0.07 to 4.5	4.30	0.013	0.04	0.064
Triethanolamine (TEA)	0.12 to 1.16	6.10	0.02	0.06	0.079

FORMULA: various

M.W.: various

ASBESTOS (bulk)

METHOD: 9002

ISSUED: 5/15/89

EPA Standard (Bulk): 1%

PROPERTIES: solid, fibrous, crystalline, anisotropic

SYNONYMS: actinolite [CAS #13768-00-8], or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos.

SAMPLING

BULK SAMPLE: 1 to 10 grams

SHIPMENT: seal securely to prevent escape of asbestos

SAMPLE STABILITY: stable

BLANKS: none required

ACCURACY

RANGE STUDIED: <1% to 100% asbestos

BIAS: not determined

PRECISION: not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, STEREO AND POLARIZED LIGHT, WITH DISPERSION STAINING

ANALYTE: actinolite asbestos, amosite, anthophyllite asbestos, chrysotile, crocidolite, tremolite asbestos

EQUIPMENT: microscope, polarized light: 100-400X dispersion staining objective, stereo microscope: 10-45X

RANGE: 1% to 100% asbestos

ESTIMATED LOD: <1% asbestos [1]

PRECISION: not determined

APPLICABILITY: This method is useful for the qualitative identification of asbestos and the semi-quantitative determination of asbestos content of bulk samples, expressed as a percent of projected area. The method measures percent asbestos as perceived by the analyst in comparison to standard area projections, photos, and drawings, or trained experience. The method is not applicable to samples containing large amounts of fine fibers below the resolution of the light microscope.

INTERFERENCES: Other fibers with optical properties similar to the asbestos minerals may give positive interferences. Optical properties of asbestos may be obscured by coating on the fibers. Fibers finer than the resolving power of the microscope (ca. 0.3 µm) will not be detected. Heat and acid treatment may alter the index of refraction of asbestos and change its color.

OTHER METHODS: This method (originally designated as method 7403) is designed for use with NIOSH Methods 7400 (phase contrast microscopy) and 7402 (electron microscopy/EDS). The method is similar to the EPA bulk asbestos method [1].

REAGENTS:

1. Refractive index (RI) liquids for Dispersion Staining: high-dispersion (HD) series, 1.550, 1.605, 1.620.
2. Refractive index liquids: 1.670, 1.680, and 1.700.
3. Asbestos reference samples such as SRM #1866, available from the National Institute of Standards and Technology.*
4. Distilled Water (optional).
5. Concentrated HCl: ACS reagent grade (optional).

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sample containers: screw-top plastic vials of 10- to 50-mL capacity.
2. Microscope, polarized light, with polarizer, analyzer, port for retardation plate, 360° graduated rotating stage, substage condenser with iris, lamp, lamp iris, and:
   a. Objective lenses: 10X, 20x, and 40X or near equivalent.
   b. Ocular lense: 10X minimum.
   c. Eyepiece reticle: crosshair.
   d. Dispersion staining objective lens or equivalent.
   e. Compensator plate: ca. 550 nm ± 20 nm, retardation: "first order red" compensator.
3. Microscope slides: 75 mm x 25 mm.
4. Cover slips: 22 mm x 22 mm.
5. Ventilated hood or negative pressure glove box.
6. Mortar and pestle: agate or porcelain.
7. Stereomicroscope, ca. 10 to 45X.
8. Light source: incandescent or fluorescent.
9. Tweezers, dissecting needles, spatulas, probes, and scalpels.
10. Glassine paper or clean glass plate.
11. Low-speed hand drill with coarse burr bit (optional).

SPECIAL PRECAUTIONS: Asbestos, a human carcinogen, should be handled only in an exhaust hood (equipped with a HEPA filter). [2] Precautions should be taken when collecting unknown samples, which may be asbestos, to preclude exposure to the person collecting the sample and minimize the disruption to the parent material [3]. Disposal of asbestos-containing materials should follow EPA Guidelines [4].

SAMPLING:

1. Place 1 to 10 g of the material to be analyzed in a sample container.
   NOTE: For large samples (i.e., whole ceiling tiles) that are fairly homogenous, a representative small portion should be submitted for analysis. Sample size should be adjusted to ensure that it is representative of the parent material.
2. Make sure that sample containers are taped so they will not open in transit.
3. Ship the samples in a rigid container with sufficient packing material to prevent damage or sample loss.

SAMPLE PREPARATION:

4. Visually examine samples in the container and with a low-magnification stereomicroscope in a hood. (If necessary, a sample may be carefully removed from the container and placed on glassine transfer paper or clean glass plate for examination). Break off a portion of the sample and examine the edges for emergent fibers. Note the homogeneity of the sample. Some hard tiles can be broken, and the edges examined for emergent fibers. If fibers are found, make an estimate of the amount and type of fibers present, confirm fiber type (steps 6 through 13) and quantify (steps 14 through 16).

5. In a hood, open sample container and with tweezers remove small, representative portions of the sample.
   a. If there are obvious separable layers, sample and analyze each layer separately.
   b. If the sample appears to be slightly inhomogeneous, mix it in the sample container with tweezers or a spatula before taking the portion for analysis. Alternatively, take small representative portions of each type of material and place on a glass slide.
   c. On hard tiles that may have thin, inseparable layers, use a scalpel to cut through all the layers for a representative sample. Then cut it into smaller pieces after placing RI liquid on it before trying to reduce the thickness. Alternatively, use a low-speed hand drill equipped with a burr bit to remove material from hard tiles. Avoid excessive heating of the sample which may alter the optical properties of the material.
   NOTE: This type of sample ofter requires ashing or other specialized preparation.
   d. If the sample has large, hard particles, grind it in a mortar. Do not grind so fine that fiber characteristics are destroyed.
   e. If necessary, treat a portion of the sample in a hood with an appropriate solvent to remove binders, tars, and other interfering materials which may be present in the sample. Make corrections for the non-asbestos material removed by this process.
   NOTE: Other methods of sample preparation such as acid and sodium metaphosphate treatment and ashing are not normally necessary. However, if needed, use as described in Reference [1].
6. After placing a few drops of RI liquid on the slide, put a small portion of sample in the liquid. Tease apart with a needle or smash small clumps with the flat end of a spatula or probe, producing a uniform thickness of particles so that better estimates of projected area percentages can be made. Mix the fibers and particles on the slide so that they are as homogeneous as possible.
   NOTE: An even dispersion of sample should cover the entire area under the cover slip. Some practice will be necessary to judge the right amount of material to place on the slide. Too little sample may not give sufficient information and too much sample cannot be easily analyzed.

CALIBRATION AND QUALITY CONTROL:

7. Check for contamination of microscope slides, cover slips and refractive index liquids once per day of operation. Record results in a separate logbook.
8. Verify the refractive indices of the refractive index liquids used once per week of operation. Record these checks in a separate logbook.
9. Follow the manufacturer's instructions for illumination, condenser alignment and other microscope adjustments. Perform these adjustments prior to each sample set.
10. Determine precent of each identified asbestos species by comparision to standard projections (Figure 1) [1]. If no fibers are detected in a homogeneous sample, examine at least two additional preparations before concluding that no asbestos is present.
11. If it appears that the preparation technique might not be able to produce a homogeneous or representative sample on the slide, prepare a duplicate slide and average the results. Occasionally, when the duplicate results vary greatly, it will be necessary to prepare additional replicate slides and average all the replicate results. Prepare duplicate slides of at least 10% of the samples analyzed. Average the results for reporting.
12. Analyze about 5% blind samples of known asbestos content.
13. Laboratories performing this analytical method should participate in the National Voluntary Labortory Accreditation Program [5] or a similar interlaboratory quality control program. Each analyst should have completed formal training in polarized light microscopy and its application to crystalline materials. In lieu of formal training, laboratory training in asbestos bulk analysis under the direction of a trained asbestos bulk analyst may be substituted. Due to the subjective nature of the method, frequent practice is essential in order to remain proficient in estimating projected area percentages.

QUALITATIVE ASSESSMENT:

14. Scan the slide to identify any asbestos minerals using the optical properties of morphology, refractive indices, color, pleochroism, birefringence, extinction characteristics, sign of elongation, and dispersion staining characteristics.
    NOTE: Identification of asbestos using polarized light microscopy is unlike most other analytical methods. The quality of the results is dependent on the skill and judgment of the analyst. This method does not lend itself easily to a step-wise approach. Various procedures devised by different analysts may yield equivalent results. The following step-wise procedure repeatedly utilizes the sample preparation procedure previously outlined.

    a. Prepare a slide using 1.550 HD RI liquid. Adjust the polarizing filter such that the polars are partially crossed, with ca. 15° offset. Scan the preparation, examining the morphology for the presence of fibers. If no fibers are found, scan the additional preparations. If no fibers are found in any of the preparations, report that the sample does not contain asbestos, and stop the analysis at this point.

    b. If fibers are found, adjust the polarizing filter such that the polars are fully crossed. If all of the fibers are isotropic (disappear at all angles of rotation) then those fibers are not asbestos. Fibrous glass and mineral wool, which are common components of suspect samples, are isotropic. If only isotropic fibers are found in the additional preparations, report no asbestos fibers detected, and stop the analysis.

    c. If anisotropic fibers are found, rotate the stage to determine the angle of extinction. Except for tremolite-actinolite asbestos which has oblique extinction at 10-20°, the other forms of asbestos exhibit parallel extinction. Tremolite may show both parallel and oblique extinction.

    d. Insert the first-order red compensator plate in the microscope and determine the sign of elongation. All forms of asbestos have a postive sign of elongation except for crocidolite. If the sign of elongation observed is negative, go to step "g".
    NOTE: To determine the direction of the sign of elongation on a particular microscope configuration, examine a known chrysotile sample and note the direction (NE-SW or NW-SE) of the blue coloration. Chrysotile has a positive sign of elongation.

    e. Remove the first-order red compensator and uncross the polarizer. Examine under plane polarized light for blue and gold-brown Becke colors at the fiber-oil interface (i.e., index of refraction match). Becke colors are not always evident. Examine fiber morphology for twisted, wavy bundles of fibers which are characteristic of chrysotile. Twisted, ribbon-like morphology with cellular internal features may indicate cellulose fibers. It may be necessary to cross the polars partially in order to see the fibers if the index of refraction is an exact match at 1.550. If the fibers appear to have higher index of refraction, go to step "h", otherwise continue.

    f. Identification of chrysotile. Insert the dispersion staining objective. Observing dispersion staining colors of blue and blue-magenta confirms chrysotile. Cellulose, which is a common interfering fiber at the 1.550 index of refraction, will not exhibit these dispersion staining colors. If chrysotile is found, go to step 15 for quantitative estimation.

    g. Identification of crocidolite. Prepare a slide in 1.700 RI liquid. Examine under plane-polarized light (uncrossed polars); check for morphology of crocidolite. Fibers will be straight, with rigid appearance, and may appear blue or purple-blue. Crocidolite is pleochroic, i.e., it will appear to change its color (blue or gray) as it is rotated through plane polarized light. Insert the dispersion staining objective. The central stop dispersion staining colors are red magenta and blue magenta, however these colors are sometimes difficult to impossible to see because of the opacity of the dark blue fibers. If observations above indicate crocidolite, go to step 15 for quantitative estimation.

h. Identification of amosite. Prepare a slide in 1.680 RI liquid. Observe the fiber morphology for amosite characteristics: straight fibers and fiber bundles with broom-like or splayed ends. If the morphology matches amosite, examine the fibers using the dispersion staining objective. Blue and pale blue colors indicate the cummingtonite form of amosite, and gold and blue colors indicate the grunerite form of amosite. If amosite is confirmed by this test, go to step 15 for quantitative estimation, otherwise continue.

i. Identification of anthophyllite-tremolite-actinolite. Prepare a slide in 1.605 HD RI liquid. Examine morphology for comparision to anthophyllite-tremolite-actinolite asbestos. The refractive indices for these forms of asbestos vary naturally within the species. Anthophyllite can be distinguished from actinolite and tremolite by its nearly parallel extinction. Actinolite has a light to dark green color under plane-polarized light and exhibits some pleochroism. For all three, fibers will be straight, single fibers possibly with some larger composite fibers. Cleavage fragments may also be present. Examine using the central stop dispersion staining objective. Anthophyllite will exhibit central stop colors of blue and gold/gold-magenta; tremolite will exhibit pale blue and yellow; and actinolite will exhibit magenta and golden-yellow colors.

NOTE: In this refractive index range, wollastonite is a common interfering mineral with similiar morphology including the presence of cleavage fragments. It has both positive and negative sign of elongation, parallel extinction, and central stop dispersion staining colors of pale yellow and pale yellow to magenta. If further confirmation of wollastonite versus anthophyllite is needed, go to step "j". If any of the above forms of asbestos was confirmed above, go to step 15 for quantitative estimation. If none of the tests above confirmed asbestos fibers, examine the additional preparations and if the same result occurs, report the absence of asbestos in this sample.

j. Wash a small portion of the sample in a drop of concentrated hydrochloric acid on a slide. Place the slide, with cover slip in place, on a warm hot plate until dry. By capillary action, place 1.620 RI liquid under the cover slip and examine the slide. Wollastonite fibers will have a "cross-hatched" appearance across the length of the fibers and will not show central stop dispersion colors. Anthophyllite and tremolite will still show their original dispersion colors.

NOTE: There are alternative analysis procedures to the step-wise approach outlined above which will yield equivalent results. Some of these alternatives are:

i. Perform the initial scan for the presence of asbestos using crossed polars as well as the first-order red compensator. This allows for simultaneous viewing of birefringent and amorphous materials as well as determining their sign of elongation. Some fibers which are covered with mortar may best be observed using this configuration.

ii. Some analysts prefer to mount their first preparation in a RI liquid different than any asbestos materials and conduct their initial examination under plane-polarized light.

iii. If alternative RI liquids are used from those specified, dispersion staining colors observed will also change. Refer to an appropriate reference for the specific colors associated with asbestos in the RI liquids actually used.

QUANTITATIVE ASSESSMENT:

15. Estimate the content of the asbestos type present in the sample using the 1.550 RI preparation. Express the estimate as an area percent of all material present, taking into account the loading and distribution of all sample material on the slide. Use Figure 1 as an aid in arriving at your estimate. If additional unidentified fibers are present in the sample, continue with the qualitative measurement (step 14).

NOTE: Point-counting techniques to determine percentages of the asbestos minerals are not generally recommended. The point-counting method only produces accurate quantitative

data when the material on the slide is homogeneous and has a uniform thickness, which is difficult to obtain [6]. The point-counting technique is, recommended by the EPA to determine the amount of asbestos in bulk [1]; however in the more recent Asbestos Hazard Emergency Response Act (AHERA) regulations, asbestos quantification may be performed by a point-counting or equivalent estimation method [7].

16. Make a quantitative estimate of the asbestos content of the sample from the appropriate combination of the estimates from both the gross and microscopic examinations. If asbestos fibers are identified, report the material as "asbestos-containing". Asbestos content should be reported as a range of percent content. The range reported should be indicative of the analyst's precision in estimating asbestos content. For greater quantities use Figure 1 in arriving at your estimate.

EVALUATION OF METHOD:

The method is compiled from standard techniques used in mineralogy [8-13], and from standard laboratory procedures for bulk asbestos analysis which have been utilized for several years. These techniques have been successfully applied to the analysis of EPA Bulk Sample Analysis Quality Assurance Program samples for more than 8 years [1,5]. However, no formal evaluation of this method, as written, has been performed.

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Figure 1. Percent estimate comparator.

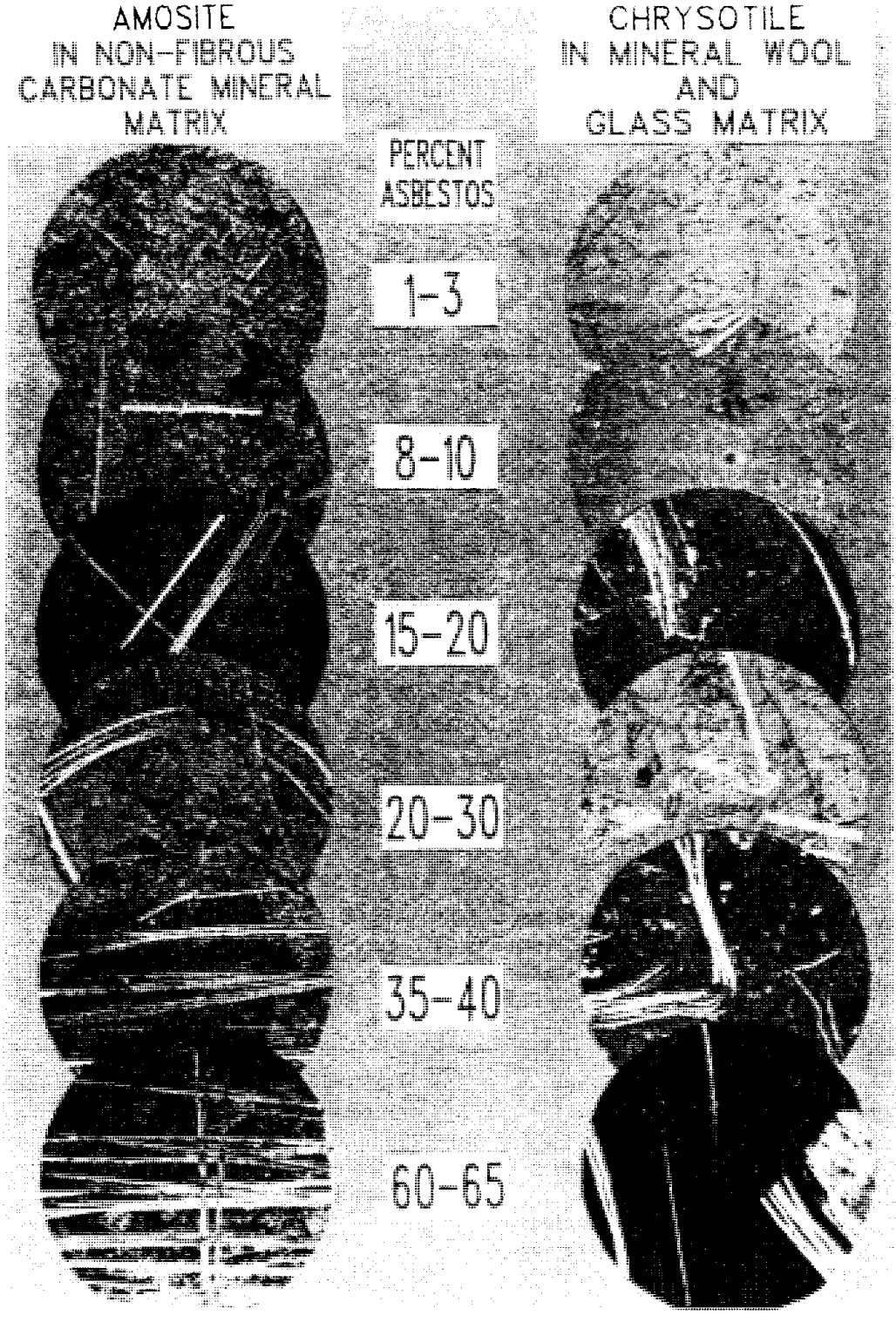

Table 1. Optical Properties of Asbestos Fibers

Mineral	Morphology and Color	Refractive Index (Approximate Values) ⊥ to Elongation	Refractive Index (Approximate Values) ∥ to Elongation	Birefringence
Chrysotile	Wavy fibers with kinks. Splayed ends on larger bundles. Colorless to light brown upon being heated. Nonpleochroic. Aspect ratio typically >10:1.	1.54	1.55	0.002 - 0.014
Cummingtonite-Grunerite (Amosite)	Straight fibers and fiber bundles. Bundle ends appear broom-like or splayed. Colorless to brown upon heating. May be weakly pleochroic. Aspect ratio typically >10:1.	1.67	1.70	0.02 - 0.03
Crocidolite (Riebeckite)	Straight fibers and fiber bundles. Longer fibers show curvature. Splayed ends on bundles. Characteristic blue color. Pleochroic. Aspect ratio typically >10:1.	1.71	1.70	0.014 - 0.016 Interference colors may be masked by blue color.
Anthophyllite	Straight fibers and fiber bundles. Cleavage fragments may be present. Colorless to light brown. Nonpleochroic to weakly pleochroic. Aspect ratio generally <10:1.	1.61	1.63	.019 - .024
Tremolite-Actinolite	Straight and curved fibers. Cleavage fragments common. Large fiber bundles show splayed ends. Tremolite is colorless. Actinolite is green and weakly to moderately pleochroic. Aspect ratio generally <10:1.	1.60 - 1.62 (tremolite) 1.62 - 1.67 (actinolite)	1.62 - 1.64 (tremolite) 1.64 - 1.68 (actinolite)	0.02 - 0.03

Table 1. Optical Properties of Asbestos Fibers (Continued)

Mineral	Extinction	Sign of Elongation	Central Stop Dispersion Staining Colors: RI Liquid	⊥ to Vibration	∥ to Vibration
Chrysotile	Parallel to fiber length	+ (length slow)	1.550 HD	Blue	Blue-magenta
Cummingtonite-Grunerite (Amosite)	Parallel to fiber length	+ (length slow)	1.670	Red magenta to blue	Yellow
			Fibers subjected to high temperatures will not dispersion-stain.		
Cummingtonite			1.680	pale blue	blue
Grunerite			1.680	blue	gold
Crocidolite (Riebeckite)	Parallel to fiber length	- (length fast)	1.700	Red magenta	Blue-magenta
			1.680	yellow	pale yellow
Anthophyllite	Parallel to fiber length	+ (length slow)	1.605 HD	Blue	Gold to gold-magenta
			1.620 HD	Blue-green	Golden-yellow
Tremolite-Actinolite	Oblique - 10 to 20° for fragments. Some composite fibers show ∥ extinction.	+ (length slow)	1.605 HD	Pale blue (tremolite)	Yellow (tremolite)
				Yellow (actinolite)	Pale yellow (actinolite)

HD = high-dispersion RI liquid series.

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FORMULA: various

M.W.: various

ASBESTOS FIBERS

METHOD: 7402
ISSUED: 8/15/87
REVISION #1: 5/15/89

PROPERTIES: solid, fibrous

OSHA: 0.2 asbestos fiber (>5 μm long)/cc
1 asbestos fiber/cc/30 minute excursion [1]
MSHA: 2 asbestos fibers (>5 μm long)/cc [2]
NIOSH: carcinogen; control to lowest level possible [3]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc [4]

SYNONYMS: actinolite [CAS #13768-00-8] or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos.

SAMPLING

SAMPLER: FILTER
(0.45-to 1.2-μm cellulose ester membrane, 25-mm diameter; conductive cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust for 100 to 1300 fibers/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted [1000-L samples]

BIAS: not determined

OVERALL PRECISION (s_r): EVALUATION OF METHOD

MEASUREMENT

!TECHNIQUE: MICROSCOPY, TRANSMISSION ELECTRON
! (TEM)
!
!ANALYTE: asbestos fibers
!
!SAMPLE PREPARATION: modified Jaffe wick
!
!EQUIPMENT: transmission electron microscope;
! energy dispersive X-ray system (EDX)
! analyzer
!
!CALIBRATION: qualitative electron diffraction;
! calibration of TEM magnification
! and EDX system
!
!RANGE: 100 to 1300 fibers/mm^2 filter
! area [5]
!
!ESTIMATED LOD: 1 confirmed asbestos fiber above
! 95% of expected mean blank value
!
!PRECISION: 0.28 when 65% of fibers are asbestos;
! 0.20 when adjusted fiber count is
! applied to PCM count [6].
!
!

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. This method is used to determine asbestos fibers in the optically visible range and is intended to complement the results obtained by phase contrast microscopy (Method 7400).

INTERFERENCES: Other amphibole particles that have aspect ratios greater than 3:1 and elemental compositions similar to the asbestos minerals may interfere in the TEM analysis. Some non-amphibole minerals may give electron diffraction patterns similar to amphiboles. High concentrations of background dust interfere with fiber identification.

OTHER METHODS: This revises Method 7402 (8/15/87). This method is designed for use with Method 7400 (phase contrast microscopy).

REAGENTS:

1. Acetone. See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl, cellulose ester membrane filter, 0.45- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean count is >5 fibers/100 fields. These are defined as laboratory blanks.
   NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects on fiber sampling and during sample shipment. Ground the cowl when possible during sampling.
   NOTE 3: 0.8-µm pore size filters are recommended for personal sampling. 0.45-µm filters are recommended for sampling when performing TEM analysis on the samples because the particles deposit closer to the filter surface. However, the higher pressure drop through these filters normally preclude their use with personal sampling pumps.
2. Personal sampling pump, 0.5 to 16 L/min, with flexible connecting tubing.
3. Microscope, transmission electron, operated at ca. 100 kV, with electron diffraction and energy-dispersive X-ray capabilities, and having a fluorescent screen with inscribed or overlaid calibrated scale (Step 15).
   NOTE: The scale is most efficient if it consists of a series of lines inscribed on the screen or partial circles every 2 cm distant from the center.
4. Diffraction grating replica with known number of lines/mm.
5. Slides, glass, pre-cleaned, 25- x 75-mm.
6. Knife, #10 surgical steel, curved-blade.
7. Tweezers.
8. Grids, 200-mesh TEM copper, (optional: carbon-coated).
9. Petri dishes, 15-mm depth. The top and bottom of the petri dish must fit snugly together. To assure a tight fit, grind the top and bottom pieces together with an abrasive such as carborundum to produce a ground-glass contact surface.
10. Foam, clean polyurethane, spongy, 12-mm thick.
11. Filters, Whatman No. 1 qualitative paper or equivalent, or lens paper.
12. Vacuum evaporator.
13. Cork borer, No. 5 (8-mm).
14. Pen, waterproof, marking.
15. Reinforcement, page, gummed.
16. Asbestos standard bulk materials for reference; e.g. SRM #1866, available from the National Institute of Standards and Technology.
17. Carbon rods, sharpened to 1 mm x 8 mm.
18. Microscope, light, phase contrast (PCM), with Walton-Beckett graticule (see method 7400).
19. Grounding wire, 22-gauge, multi-strand.
20. Tape, shrink- or adhesive-.

SPECIAL PRECAUTIONS: Acetone is extremely flammable (flash point = 0 °F). Take precautions not to ignite it. Heating of acetone must be done in a fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [7].
2. For personal sampling, fasten sampler to worker's lapel near worker's mouth. Remove the top cover from cowl extension ("open-face") and orient sampler face down. Wrap joint between extender and monitor body with tape to help hold the cassette together and provide a marking surface to identify the cassette. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.

17. Acquire energy-dispersive X-ray (EDX) spectra on approximately 5 fibers having diameters between 0.25 and 0.5 μm of each asbestos variety obtained from standard reference materials [12].
    NOTE: The sample may require tilting to obtain adequate signal. Use same tilt angle for all spectra.
    a. Prepare TEM grids of all asbestos varieties.
    b. Use acquisition times (at least 100 sec) sufficient to show a silicon peak at least 75% of the monitor screen height at a vertical scale of ≥500 counts per channel.
    c. Estimate the elemental peak heights visually as follows:
        (1) Normalize all peaks to silicon (assigned an arbitrary value of 10).
        (2) Visually interpret all other peaks present and assign values relative to the silicon peak.
        (3) Determine an elemental profile for the fiber using the elements Na, Mg, Si, Ca, and Fe. Example: 0-4-10-3-<1 [12].
        NOTE: In fibers other than asbestos, determination of Al, K, Ti, S, P, and F may also be required for fiber characterization.
        (4) Determine a typical range of profiles for each asbestos variety and record the profiles for comparison to unknowns.

MEASUREMENT:

18. Perform a diffraction pattern inspection on all sample fibers counted under the TEM, using the procedures given in step 17. Assign the diffraction pattern to one of the following structures:
    a. chrysotile;
    b. amphibole;
    c. ambiguous;
    d. none.
    NOTE: There are some crystalline substances which exhibit diffraction patterns similar to those of asbestos fibers. Many of these, (brucite, halloysite, etc.) can be eliminated from consideration by chemistry. There are, however, several minerals (e.g., pyroxenes, massive amphiboles, and talc fibers) which are chemically similar to asbestos and can be considered interferences. The presence of these substances may warrant the use of more powerful diffraction pattern analysis before positive identification can be made. If interferences are suspected, morphology can play an important role in making positive identification.
19. Obtain EDX spectra in either the TEM or STEM modes from fibers on field samples using the procedure of step 18. Using the diffraction pattern and EDX spectrum, classify the fiber:
    a. For a chrysotile structure, obtain EDX spectra on the first five fibers and one out of ten thereafter. Label the range profiles from 0-5-10-0-0 to 0-10-10-0-0 as "chrysotile."
    b. For an amphibole structure, obtain EDX spectra on the first 10 fibers and one out of ten thereafter. Label profiles ca. 0-2-10-0-7 as "possible amosite"; profiles ca. 1-1-10-0-6 as "possible crocidolite"; profiles ca. 0-4-10-3-<1 as "possible tremolite"; and profiles ca. 0-3-10-0-1 as "possible anthophyllite."
        NOTE: The range of profiles for the amphiboles will vary up to ±1 unit for each of the elements present according to the relative detector efficiency of the spectrometer.
    c. For an ambiguous structure, obtain EDX spectra on all fibers. Label profiles similar to the chrysotile profile as "possible chrysotile." Label profiles similar to the various amphiboles as "possible amphiboles." Label all others as "unknown" or "non-asbestos."
20. Counting and Sizing:
    a. Insert the sample grid into the specimen grid holder and scan the grid at zero tilt at low magnification (ca. 300 to 500X). Ensure that the carbon film is intact and unbroken over ca. 75% of the grid openings.

b. In order to determine how the grids should be sampled, estimate the number of fibers per grid opening during a low-magnification scan (500 to 1000X). This will allow the analyst to cover most of the area of the grids during the fiber count and analysis. Use the following rules when picking grid openings to count [12,13]:
   (1) Light loading (<5 fibers per grid opening): count total of 40 grid openings.
   (2) Moderate loading (5 to 25 fibers per grid opening): count minimum of 40 grid openings or 100 fibers.
   (3) Heavy loading (>25 fibers per opening): count a minimum of 100 fibers and at least 6 grid openings.

   Note that these grid openings should be selected approximately equally among the three grid preparations and as randomly as possible from each grid.

c. Count only grid openings that have the carbon film intact. At 500 to 1000X magnification, begin counting at one end of the grid and systematically traverse the grid by rows, reversing direction at row ends. Select the number of fields per traverse based on the loading indicated in the initial scan. Count at least 2 field blanks per sample set to document possible contamination of the samples. Count fibers using the following rules:
   (1) Count all particles with diameter greater than 0.25 µm that meet the definition of a fiber (aspect ratio ≥3:1, longer than 5 µm). Use the guideline of counting all fibers that would have been counted under phase contrast light microscopy (Method 7400). Use higher magnification (10000X) to determine fiber dimensions and countability under the acceptance criteria. Analyze a minimum of 10% of the fibers, and at least 3 asbestos fibers, by EDX and SAED to confirm the presence of asbestos. Fibers of similar morphology under high magnification can be identified as asbestos without SAED. Particles which are of questionable morphology should be analyzed by SAED and EDX to aid in identification.
   (2) Count fibers which are partially obscured by the grid as half fibers.
   NOTE: If a fiber is partially obscured by the grid bar at the edge of the field of view, count it as a half fiber only if more than 2.5 µm of fiber is visible.
   (3) Size each fiber as it is counted and record the diameter and length:
      (a) Move the fiber to the center of the screen. Read the length of the fiber directly from the scale on the screen.
      NOTE 1: Data can be recorded directly off the screen in mm and later converted to µm by computer.
      NOTE 2: For fibers which extend beyond the field of view, the fiber must be moved and superimposed upon the scale until its entire length has been measured.
      (b) When a fiber has been sized, return to the lower magnification and continue the traverse of the grid area to the next fiber.

d. Record the following fiber counts:
   (1) f_s, f_b = number of asbestos fibers in the grid openings analyzed on the sample filter and corresponding field blank, respectively.
   (2) F_s, F_b = number of fibers, regardless of indentification, in the grid openings analyzed on the sample filter and corresponding field blank, respectively.

CALCULATIONS:

21. Calculate and report the fraction of optically visible asbestos fibers on the filter, $(f_s - f_b)/(F_s - F_b)$. Apply this fraction to fiber counts obtained by PCM on the same filter or on other filters for which the TEM sample is representative. The final result is an asbestos fiber count. The type of asbestos present should also be reported.
22. As an integral part of the report, give the model and manufacturer of the TEM as well as the model and manufacturer of the EDX system.

EVALUATION OF METHOD:

The TEM method, using the direct count of asbestos fibers, has been shown to have a precision of 0.275 (s_r) in an evaluation of mixed amosite and wollastonite fibers. The estimate of the asbestos fraction, however, had a precision of 0.11 (s_r). When this fraction was applied to the PCM count, the overall precision of the combined analysis was 0.20 [6].

REFERENCES:

[1] Occupational Safety and Health Administration, U.S. Department of Labor, Occupational Exposure to Asbestos, Tremolite, Anthophyllite, and Actinolite Asbestos; Final Rules, 29 CFR Part 1910.1001 Amended June 20, 1986; Sept. 14, 1988. Final Rules 29 CFR 1926.58 Amended Sept 14, 1988.

[2] Mine Safety and Health Administration, U.S. Department of Commerce, Exposure Limits for Airborne Contaminants; Part 56.5001 Amended July 1, 1988.

[3] Revised Recommended Asbestos Standard, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-169 (1976); as amended in NIOSH statement at OSHA Public Hearing, June 21, 1984.

[4] American Conference of Governmental Industrial Hygienists, "Threshold Limit Values and Biological Exposure Indices for 1988-1989," ACGIH (1988).

[5] Walton, W. H. "The Nature, Hazards, and Assessment of Occupational Exposure to Airborne Asbestos Dust: A Review," Ann. Occup. Hyg., 25, 115-247 (1982).

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[7] Leidel, N. A., S. G. Bayer, R. D. Zumwalde, and K. A. Busch. USPHS/NIOSH Membrane Filter Method for Evaluating Airborne Asbestos Fibers, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-127 (1979).

[8] Johnston, A. M., A. D. Jones, and J. H. Vincent. "The Influence of External Aerodynamic Factors on the Measurement of the Airborne Concentration of Asbestos Fibres by the Membrane Filter Method," Ann. Occup. Hyg., 25, 309-316 (1982).

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[10] Baron, P. A. and G. C. Pickford. "An Asbestos Sample Filter Clearing Procedure," Appl. Ind. Hyg.,1:169-171,199 (1986).

[11] LeGuen, J. M. and S. Galvin "Clearing and Mounting Techniques for the Evaluation of Asbestos Fibres by the Membrane Filter Method" Ann. Occup. Hyg. 24, 273-280 (1981).

[12] Yamate, G., S. A. Agarwal, and R. D. Gibbons. "Methodology for the Measurement of Airborne Asbestos by Electron Microscopy," EPA Contract No. 68-02-3266 (in press).

[13] Steel, E. B. and J. A. Small. "Accuracy of Transmission Electron Microcopy for the Analysis of Asbestos in Ambient Environments," Anal. Chem., 57, 209-213 (1985).

METHOD REVISED BY: Paul A. Baron, Ph.D.; NIOSH/DPSE.

FORMULA: $CH_3(CH_2)_3SH$; C_4H_9SH

M.W.: 90.19

1-BUTANETHIOL

METHOD: 2525

ISSUED: 5/15/89

OSHA: 0.5 ppm
NIOSH: C 0.5 ppm
ACGIH: 0.5 ppm
(1 ppm = 3.69 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.842 g/ml @ 25 °C; BP 98 °C;
VP 4.7 kPa (35 mm Hg; 4.6% v/v) @ 20 °C

SYNONYMS: n-butyl mercaptan; thiobutyl alcohol; CAS #109-79-5.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Chromosorb 104, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L
-MAX: 4 L

SHIPMENT: routine

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

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 17 to 74 mg/m^3 [1]
(1.5-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.062 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD (S-mode)

ANALYTE: 1-butanethiol

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 200 °C
-COLUMN: 140 °C isothermal

GASES:
CARRIER: N_2, 50 mL/min
OTHER: H_2, 150 mL/min; O_2, 20 mL/min;
Air, 30 mL/min

COLUMN: 1.2 m x 2-mm ID glass;
60/80 mesh Chromosorb 104

CALIBRATION: standard solutions of 1-butanethiol in acetone

RANGE: 0.02 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.003 mg per sample [1]

PRECISION (s_r): 0.015 @ 0.03 to 0.11 mg per sample [1]

APPLICABILITY: The working range is 5 to 50 mg/m^3 (1.4 to 14 ppm) for a 4-L air sample. The maximum sample size is based on the capacity of the Chromosorb 104 to collect vapors of 1-butanethiol in air at high relative humidity (94%) [1]. Smaller concentrations may be determined if desorption efficiency is adequate.

INTERFERENCES: None identified.

OTHER METHODS: This revises NIOSH Method S350 [2].

REAGENTS:

1. Acetone, chromatographic quality.
2. n-hexane, reagent grade.
3. 1-Butanethiol.*
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Oxygen, purified.
7. Air, filtered, compressed.
8. Calibration stock solution, 13.47 mg/mL. Add 160 µL of pure 1-butanethiol to acetone and dilute to 10 mL. Prepare in duplicate.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 8.5 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps containing two sections of 60/80 mesh Chromosorb 104 (front = 150 mg; back = 75 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 0.025 L/min airflow must be less than 3.4 kPa (25 mm Hg). The sampling tubes are commercially available (SKC, Inc. Cat. # 226-49-40-104).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector with sulfur filter, integrator and column (see Page 2525-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL (readable to 0.1 µL) and 50-µL.
6. Flasks, volumetric, 10-mL.
7. Pipet, 1.0-mL.
8. File, triangular.

SPECIAL PRECAUTIONS: Store 1-butanethiol away from oxidizing and flammable materials [3,4]. The analyte is highly flammable and irritating to the eyes and mucous membranes. Work in a hood.

SAMPLING:

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

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Attach cap to each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards covering the range 0.0003 to 0.02 mg/mL.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area squared vs. mg 1-butanethiol).
9. Determine desorption efficiency (DE) at least once for the batch of Chromosorb 104 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels

plus three media blanks.

a. Remove and discard back sorbent section of a media blank sampler.
b. Inject calibration stock solution (2 to 20 µL) containing known amount of 1-butanethiol directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg 1-butanethiol recovered.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2525-1. Inject sample aliquot manually using solvent flush technique. Vent the acetone peak so that it will not extinquish the flame in the detector.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 1-butanethiol found in the sample front (W_f) and back (W_b) sorbent sections, and in the average blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b \geq W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1-butanethiol in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was validated over the range 17 to 74 mg/m^3 at 22 °C and 759 mm Hg using a 1.5-L sample [1]. Overall precision, s_r, was 0.062 with an average recovery of 0.98, representing a non-significant bias. The concentration of 1-butanethiol was independently determined from the syringe delivery rate and dilution flow rates. Desorption efficiency was 0.90 in the range 0.028 to 0.11 mg per sample. The breakthrough volume (effluent concentration = 5% of influent concentration) was 4.0 L; this was determined by sampling humid air (94% relative humidity), containing 74 mg/m^3 1-butanethiol at 0.023 L/min.

REFERENCES:

[1] Backup Data Report for S350, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, method S350, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Material Safety Data Sheet, #504 Butyl Mercaptan, General Electric, Schenectady, N.Y. 12305 (1982).
[4] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD WRITTEN BY: James E. Arnold, NIOSH/DPSE; S350 originally validated under NIOSH Contract 210-76-0123.

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FORMULA: $C_{10}H_6Cl_8$

M.W.: 409.80

CHLORDANE

METHOD: 5510
ISSUED: 5/15/89

OSHA: 0.5 mg/m^3 (skin)
NIOSH: carcinogen; 0.5 mg/m^3
ACGIH: 0.5 mg/m^3 (skin), suspect human carcinogen

PROPERTIES: liquid; d 1.59 to 1.63 g/mL @ 25 °C; BP 175 °C; VP 0.13 x 10^{-5} kPa (1.0×10^{-5} mm Hg) @ 20 °C

SYNONYMS: 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane and isomers; Toxichlor; Octachlor; CAS #57-74-9.

SAMPLING

SAMPLER: FILTER AND SOLID SORBENT TUBE
(0.8-µm cellulose ester membrane; Chromosorb 102, 100/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 10 L @ 0.5 mg/m^3
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: >1 week @ 25 °C [1]

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 2 per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 0.16 to 1.17 mg/m^3 [1,2] (120-L samples)

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): 0.070 [1,2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTRON CAPTURE DETECTOR (GC/ECD)

ANALYTE: Chlordane

EXTRACTION: 10 mL toluene, stand 30 min

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 205 °C

CARRIER GASES: 95% argon/5% methane @ 75 mL/min

COLUMN: 2 m x 4-mm ID glass packed with 1.5%, SP2250/1.95% SP2401 on 100/120 mesh Chromosorb WHP

CALIBRATION: solution of analyte in toluene or hexane with internal standard

RANGE: 5 to 150 µg per sample [2]

ESTIMATED LOD: 0.1 µg per sample [3]

PRECISION (s_r): 0.02 @ 6 to 120 µg per sample [2]

APPLICABILITY: The working range is 0.04 to 1.2 mg/m^3 for a 120-L air sample. Chlordane, accompanied by a mixture of penta-, hexa-, hepta-, and nonachlorinated compounds, is defined by a group of five chromatographic peaks. It is necessary to determine the percentage of Chlordane and its isomers in the standards used.

INTERFERENCES: None identified; an alternate column is 2-m x 2-mm ID glass packed with 3% QF-1 on 100/120 mesh Chrom Q.

OTHER METHODS: This replaces NIOSH method S278. [2]

REAGENTS:

1. Toluene, distilled in glass.
2. Hexane, distilled in glass.
3. Chlordane, 95%.
4. Calibration stock solution, ca. 6 mg/mL. Dissolve 10 mg Chlordane in 1 mL toluene. NOTE: Since Chlordane is available only as a mixture, standardize the solution as follows:
   a. Dilute 10 µL calibration stock solution to 10 mL.
   b. Analyze by steps 11-13.
   c. Divide combined area of Chlordane peaks (Fig. 1) by total area of all peaks to determine fraction Chlordane, f.
   d. Multiply f by 10 mg/mL to determine calibration stock solution concentration.
5. Internal standard, p,p'-DDT, 98%.
6. 95% Argon/5% methane mixture, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: train consisting of a 37-mm, 0.8-µm pore size cellulose ester membrane filter supported by a stainless steel screen in a two-piece filter cassette holder followed by a 10 cm x 8 mm OD x 6 mm ID, 20/40 Chromosorb 102 tube (front = 100 mg; back = 50 mg), separated by 3-mm silanized glass wool plug, with plastic caps. Pressure drop across the tube at 1 L/min must not exceed 2.5 cm Hg. Filters and tubes are commercially available.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator and column (page 5510-1).
4. Vials, scintillation, 20-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Flasks, volumetric 10-mL.
7. Bottle, 60 mL, 40-mm ID, straight-sided with a PTFE-lined cap for extracting filter holder and screen.
8. Stopwatch.
9. Manometer.
10. Pipets, 1- and 10-mL and other convenient sizes for preparing standards.
11. Tweezers.

SPECIAL PRECAUTIONS: Chlordane and p,p'-DDT are toxic and rapidly absorbed through the skin [4]. Use gloves and eyeglasses to avoid direct contact with these compounds. Handle these chemicals and organic solvents with care in the laboratory hood. Chlordane is a potential human carcinogen [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Assemble the sampler and connect the sorbent tube (ends broken just before connection) to the sampling pump with backup section nearest the sampling pump. Keep the sampler in a vertical position during sampling. Assure that the air being sampled is not passed through any hose or tubing before entering the filter cassette.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 10 to 200 L.
4. Remove the sorbent tube from the outlet of the cassette and connect it to the inlet side of the cassette. Cap the open end of the sorbent tube and plug the outlet of the cassette. Ship sampler with appropriate blanks to laboratory.
5. In separate package, ship bulk sample of the suspected material.

SAMPLE PREPARATION:

6. Separate the sampler components for extraction as follows:
   a. Into a bottle, transfer the filter, front sorbent section and glass wool plugs. Add 10.0 mL toluene. After desorption is complete, dilute a 1-mL aliquot to 10 mL for analysis.
   b. Into a second bottle, transfer the stainless steel screen. Using a 10-mL volumetric pipet, rinse the inner surfaces of the cassette into the bottle with hexane.
   c. Into a scintillation vial, transfer the back sorbent section. Add 10.0 mL toluene.
7. Cap each container and allow to stand 30 min with occasional swirling.
   NOTE: A suitable internal standard such as p,p'-DDT may be added, at 0.4 µg/mL, at this point.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to toluene containing internal standard in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain Chlordane concentrations in the range 0.01 to 15 µg/mL.
   b. Analyze the samples and blanks (steps 11 through 13).
   c. Prepare a calibration graph (ratio of the total Chlordane peak areas to peak area of internal standard vs. µg Chlordane).
9. Determine recovery at least once for each lot of filter and Chromosorb 102 used. Prepare three samplers at each of five levels plus three media blanks.
   a. Place cellulose ester membrane filter and 100 mg of Chromosorb 102 in a bottle.
   b. Add calibration stock solution to the filter and Chromosorb 102 in the container with a microliter syringe. Prepare parallel blank samples with no added analyte.
   c. Cap the bottle. Allow to stand overnight.
   d. Desorb (steps 6 and 7) and analyze with working standards (steps 11 through 13).
   e. Prepare a graph of recovery vs. µg Chlordane recovered.
10. Check recovery at two levels for each sample set in duplicate. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5510-1,
12. Inject 2-µL sample aliquot using solvent flush technique or with autosampler. Make duplicate injections of sample and standards.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the solution, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak areas. Divide the total Chlordane peak area (sum of five peaks; see Fig. 1) by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

14. Calculate the mass of Chlordane found on the sampler (filter plus front section of Chromosorb 102 tube), W (µg), the media blank (filter plus adsorbent tube, B (µg), and the extract from filter holder and screen, F(µg), from the measured peak areas and the calibration graph.
15. Calculate the concentration of Chlordane, C (mg/m^3), in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S278 was validated on June 8, 1979, [1,2,6]. The substance used to dynamically generate test atmospheres at 25 °C and 760 mm Hg was Ortho-Klor-72 (40% Chlordane), Velsicol Chemical Corporation. Collection efficiencies and recoveries were close to 1.00 in the range 6 to 120 µg per sample. No significant breakthrough was observed after 240 min of sampling an atmosphere of 1.1 mg/m^3 Chlordane at a flow rate of approximately 1 L/min. Samples spiked with Chlordane, extracted with toluene, and stored one week at room temperature gave recoveries of 96 to 100%. Overall precision (s_r) was 0.07. No significant bias was found.

REFERENCES:

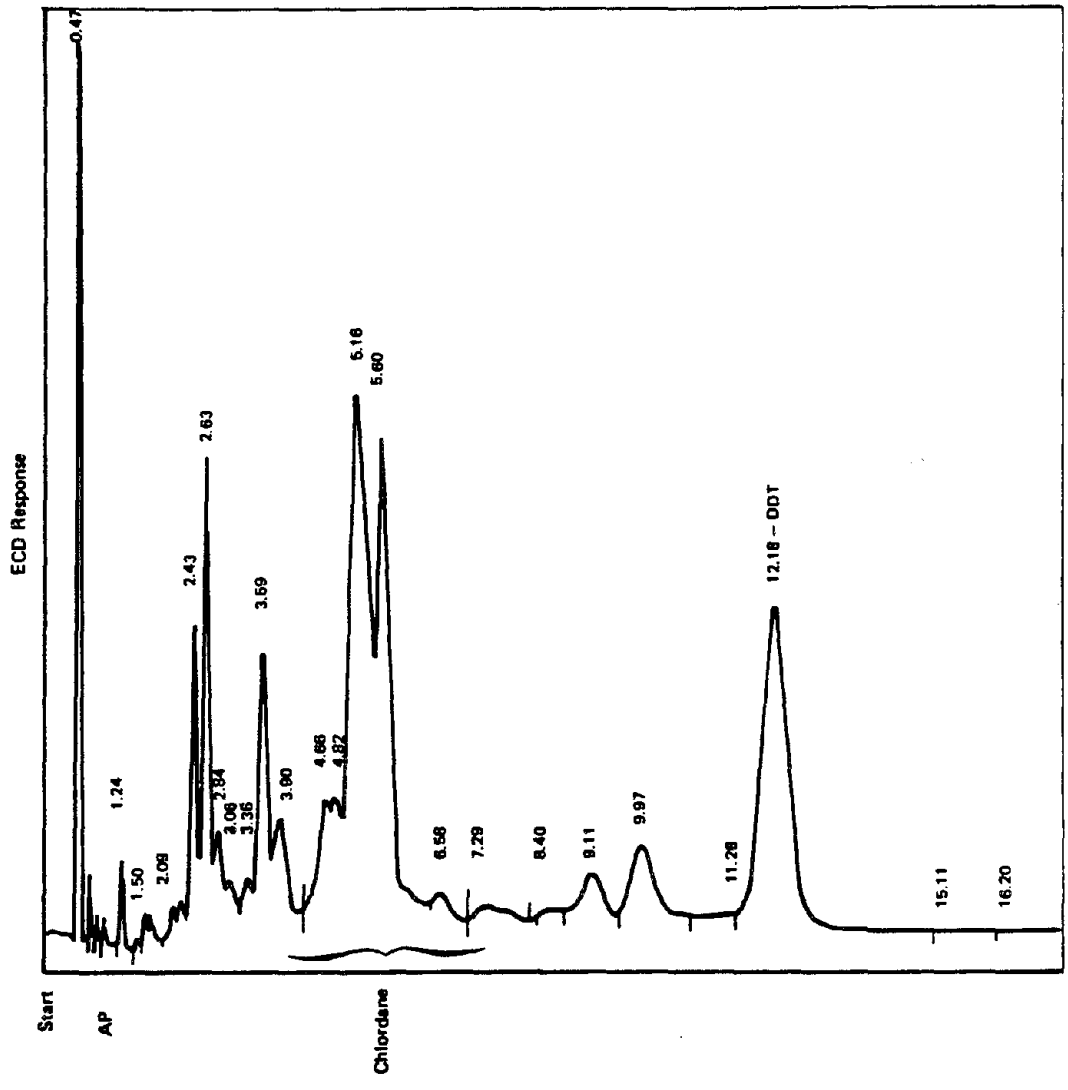
[1] NIOSH Backup Data Report S278 (June 8, 1979).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S278, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[3] UBTL, Inc. NIOSH Seq. Report 4-999-K (July 19, 1985, unpubl).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 from NTIS, Springfield, VA 22161.

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

METHOD REVISED BY: Gangadhar Choudhary, Ph.D., NIOSH, DPSE; S278 originally validated under NIOSH Contract No. 210-76-0123.

Figure 1. Chromatogram of Chlordane analytical standard.



FORMULA: Cr(VI)

M.W.: 52.00 (Cr); 99.99 (CrO_3)

CHROMIUM, HEXAVALENT

METHOD: 7600
ISSUED: 2/15/84
REVISION #1: 5/15/89

OSHA: C 0.1 mg/m^3
NIOSH: carcinogen; 0.001 mg/m^3; C 0.05 [1]
ACGIH: 0.050 mg/m^3; some insoluble chromates are carcinogens

PROPERTIES (Cr metal): oxidizing agent

SYNONYMS: vary depending upon the compound; CAS #1333-82-0 (chromic acid; chromium trioxide).

SAMPLING

SAMPLER: FILTER
(5.0-µm PVC membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 8 L @ 0.025 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: analyze within 2 weeks [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.05 to 0.2 mg/m^3 [3]
(22-L samples)

BIAS: not significant

OVERALL PRECISION (s_r): 0.084 [3]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: CrO_4^{-2}-diphenylcarbazide complex

WAVELENGTH: 540 nm; 5-cm path length

EXTRACTION SOLUTION: 0.5 N H_2SO_4 or 2% NaOH-3% Na_2CO_3 (see steps 4 and 5)

CALIBRATION: standard solutions of K_2CrO_4 in 0.5 N H_2SO_4

RANGE: 0.2 to 7 µg per sample

ESTIMATED LOD: 0.05 µg per sample

PRECISION (s_r): 0.029 @ 0.3 to 1.2 µg per sample [4]

APPLICABILITY: The working range is 0.001 to 5 mg/m^3 for a 200-L air sample. This method may be used for the determination of soluble Cr(VI) (using 0.5 N H_2SO_4 as extraction solution) or insoluble Cr(VI) (using 2% NaOH - 3% Na_2CO_3) [4].

INTERFERENCES: Possible interferents are iron, copper, nickel, and vanadium; 10 µg of any of these causes an absorbance equivalent to about 0.02 µg Cr(VI) due to formation of colored complexes. Interference due to reducing agents (e.g., Fe, Fe^{++}) is minimized by alkaline extraction (step 5).

OTHER METHODS: This method combines and replaces P&CAM 169 [2], S317 [3] and P&CAM 319 [4]; the Cr(VI) criteria document [1] contains a method similar to P&CAM 169. Method 7604 uses ion chromatography for measurement.

REAGENTS:

1. Sulfuric acid, conc. (98% w/w).
2. Sulfuric acid, 6 N. Add 167 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
3. Sulfuric acid, 0.5 N. Add 14.0 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
4. Sodium carbonate anhydrous.
5. Sodium hydroxide.
6. Potassium chromate, K_2CrO_4.
7. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 mL acetone and 100 mL water.
8. Cr(VI) standard, 1000 µg/mL. Dissolve 3.735 g K_2CrO_4 in deionized water to make 1 L, or use commercially available solution.*
9. Calibration stock solution, 10 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:100 with deionized water.
10. Extraction solution, 2% NaOH-3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
11. Nitrogen, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder (FWSB [MSA] or VM-1 [Gelman] or equivalent).
   NOTE: BSWP PVC filters (Millipore) are not acceptable for sampling Cr(VI). This filter has been found to reduce a significant amount of an aqueous 5 µg Na_2CrO_4 spike within 24 hrs. Check new lots of filters for recovery.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Vials, scintillation, 20-mL glass, PTFE-lined, screw cap.**
4. Forceps, plastic.
5. Spectrophotometer, visible (540 nm), with cuvettes, 5-cm path length.
6. Filtration apparatus, vacuum.**
7. Beakers, borosilicate, 50-mL.**
8. Watchglass.**
9. Volumetric flasks, 25-, 100- and 1000-mL.**
10. Hotplate, 120 to 400 °C.
11. Micropipettes, 10-µL to 1-mL.
12. Centrifuge tubes, 40-mL, graduated, with plastic stoppers.**
13. Buchner funnel.**
14. Pipettes, TD 5 mL.**

**Clean all glassware with 1:1 HNO_3 and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [1,5]. All sample preparation should be performed in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 8 to 400 L. Do not exceed 1 mg total dust loading on the filter.
3. Remove the filter from the cassette within 1 h of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

NOTE: There are two sample preparation techniques outlined below. For soluble chromates or chromic acid, follow step 4; for insoluble chromate or Cr(VI) in the presence of Cr(III), Fe, Fe^{++} or other reducing agents, follow step 5.

4. Sample preparation for soluble chromates and chromic acid.
   a. Remove the blank and sample filters from the vials, then fold and place them into centrifuge tubes.

b. Add 6 or 7 mL 0.5 N H_2SO_4 to each tube and shake it to wash all surfaces of the filter. Allow filter to remain in tube 5 to 10 min [6].
c. Remove the filter from the tube with plastic forceps, carefully washing all surfaces with an additional 1 to 2 mL 0.5 N H_2SO_4. Discard the filters. Start reagent blanks at this point.
d. Filter the solution through a moistened PVC filter in a Buchner funnel to remove interferences from suspended dust. Collect the filtrate in a clean centrifuge tube. Rinse the bottle, which contained the filter, with 2 to 3 mL 0.5 N H_2SO_4 and pour into the funnel. Rinse the funnel and filter with 5 to 8 mL 0.5 N H_2SO_4.
e. Add 0.5 mL diphenylcarbazide solution to each centrifuge tube. Bring the total volume in each centrifuge tube to 25 mL with 0.5 N H_2SO_4. Shake to mix and allow a few minutes (at least 2 min but no longer than 40 min [6]) for the color to develop. Transfer the solution to a clean cuvette and analyze within 40 min of mixing (steps 9 through 11).

5. Sample preparation for insoluble chromates and for Cr(VI) in the presence of Cr(III), iron or other reducing agents:
NOTE: If significant amounts of Cr(III) are expected to be present, degas the sample solution by bubbling a slow stream of nitrogen through it for 5 min before proceeding.
a. Remove the PVC filter from the bottle, place it in a 50-mL beaker, and add 5 mL extraction solution, 2% NaOH - 3% Na_2CO_3. Start reagent blanks at this point.
b. Purge the headspace above the solution with nitrogen throughout the extraction process to avoid oxidation of any Cr(III). Cover the beaker with a watchglass and heat it to near the boiling point on a hotplate with occasional swirling for 30 to 45 min. Do not boil the solution or heat longer than 45 min. Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost due to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.
c. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask, keeping the total volume about 20 mL.
NOTE: If the solution is cloudy, filter it through a PVC filter in a vacuum filtration apparatus using distilled water rinses.
d. Add 1.90 mL 6 N sulfuric acid to the volumetric flask and swirl to mix.
CAUTION: CARBON DIOXIDE WILL BE EVOLVED CAUSING INCREASED PRESSURE IN THE FLASK. LET THE SOLUTION SIT FOR SEVERAL MINUTES UNTIL VIGOROUS GAS EVOLUTION CEASES.
e. Add 0.5 mL diphenylcarbazide solution, dilute to the mark with distilled water and invert several times to mix thoroughly. Pour out and discard about one-half of the contents of the flask, stopper the flask and shake it vigorously several times, removing the stopper each time to relieve pressure.
NOTE: This step releases bubbles of carbon dioxide which would otherwise cause high and erratic absorbance readings.

CALIBRATION AND QUALITY CONTROL:

6. Transfer 6 or 7 mL 0.5 N H_2SO_4 to each of a series of 25-mL volumetric flasks. Pipet 0 to 0.7 mL of 10 µg/mL calibration stock solution into the volumetric flasks. Add 0.5 mL diphenylcarbazide solution to each and sufficient 0.5 N H_2SO_4 to bring the volume to 25 mL. These working standards contain 0 to 7 µg Cr(VI).
7. Analyze the working standards (steps 9 through 11).
8. Prepare a calibration graph [absorbance vs. µg Cr(VI)].

MEASUREMENT:

9. Set wavelength on the spectrophotometer to 540 nm.
10. Set to zero using a 0.5 N H_2SO_4 reagent blank.

11. Transfer sample solution to a cuvette and record the absorbance.
    NOTE 1: A sample containing 1.5 µg Cr(VI)/25 mL gives ca. 0.2 absorbance.
    NOTE 2: If the absorbance values for the samples are higher than the standards, dilute using 0.5 N H_2SO_4 and multiply the resulting absorbance by the appropriate dilution factor.

CALCULATIONS:

12. From the calibration graph, determine the mass of Cr(VI) in each sample, W (µg), and in the average media blank, B (µg).
13. Calculate the concentration, C (mg/m^3), of Cr(VI) in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

P&CAM 169 and S317 are essentially the same method and are suitable for soluble chromate and chromic acid. Method S317 was validated with generated samples of chromic acid mist [3,7], and P&CAM 169 was tested with field samples [2,8]. P&CAM 319 was developed because a method was needed to analyze for insoluble chromates [4]. This method was tested with insoluble chromates in matrices such as paints, primer and ceramic powders [4].

Precision, analytical range, recovery data, etc., for the three methods pooled are as follows:

Total s_r:	0.084
Measurement s_r [2,3,4]:	0.02 to 0.04
Range [4]:	0.5 to 10 $\mu g/m^3$
Collection Efficiency [5]:	94.5%
Sampling Rate [2,3,4]:	1.5 to 2.5 L/min
Stability (two weeks) [2]:	96% recovery
Acceptable Filters [4]:	FWSB (MSA); VM-1 (Gelman).

REFERENCES:

[1] NIOSH Testimony on the OSHA Proposal Rules on Air Contaminants, Docket #H-020, August 1, 1988.
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Ibid, V. 3, S317, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] Ibid, V. 6, P&CAM 319, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[5] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[6] Lewis, B., NIOSH/DPSE, unpublished data (1989).
[7] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[8] Abell, M. T. and J. R. Carlberg. A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium, Am. Ind. Hyg. Assoc. J., 35:229 (1974).

METHOD REVISED BY: Daniel Molina and Martin T. Abell, NIOSH/DPSE; Method S317 validated under NIOSH Contract CDC-99-74-45.

FORMULA: Cr (VI)

M.W.: 52.00 (Cr); 99.99 (CrO_3)

CHROMIUM, HEXAVALENT

METHOD: 7604

ISSUED: 5/15/89

OSHA: C 0.1 mg/m^3 (as CrO_3)
NIOSH: carcinogen; 0.001 mg/m^3; C 0.5 mg/m^3 [1]
ACGIH: 0.050 mg/m^3 (some insoluble Cr(VI) are human carcinogens)

PROPERTIES: oxidizing agent

SYNONYMS: vary according to the compound; CAS #1333-82-0 (chromic acid; chromium trioxide).

SAMPLING

SAMPLER: FILTER
(5.0-µm PVC membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 100 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: analyze within 2 weeks [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.05 to 0.15 µg/m^3
(400-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: chromate ion

EXTRACTION SOLUTION: 5 mL 2% NaOH/3% Na_2CO_3

INJECTION VOLUME: 50 µL

COLUMN: Dionex HPIC-AG5 guard, HPIC AS5 separator, and anion suppressor, or equivalent

DETECTOR SETTING: 1 µS

MOBILE PHASE: 7.0 mM Na_2CO_3/0.5 mM NaOH, 2.0 mL/min

CALIBRATION: standard solutions of Cr(VI) in 0.4% NaOH/0.6% Na_2CO_3

RANGE: 10 to 250 µg per sample [2]

ESTIMATED LOD: 3.5 µg per sample [2]

PRECISION (s_r): 0.043 @ 22 to 62 µg per sample [2]

APPLICABILITY: The working range is 0.01 to 4 mg/m^3 for a 500-L air sample. This method is less sensitive than method 7600 (colorimetric), but it contains fewer sample preparation steps and was found free from interferences when used for samples of five chromate-containing paints. This method may be used for the determination of insoluble or soluble Cr(VI).

INTERFERENCES: Interferences due to reducing agents (e.g., Fe, Fe^{++}) are eliminated by alkaline extraction. Cations of metals, interfering with the colorimetric method, do not interfere with this method. Inadequately-cleaned glassware may create a negative bias.

OTHER METHODS: This method is an alternative to NIOSH Method 7600 (colorimetric).

REAGENTS:

1. Sodium carbonate, anhydrous.
2. Sodium hydroxide, reagent grade.
3. Extraction solution, 2% NaOH/3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
4. Mobile phase, 7.0 mM Na_2CO_3-0.5 mM NaOH. Dissolve 2.97 g Na_2CO_3 in 4 L deionized water. Add 20 mL of 0.1 M NaOH (8 g/L).
5. Suppressor regenerant, 0.025 N H_2SO_4. Dilute 2.8 mL of conc. H_2SO_4 in deionized water to 4 L.
6. Cr(VI) standard, 1000 µg/mL.
7. Calibration stock solution, 100 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:100 with distilled or deionized water.
8. Nitrogen, purified.
9. Water, distilled or deionized.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter (FWSB [MSA] or VM-1 [Gelman], or equivalent) with fiber-type backup pad in polystyrene cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ion chromatograph, with Dionex AG5, AS5, and ion suppressor, or equivalent.
4. Vials, scintillation 20-mL glass, PTFE-lined screw cap.
5. Forceps, plastic.
6. Syringe, 10-mL, with in-line membrane filter 0.45-µm pore size.
7. Beakers, borosilicate, 50-mL.
8. Watchglass.
9. Volumetric, flasks, 25-, 100-, and 1000-mL.
10. Hotplate, 120 to 400 °C.
11. Micropipette,, 20-µL, and other sizes.
12. Centrifuge tubes, 40-mL, graduated, with plastic, screw caps.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [1]. All sample preparation should be performed in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 100 to 1000 L. Do not exceed 2 mg of particulate loading on the filter.
3. Remove the filter from the cassette within 1 hour of completion of sampling, and place it in a vial to be shipped to the laboratory. Handle the filters only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

4. Place the filter face down in a 50-mL beaker, and add 5.0 mL extraction solution. Start reagent blanks at this point.
   NOTE 1: If significant amounts of Cr(III) are expected to be present, degas the extraction solution by bubbling a slow stream of nitrogen through it for 5 min before proceeding and purge the headspace above the solution with nitrogen during this step.
   NOTE 2: If only soluble chromates are of interest use distilled water in place of extraction solution.
5. Cover the beaker with a watchglass and place on a hotplate preheated to 135 °C. Heat the samples for 45 min with occasional swirling. Do not allow the solution to boil or to evaporate to dryness, because if this happens, hexavalent chromium may be lost due to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.
   NOTE: Longer heating times, up to 90 min. may be necessary for some samples (e.g., point spray [2].
6. Cool the solution and transfer it quantitatively with distilled water rinses to a centrifuge tube. Adjust the final volume to 25 mL with distilled water.

CALIBRATION AND QUALITY CONTROL:

7. Pipet 0 to 2.5 mL calibration stock solution into each of a series of 25-mL volumetric flasks. Add 5 mL extraction solution to each flask and dilute to the mark with deionized water. These working standards contain 0 to 250 µg Cr(VI).
8. Analyze the working standards (steps 10 through 12).
9. Prepare a calibration graph [peak height vs. µg Cr(VI) per sample].

MEASUREMENT:

10. Set the ion chromatograph according to manufacturer's recommendations (page 7604-1).
11. Set the regenerant flow rate to 3 mL/min. Set the ion chromatograph output range to 1 µS full scale. Set the detector output to zero, after the system equilibrates.
12. Inject 50 µL of sample or standard solution into the injection port using an in-line filter to remove solids. Record the peak height of the Cr(VI) peak, which elutes at approximately 12 minutes under these conditions.

CALCULATIONS:

13. From the calibration graph, determine the mass of Cr(VI) in each sample, W (µg), and in the average blank, B (µg).
14. Calculate the concentration, C (mg/m^3), of Cr(VI) in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated with three sets of 16 filter samples which were collected from a chromate-containing paint aerosol [2]. The average amount of Cr(VI) on the filter ranged from 24 to 62 micrograms. Half of the samples were analyzed by this method while the other half were analyzed by Method 7300 (ICP). The results were not significantly different at the 95% confidence level. To examine sample stability, selected members of a fourth set of filters were analyzed and the remainder were stored for two weeks under cover in a constant temperature and constant humidity environment. Comparison of the results of analysis before and after storage indicated that the amount of Cr(VI) did not change during this period.

REFERENCES:

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

[2] Molina, D. and M. T. Abell. An Ion Chromatographic Method for Isoluble Chromium in Paint Aerosol. Am. Ind. Hyg. Assoc. J. 48:830-835 (1987).

METHOD WRITTEN BY: Daniel Molina and Martin T. Abell, NIOSH/DPSE.

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FORMULA: $C_3H_3N_3O_3$

M.W.: 129.08

CYANURIC ACID

METHOD: 5030

ISSUED: 5/15/89

OSHA: no standard
NIOSH: no recommended exposure limit
ACGIH: no TLV

PROPERTIES: solid; d 2.50 g/mL @ 20 °C; MP >330 °C; VP not significant

SYNONYMS: 2,4,6-trihydroxy-1,3,5-triazine; isocyanuric acid; 1,3,5-triazine-2,4,6(1H,3H,5H)-trione; CAS #108-80-5.

SAMPLING

SAMPLER: FILTER
(5-µm PVC membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: ≥69 days at 25 °C [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: cyanuric acid

EXTRACTION: 3 mL 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water (pH = 7.0), 10 min ultrasonic

INJECTION VOLUME: 15 µL

MOBILE PHASE: 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water (pH = 7.0)

DETECTOR: UV, 225 nm

FLOW RATE: 1.5 mL/min

COLUMN: µ-Bondapak C_{18}, 10-µm particles, size; Radial PAK cartridge, 11 cm x 8-mm ID

CALIBRATION: standard solutions of cyanuric acid in mobile phase

RANGE: 1 to 750 µg per sample

ESTIMATED LOD: 0.3 µg per sample

PRECISION (s_r): 0.020 @ 12 to 412 µg per sample [1]

APPLICABILITY: The working range is 0.01 to 10 mg/m^3 for a 100-L air sample.

INTERFERENCES: Trichloroisocyanuric acid interferes because it reacts with water (which is present in the eluent used for recovery) to form cyanuric acid.

OTHER METHODS: None identified for air analysis. HPLC method for measurement in solution is a variation of the method of Briggle et al. [2].

REAGENTS:

1. Cyanuric acid, ≥98% pure.*
2. Water, distilled.
3. Methanol, chromatographic quality.*
4. $Na_2HPO_4 \cdot 7H_2O$, reagent grade.
5. HCl, 1 M (aqueous).
6. Eluent and mobile phase: 0.005 M Na_2HPO_4, 5:95 (v:v) methanol:water at pH = 7.0. Dissolve 5.36 g of $Na_2HPO_4 \cdot 7H_2O$ in 2000 mL water. Add 200 mL methanol. Add water until total volume is 3990 mL. Add 1 M HCl until pH is 7.0.
7. Calibration stock solution, 1 mg/mL. Dissolve 25 mg cyanuric acid in eluent to make 25 mL solution. Prepare fresh monthly.
   NOTE: Ultrasonic bath will facilitate dissolution of cyanuric acid.
8. Recovery stock solution, 1.7 µg/µL. Dissolve 42.5 mg cyanuric acid in water to make 25 mL solution.
   NOTE: Ultrasonic bath will facilitate dissolution of cyanuric acid.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm, 5-µm polyvinyl chloride (PVC) membrane filter in 2-piece cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC), UV absorption detector, 225 nm, recorder, intergrator and column (page 5030-1).
4. Vials, 4-mL, with PTFE-lined caps.
5. Volumetric flasks, 25-mL.
6. Carboy, 4-L.
7. Graduated cylinders, 1-L, readable to 10-mL; 250-mL; readable to 2 mL.
8. Syringes, 500-µL, readable to 10 µL; 100-µL, readable to 1 µL; 10-µL, readable to 0.1 µL.
9. Beakers, 50-mL, internal diameter ≥37 mm.
10. Ultrasonic water bath.
11. Film, plastic, flexible, water-resistant.
12. Filter units, 25-mm PTFE membrane, 0.45-µm pore size, in polypropylene housing.
13. Vacuum oven.
14. Tweezers.
15. pH meter.
16. Adhesive tape.

SPECIAL PRECAUTIONS: Cyanuric acid is a possible tumorigenic agent and a slight eye irritant [3,4]. Methanol is toxic. Ingestion of methanol may cause blindness or death. Methanol is a fire hazard (flash point 12 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 1000 L. Limit the maximum loading of particulate matter on the filter to about 1 mg.
4. Seal the ends of the sampler with plugs. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the PVC filter face down into a 50-mL beaker (the filter should lie flat on the bottom of the beaker). Retain the cassette filter holder (step 9).
6. Add 3 mL eluent to the beaker. Seal the mouth of the beaker with plastic film.
   NOTE: The volume of 3 mL is sufficient when the quantity of cyanuric acid on the filter is 1 mg or less. The limit of solubility of cyanuric acid in eluent is about 2 mg/mL at room temperature.
7. Place the beaker into an ultrasonic bath for 10 min.
8. Filter the solution.

9. If cyanuric acid is found on the PVC filter (steps 13 and 14), prepare additional sample solution by treatment of the interior surface of the front piece of the cassette filter holder with eluent.
   NOTE: The quantity of cyanuric acid collected on the interior surface of the front piece of the cassette filter holder may be significant (see EVALUATION OF METHOD).
   a. Use adhesive tape to secure in place the plug in the inlet of the front piece of the cassette filter holder.
   b. Add eluent (ca. 6 mL) to the front piece until about 95% of the interior surface is in contact with eluent.
   c. Place the front piece into an ultrasonic bath for 5 min.
   d. Transfer the solution from the front piece to a beaker, seal the mouth of the beaker with plastic film, and place the beaker into an ultrasonic water bath for 10 min.
      NOTE: Solid particles may be present in the solution after the first 5 min of ultrasonic agitation. Transfer of the solution to a beaker helps protect the solution from contamination.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least eight working standards over the range 0.1 to 250 µg cyanuric acid per mL of solution.
    a. Prepare a series of working standards in vials from calibration stock solution and eluent by serial dilution.
       NOTE: Working standards may be stored at -3 °C for at least 18 days without deterioration.
    b. Analyze together with samples and blanks (steps 13 and 14).
    c. Prepare calibration graph (peak area or height vs. concentration of cyanuric acid).
11. Determine recovery (R) at least once for each lot of PVC membrane filters used for sampling in the calibration range (step 10). Prepare three filters at each of five levels plus three media blanks.
    a. Place an aliquot of recovery stock solution onto a PVC filter which is situated in the back piece of a cassette filter holder. If the volume of the aliquot is greater than 15 µL, transfer the aliquot to the filter in portions which are about 15 µL in size.
       NOTE: Portions of stock solution will appear as beads on the filter. A maximum of about sixteen 15-µL portions of solution can be distributed on the filter. Thus, a maximum of about 400 µg of cyanuric acid can be applied to the filter with the recovery stock solution. A recovery stock solution which has a much higher concentration of cyanuric acid in water at room temperature can not be prepared because the limit of solubility of cyanuric acid in water at room temperature is about 2.5 mg/mL. If higher loadings are needed, allow the first portions to dry and repeat the process.
    b. Join the front piece of the cassette filter holder with the back piece. Remove the plug from the inlet.
    c. Carefully transfer the filter holder to a vacuum oven.
    d. Dry the filter at about 65 °C and 40 kPa (300 mm Hg). Filter will be dry in ca. 0.3 to 4.5 hrs.
    e. Prepare sample (steps 5 through 8) and analyze with working standards (steps 13 and 14).
    f. Prepare a graph of R vs. µg cyanuric acid recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

13. Set liquid chromatograph to manufacturer's recommendations and to conditions given on page 5030-1. Inject sample aliquot manually or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
14. Measure peak area or peak height.

CALCULATIONS:

15. Determine the mass, µg (corrected for R), of cyanuric acid found on the filter (W_f) and on the average media blank (B_f).
16. Determine the mass, µg, of cyanuric acid found on the interior surface of the cassette filter holder (W_c) and on the interior surface of a blank cassette filter holder (B_c).
17. Calculate concentration, C, of cyanuric acid in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Average recoveries after fortification of 37-mm PVC membrane filters with 12-, 36-, and 412-µg quantities of cyanuric acid were 0.98, 1.00, and 1.00, respectively; precision (s_r) was 0.020 (16 samples, pooled). The average recovery of 36-µg quantities of cyanuric acid from PVC filters after 22 days of storage at room temperature was 1.08; s_r was 0.065 (5 samples). Recovery of 1.08 was not significantly different from 1.00 at the 95% confidence level. Recoveries of 10-, 80-, 200-, and 400-µg quantities of cyanuric acid were 0.88, 1.04, 0.98 and 0.98, respectively, after storage of fortified PVC filters for 69 days at room temperature (one sample at each level). This method was not evaluated with controlled atmospheres in a laboratory. However, the method was employed for measurement of cyanuric acid in air at a plant in which trichloroisocyanuric acid was manufactured from cyanuric acid [5]. Significant quantities (ca. 40% of the totals) of cyanuric acid were found on interior surfaces of the front pieces of cassette filter holders.

Working standards of cyanuric acid at concentrations near 1 µg/mL in eluent deteriorated in about 3 weeks during storage at room temperature; standards were stable for at least 18 days during storage at -3 °C. Deterioration of a C_{18} analytical column took place and caused the LOD of cyanuric acid to increase from 0.1 to 0.25 µg/mL during 6 weeks.

Trichloroisocyanuric acid is an interference because it reacts with water (present in the eluent) to form cyanuric acid. Average yields of cyanuric acid after treatment of 8.4-, 64-, and 424-µg quantities of trichloroisocyanuric acid with eluent in glass vials were 74%, 89%, and 93%, respectively.

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METHOD WRITTEN BY: Samuel P. Tucker, Ph.D., NIOSH/DPSE.

FORMULA: Table 1 | DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE

METHOD: 2540

M.W.: Table 1 | ISSUED: 5/15/89

OSHA/NIOSH/ACGIH: Table 1 | PROPERTIES: Table 1

SYNONYMS: Diethylenetriamine: DETA; aminoethylethandiamine; 3-azapentane-1,5-diamine; bis(2-aminoethyl)amine; CAS #111-40-0.
Ethylenediamine: EDA; 1,2-diaminoethane, 1,2-ethanediamine, CAS #107-15-3.
Triethylenetetramine: TETA; 1,4-diazabicyclo(2,2,2)octane; DABCO; 1,4-ethylenepiperazine; CAS #280-57-9.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (1-naphthylisothiocyanate-coated XAD-2, 80 mg/40 mg)

FLOW RATE: 0.01 to 0.1 L/min [1]

VOL-MIN: 1 L @ 10 ppm
-MAX: 20 L

SHIPMENT: routine

SAMPLE STABILITY: >30 days @ 20 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: DETA: 0.016 to 8 mg/m^3;
EDA: 0.040 to 47 mg/m^3;
TETA: 0.026 to 12 mg/m^3 [1]
(10-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.06 [1]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: naphthylisothiourea derivative of analytes

DESORPTION: 2 mL dimethylformamide (DMF), ultrasonic 30 min

INJECTION VOLUME: 10 µL

COLUMN: 10 µm radial cyano, 10 cm x 8 mm ID in Waters RCM-100 radial compression module

MOBILE PHASE: EDA, 80/20 isoctane/isopropanol; DETA and TETA, 50/50 isoctane/isopropanol at 3 mL/min

CALIBRATION: standard solutions of derivatives in DMF

RANGE: DETA: 1 to 80 µg per sample;
EDA: 5 to 465 µg per sample;
TETA: 1 to 119 µg per sample

ESTIMATED LOD: DETA: 0.16 µg per sample;
EDA: 0.9 µg per sample;
TETA: 0.3 µg per sample

PRECISION (s_r): DETA: 0.007; EDA: 0.013; TETA: 0.018 (see EVALUATION OF METHOD)

APPLICABILITY: The working ranges for DETA, EDA and TETA are 0.05 to 150 mg/m^3, 1 to 130 mg/m^3 and 0.08 to 160 mg/m^3 respectively for 10-L air samples. This method is the result of evaluation [2] of OSHA Method #60 for DETA, EDA, TETA [1]. The theoretical capacity of each front section is 1.5 mg of DETA, 1.3 mg of EDA, or 1.6 mg of TETA.

INTERFERENCES: Other primary or secondary amines may react with the sampler coating reagent, and thereby reduce the sampler capacity.

OTHER METHODS: This replaces NIOSH Method P&CAM 276 [3]. The method of Anderson, et al., for EDA [4] is an alternate method using thiourea derivatization and HPLC analysis.

REAGENTS:

1. XAD-2 resin, reagent grade.
2. 1-Naphthylisothiocyanate (NTIC), reagent grade.
3. Methylene chloride, reagent grade.
4. Dimethylformamide (DMF), HPLC grade.
5. Isooctane, HPLC grade.
6. Isopropanol, HPLC grade.
7. Ethylenediamine (EDA),* high purity.
8. Diethylenediamine (DETA),* high purity.
9. Triethylenetetramine (TETA),* high purity.
10. Calibration stock solution, 4.8 mg/mL DETA, 4.50 mg/mL EDA, 4.9 mg/mL TETA. Dissolve 95.4 mg DETA, 90.0 mg EDA and 98.2 mg TETA in 600 mg of NTIC, allow to react for at least 60 minutes, and dilute to 20 mL with DMF.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing 2 sections of 16/50 mesh XAD-2 resin coated with 10% 1-naphthyl-isothiocyanate (front = 80 mg; back = 40 mg) separated by a plug of PTFE wool (see APPENDIX).
2. Personal sampling pump calibrated to 0.01 to 0.1 L/min.
3. High performance liquid chromatograph (HPLC), UV, 254 nm, cyano column and integrator (page 2540-1).
4. Vials, 4-mL.
5. Syringes, microliter, readable to 0.1 µL
6. Pipets, 2-mL..
7. Flasks, volumetric, 25- and 50-mL.
8. Ultrasonic water bath.

SPECIAL PRECAUTIONS: The vapors of these amines are painful and irritating to the eyes, nose, throat, and respiratory system. The liquids can cause severe damage to the eye and serious burns to the skin. [1,5]

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling.
3. Attach the sampler to personal sampling pump with flexible tubing.
4. Sample at an accurately known flow rate between 0.01 to 0.1 L/min for a total sample size of 1 to 20 L.
5. Cap the sampler and pack securely for shipment.

SAMPLE PREPARATION:

6. Transfer each sorbent section individually to 4-mL sampling vials.
7. Add 2.0 mL DMF to each vial.
8. Agitate in an ultrasonic water bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards in the range of the samples.
   a. Prepare working standards by serial dilution of the stock standards with DMF.
   b. Analyze together with samples, blanks, and QC samples (steps 12 and 13).
   c. Prepare separate calibration graph (peak area vs. µg per sample) for EDA, DETA, TETA.
10. Determine the desorption efficiency (DE) at least once for each lot of XAD-2 resin used for sampling. Prepare three tubes at each of five levels plus 3 media blanks.
    a. Inject a known amount of analyte onto the NTIC-coated resin.
    b. Allow to stand overnight.
    c. Desorb and analyze together with working standards.
    d. Prepare a graph of DE vs. µg amine recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration curve and DE graph are in control.

MEASUREMENT:

12. Set liquid chromatograph according to manufacturer's recommendations and conditions given on page 2540-1.
13. Inject sample aliquot manually or with autosampler. Measure peak area.
    NOTE: If the peak response is above the range of the working standards, dilute the standards with DMF, reanalyze and apply the appropriate dilution factors in calculations.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of each analyte found in the sample front sorbent (W_f) and the sample back sorbent (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.
15. Calculate concentration, C, of each analyte in the air volume sampled, (L):

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

EVALUATION OF METHOD:

This method was developed by and subjected to the evaluation procedures of the OSHA Organics Methods Evaluation Branch [1]. NIOSH evaluated the method for recovery, storage stability, precision, and accuracy and found comparable results [2]. The detection limits obtained by OSHA [1] corresponded to air concentrations of 0.004 ppm, 0.15 ppm, and 0.004 ppm for DETA, EDA, and TETA repectively for a 10-L air volume. The method was validated over the range of 0.8 to 80 µg/sample for DETA, 4.6 to 465 µg/sample for EDA, and 1.3 to 119 µg/sample for TETA [1]. Desorption efficiency studies as performed by OSHA [1] using 6 samples at 3 levels gave a recovery of 99.0% for DETA, 99.2% for EDA, and 99.8% for TETA. The recovery of DETA, EDA, and TETA from samples used in a 15-day storage study was 87, 92, and 89% respectively. These samples were generated by spiking the amines onto a glass wool plug in front of a sampling tube and drawing approximately 10 liters of air at 80% relative humidity through them. A 30-day storage study conducted by NIOSH [2] showed similar recoveries. Collection efficiency studies were done [1] by drawing 10-L of air at 80% relative humidity through Teflon wool plugs positioned ahead of the samplers and spiked with the pure amine. No DETA or TETA was found on the back section with a loading of 57.2 µg of DETA or 32.5 µg of TETA. At a loading of 414 µg of EDA, the back section was found to contain 12.2 µg of EDA.

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METHOD WRITTEN BY: Charles Neumeister, NIOSH/DPSE.

Table 1. General information:

Compound [Formula]	M.W.	Exposure Limits, ppm OSHA	NIOSH	ACGIH	Properties
Diethylenetriamine (DETA) $[H_2N(CH_2)_2NH(CH_2)_2NH_2]$	103.2	1	1 (skin)	1 (skin)	liquid; 0.96 g/mL @ 20 °C; BP 206.7 °C; VP 0.05 kPa (0.37 mm Hg); flash point 98 °C
Ethylenediamine (EDA) $[H_2N(CH_2)_2NH_2]$	60.1	10	10	10 TWA	liquid; 0.90 g/mL @ 20 °C; BP 116–117 °C; VP 1.43 kPa (10.7 mm Hg); flash point 40 °C
Triethylenetetramine (TETA) $[H_2N(CH_2CH_2NH)_2(CH_2)_2NH_2]$	146.2	No PEL	No REL	No TLV	liquid; 0.98 g/mL @ 20 °C; BP 277.4 °C; VP unknown; flash point 118 °C

APPENDIX:

PREPARATION OF NTIC-COATED XAD-2 RESIN:

a. Weigh sufficient XAD-2 resin (16/50 mesh) to allow preparation of tubes for sampling, blanks, quality control, and recovery studies. (@ 120 mg XAD resin per tube).
b. Dissolve sufficient 1-naphthylisothiocyanate in methylene chloride to coat the XAD-2 resin at a 10% loading (w/w).
c. Place the XAD-2 resin in the NTIC solution, mix, and remove methylene chloride using rotary evaporation.
d. Load the coated XAD-2 resin into 7 cm long, 6-mm OD, 4-mm ID, glass tubes so that the front section contains 80 mg and back section contains 40 mg. Use PTFE-wool plugs to separate and contain the two sections. Cap the finished tubes with plastic caps.

FORMULA: $C_{12}H_8OCl_6$

ENDRIN

NIOSH METHOD: 5519

M.W.: 380.93

ISSUED: 5/15/89

OSHA: 0.1 mg/m^3 (skin)
NIOSH: 0.1 mg/m^3 (skin)
ACGIH: no TLV

PROPERTIES: crystals; MP 200 °C; decomposes @ 245 °C; VP 0.27 x 10^{-7} kPa (2×10^{-7} mm Hg) @ 25 °C

SYNONYMS: CAS #72-20-8.

SAMPLING

SAMPLER: FILTER AND SOLID SORBENT TUBE
(0.8 µm cellulose ester membrane + Chromosorb 102, 100/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 12 L @ 0.1 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovered after 1 week @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.06 to 0.31 mg/m^3 [1,2]
[120-L samples]

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): 0.071 [1,2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: endrin

EXTRACTION: 5 mL toluene, stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 280 °C
-COLUMN: 160 °C

CARRIER GAS: 95% argon/5% methane @ 60 mL/min

COLUMN: 2 m x 4-mm ID glass, packed with 3% OV-1 on 100/120 Chromosorb Q

CALIBRATION: standard solutions of endrin in toluene

RANGE: 1.2 to 36 µg per sample [1]

ESTIMATED LOD: 0.02 µg per sample [2]

PRECISION (s_r): 0.016 @ 1.2 to 24.5 µg per sample [2]

APPLICABILITY: The working range is 0.01 to 0.33 mg/m^3 for a 120-L air sample. Smaller concentrations can be determined if desorption efficiency is satisfactory.

INTERFERENCES: None identified.

OTHER METHODS: This is a modification of the method of Hill and Arnold [3] and it replaces NIOSH method S284 [1].

REAGENTS:

1. Toluene, ACS reagent grade or better.
2. Hexane, ACS reagent grade or better.
3. Xylene, ACS reagent grade or better.
4. Endrin.*
5. Calibration stock solution, 3 mg/mL. Dissolve 30 mg endrin in 1 mL xylene and dilute to 10 mL with hexane.
6. 95% Argon/5% methane mixture, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: train consisting of a 37-mm, 0.8-µm pore size MCEF filter supported by a stainless steel screen in cassette filter holder followed by a 7 cm x 8-mm OD x 6-mm ID, glass tube, flame-sealed with plastic caps, containing 20/40 mesh Chromosorb 102 (front = 100 mg; back = 50 mg), separated by 3-mm silanized glass wool plug. Pressure drop across the tube at 1 L/min must not exceed 2.5 cm of mercury. Tubes commercially available (SKC #226-49-20-102 or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator and column (page 5519-1).
4. Vials, glass, scintillation, 20-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1-µL.
6. Volumetric flasks, 10-mL.
7. File, triangular.
8. Pipets, 5- and 10-mL.
9. Tweezers.

SPECIAL PRECAUTIONS: Endrin is absorbed through the skin. Gloves and eyeglasses must be used to avoid direct contact with this compound. Handle all chemicals and organic solvents in the laboratory hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the Chromosorb tube (ends broken just before connection) to the cassette. Connect the tube to the pump with backup section nearest the sampling pump.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 12 to 400 L.
4. Remove the cassette from the sampling train, carefully remove the filter from the cassette with tweezers and place it in a clean vial. Reassemble the cassette and plug the inlet and outlet.
5. Score the Chromosorb tube in front of the front section and break the tube at score line. Transfer the front (larger) section of sorbent and the glass wool plug into the scintillation vial containing the filter.
6. Cap the ends of the sampling tube containing the backup section and ship along with the sample vial.
7. In a separate package, ship bulk sample of the suspected material in a vial.

SAMPLE PREPARATION:

8. Transfer the backup sorbent section and associated glass wool plugs to a clean vial.
9. Add 5.0 mL toluene to each vial containing filter + front sorbent section or back sorbent section. Cap each vial. Allow to stand, with occasional swirling, for 15 min.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (e.g., closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 0.5 to 16 L/min [8]. Adjust sampling rate, Q (L/min), and time, t (min), to produce fiber density, E, of 100 to 1300 fibers/mm^2 [$3.85 \bullet 10^4$ to $5 \bullet 10^5$ fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum accuracy. Do not exceed ca. 0.5 mg total dust loading on the filter. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \bullet E}{Q \bullet L \bullet 10^3}, \text{ min.}$$

   NOTE: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs (700 to 2800 L) is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust [8].
5. At the end of sampling, replace top cover and small end caps.
6. Ship samples upright with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

7. Remove three circular sections from any quadrant of each sample and blank filter using a cork borer [9]. The use of three grid preparations reduces the effect of local variations in dust deposit on the filter.
8. Affix the circular filter sections to a clean glass slide with a gummed page reinforcement. Label the slide with a waterproof marking pen.
   NOTE: Up to eight filter sections may be attached to the same slide.
9. Place the slide in a petri dish which contains several paper filters soaked with 2 to 3 mL acetone. Cover the dish. Wait 2 to 4 min for the sample filter(s) to fuse and clear.
   NOTE: The "hot block" clearing technique [10] of Method 7400 or the DMF clearing technique [11] may be used instead of steps 8 and 9.
10. Transfer the slide to a rotating stage inside the bell jar of a vacuum evaporator. Evaporate a 1- by 5-mm section of a graphite rod onto the cleared filter(s). Remove the slide to a clean, dry, covered petri dish [9].
11. Prepare a second petri dish as a Jaffe wick washer with the wicking substrate prepared from filter or lens paper placed on top of a 12-mm thick disk of clean, spongy polyurethane foam [12]. Cut a V-notch on the edge of the foam and filter paper. Use the V-notch as a reservoir for adding solvent.
    NOTE: The wicking substrate should be thin enough to fit into the petri dish without touching the lid.
12. Place the TEM grids face up on the filter or lens paper. Label the grids by marking with a pencil on the filter paper or by putting registration marks on the petri dish halves and marking with a waterproof marker on the dish lid. In a fume hood, fill the dish with acetone until the wicking substrate is saturated.
    NOTE: The level of acetone should be just high enough to saturate the filter paper without creating puddles.

13. Remove about a quarter section of the carbon-coated filter from the glass slide using a surgical knife and tweezers. Carefully place the excised filter, carbon side down, on the appropriately-labeled grid in the acetone-saturated petri dish. When all filter sections have been transferred, slowly add more solvent to the wedge-shaped trough to raise the acetone level as high as possible without disturbing the sample preparations. Cover the petri dish. Elevate one side of the petri dish by placing a slide under it (allowing drops of condensed acetone to form near the edge rather than in the center where they would drip onto the grid preparation).

CALIBRATION AND QUALITY CONTROL:

14. Determine the TEM magnification on the fluorescent screen:
    a. Define a field of view on the fluorescent screen either by markings or physical boundaries.
       NOTE: The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric) [12].
    b. Insert a diffraction grating replica into the specimen holder and place into the microscope. Orient the replica so that the grating lines fall perpendicular to the scale on the TEM fluorescent screen. Ensure that goniometer stage tilt is zero.
    c. Adjust microscope magnification to 10,000X. Measure the distance (mm) between the same relative positions (e.g., between left edges) of two widely-separated lines on the grating replica. Count the number of spaces between the lines.
       NOTE: On most microscopes the magnification is substantially constant only within the central 8- to 10-cm diameter region of the fluorescent screen.
    d. Calculate the true magnification (M) on the fluorescent screen:

$$M = \frac{X \cdot G}{Y}$$

       where: X = total distance (mm) between the two grating lines;
              G = calibration constant of the grating replica (lines/mm);
              Y = number of grating replica spaces counted
    e. After calibration, note the apparent sizes of 0.25 and 5.0 µm on the fluorescent screen. (These dimensions are the boundary limits for counting asbestos fibers by phase contrast microscopy.)
15. Measure 20 grid openings at random on a 200-mesh copper grid by placing a grid on a glass slide and examining it under the PCM. Use the Walton-Beckett graticule to measure the grid opening dimensions. Calculate an average graticule field dimension from the data and use this number to calculate the graticule field area for an average grid opening.
    NOTE: A grid opening is considered as one graticule field.
16. Obtain reference selected area electron diffraction (SAED) or microdiffraction patterns from standard asbestos materials prepared for TEM analysis.
    NOTE: This is a visual reference technique. No quantitative SAED analysis is required [12]. Microdiffraction may produce clearer patterns on very small fibers or fibers partially obscured by other material.
    a. Set the specimen holder at zero tilt.
    b. Center a fiber, focus, and center the smallest field-limiting aperture on the fiber. Use a 20-cm camera length and 10X binocular head. Obtain a diffraction pattern. Photograph each distinctive pattern and keep the photo for comparison to unknowns.
       NOTE: Not all fibers will present diffraction patterns. The objective lens current may need adjustment to give optimum pattern visibility. There are many more amphiboles which give diffraction patterns similar to the analytes named on p.7402-1. Some, but not all, of these can be eliminated by chemical separations. Also, some non-amphiboles (e.g., pyroxenes, some talc fibers) may interfere.

10. Wash the filter cassette parts as follows: Pipet 10.0 mL hexane into a clean vial and mark the level. Remove the contents and allow to dry. Place the bottom part-cassette on the open, marked vial. Invert the top part-cassette and place it on the bottom part-cassette. Hold the metal screen over the set-up with clean tweezers. Rinse the screen with 10.0 mL hexane, allowing the rinse to drain from top cassette through bottom cassette to the marked vial. Remove any remaining rinse from the cassette parts with clean disposable pipet and deposit in the marked vial. Dilute with hexane to the marked levels. Cap immediately. NOTE: Analysis should be done within 24 hours of desorption.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least five working standards covering the range of samples.
    a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark. Use serial dilution as needed to obtain endrin concentration in the range 0.004 to 7 µg/mL.
    b. Analyze (steps 14 through 16) the working standards and blank in duplicate.
    c. Prepare a calibration graph (peak area vs. mg/mL endrin); analyze two additional check standards for each ten sample injections.
12. Determine the analytical method recovery at least once for each lot of filter and Chromosorb 102 used. Prepare four samplers at each of five levels plus three media blanks.
    a. Place a MCEF filter and 100 mg of Chromosorb 102 in a vial.
    b. Inject calibration stock solution onto the combined filter and Chromosorb 102 in the container with a microliter syringe. Include blank samples.
    c. Cap the vial and let stand overnight.
    d. Analyze in duplicate; prepare graph of recovery vs. mass of endrin.
13. Check recovery at two levels for each sample set in duplicate. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

14. Set gas chromatograph to conditions given on page 5519-1.
15. Inject 5 µL sample aliquot using solvent flush technique. Make duplicate injections of sample and standards.
    NOTE: Under these conditions, t_r for endrin is ca. 5 min.
16. Measure peak areas.

CALCULATIONS:

17. Calculate the mass of endrin found on the sampler (filter plus front section of Chromosorb 102), W_1 (µg); back section of Chromosorb tube, W_2 (µg); media blank (filter plus Chromosorb 102 tube), B (µg); and the rinse from cassette holder and screen, F(µg), from the measured peak areas and the calibration graph.
18. Calculate the concentration of endrin, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_1 + W_2 + F - B)}{V}, \ mg/m^3$$

EVALUATION OF METHOD:

Method S284 was validated on July 8, 1979 [1,2,4]. The substances used to dynamically generate test atmospheres at 25 °C and 760 mm Hg was: 1.6 EC, Velsicol Chemical Corporation. Collection efficiencies were close to 1.00 in the range 28 to 33 µg per sample. The analytical recoveries from sorbent tubes (range: 1.2 to 6.1 µg per sample) and from the filter sampler (range: 6.1 to 24.5 µg per sample) were 99% with a combined precision of 0.016. No significant breakthrough was observed after 240 min of sampling an atmosphere containing 0.257 mg/m^3 endrin at a flow rate of approximately 1 L/min. Samples stored one week at room temperature and extracted with toluene gave recoveries of 96 to 100%. Overall precision (s_r) was 0.07. No significant bias was found.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, S284, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[2] NIOSH Backup Data Report S284 (July 8, 1979).

[3] Hill, R. H. and J. E. Arnold., "A Personal Air Sampler for Pesticides", Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).

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

METHOD REVISED BY: Gangadhar Choudhary, Ph.D., NIOSH/DPSE; S284 originally validated under NIOSH Contract NO. 210-76-0123.

FORMULA: various

M.W.: various

FIBERS

METHOD: 7400

ISSUED: 2/15/84

REVISION #3: 5/15/89

PROPERTIES: solid, fibrous

OSHA: 0.2 asbestos fiber (≥5 µm long)/cc;
1 asbestos fiber/cc/30 minute excursion [1]

MSHA: 2 asbestos fibers (>5 µm long)/cc [2]

NIOSH: carcinogen; control to lowest level possible [3]; 3 glass fibers (>10 µm x <3.5 µm)/cc [4]

ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc [5]

SYNONYMS: actinolite [CAS #13768-00-8] or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos; fibrous glass.

SAMPLING

SAMPLER: FILTER
(0.45- to 1.2-µm cellulose ester membrane, 25-mm diameter; conductive cowl on cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust to give 100 to 1300 fibers/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.115 to 0.13 [7]

MEASUREMENT

TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone/triacetin "hot block" method [6]

COUNTING RULES: Described in previous version of this method as A rules [1,7]

EQUIPMENT: 1. Positive phase-contrast microscope
2. Walton-Beckett graticule (100-µm field of view) Type G-22
3. phase-shift test slide (HSE/NPL)

CALIBRATION: HSE/NPL test slide

RANGE: 100 to 1300 fibers/mm^2 filter area

ESTIMATED LOD: 7 fibers/mm^2 filter area

PRECISION: 0.10 to 0.12 [7]; see EVALUATION OF METHOD

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. The method gives an index of airborne fibers. It is primarily used for estimating asbestos concentrations, though PCM does not differentiate between asbestos and other fibers. Use this method in conjuction with electron microscopy (e.g., Method 7402) for assistance in identification of fibers. Fiber <ca. 0.25 µm diameter will not be detected by this method [8]. This method may be used for other materials such as fibrous glass by using alternate counting rules (see Appendix C).

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility. It replaces P&CAM 239 [7,9] and NIOSH Method 7400, Revision #2 (dated 8/15/87).

REAGENTS:

1. Acetone.*
2. Triacetin (glycerol triacetate), reagent grade.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl and cellulose ester filter, 0.45- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean is ≥5 fibers per 100 graticule fields. These are defined as laboratory blanks. Manufacturer-provided quality assurance checks on filter blanks are normally adequate as long as field blanks are analyzed as described below.
   NOTE 2: The electrically-conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling [10].
   NOTE 3: Use 0.8-µm pore size filters for personal sampling. The 0.45-µm filters are recommended for sampling when performing TEM analysis on the same samples. However, their higher pressure drop precludes their use with personal sampling pumps.
2. Sampling pump, 0.5 to 16 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, positive phase (dark) contrast, with green or blue filter, adjustable field iris, 8 to 10X eye-piece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, frosted-end, pre-cleaned, 25- x 75-mm.
5. Cover slips, 22- x 22-mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Lacquer or nail polish.
7. Knife, #10 surgical steel, curved blade.
8. Tweezers.
9. Heated aluminum block for clearing filters on glass slides (see ref. [6] for specifications or see manufacturer's instructions for equivalent devices).
10. Micropipets, 5-µL and 100- to 500-µL.
11. Graticule, Walton-Beckett type, 100-µm diameter circular field (area = 0.00785 mm^2) at specimen plane (Type G-22). Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 [phone (617) 891-6000] and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. (See Appendix A for the custom-ordering procedure).
12. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd. (address above).
13. Telescope, ocular phase-ring centering.
14. Stage micrometer (0.01-mm divisions).
15. Wire, multi-stranded, 22-gauge.
16. Tape, shrink- or adhesive-.

SPECIAL PRECAUTIONS: Acetone is extremely flammable. Take precautions not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. For personal sampling, fasten sampler to the worker's lapel near the worker's mouth. Remove top cover from cowl extension ("open-face") and orient face down. Wrap joint between cowl and monitor body with tape to help hold the cassette together, keep the joint free of dust, and provide a marking surface to identify the cassette.

   NOTE: If possible, ground the cassette to remove any surface charge, using a wire held in contact (e.g., with a hose clamp) with the conductive cowl and an earth ground such as a cold-water pipe.
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Handle field blanks in the same fashion as other samplers. Open field blank cassettes at the same time as other cassettes just prior to sampling. Store top covers and cassettes in a clean area with the top covers from the sampling cassettes during the sampling period.
4. Sample at 0.5 L/min or greater [11]. Adjust sampling flow rate, Q (L/min), and time, t(min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 ($3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area A_c= 385 mm^2) for optimum accuracy. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

   NOTE 1: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absense of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If $\geq$ 50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.

   NOTE 2: OSHA regulations specify a maximum sampling rate of 2.5 L/min [1].

   NOTE 3: OSHA regulations specify a minimum sampling volume of 48 L for an excursion measurement [1].
5. At the end of sampling, replace top cover and end plugs.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.

   NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE 1: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index of $\leq$1.46. This method collapses the filter for easier focusing and produces relatively permanent mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" or similar flash vaporization techniques may be used outside the laboratory [6]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [3,7,9,12]). A videotape of the mounting procedure is available from the NIOSH Publication Office [13].

NOTE 2: Excessive water in the acetone may slow the clearing of the filters, causing material to be washed off the surface of the filter. Also, filters that have been exposed to high humidities prior to clearing may have a grainy background.

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [6].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.
   b. Insert slide with wedge into the receiving slot at the base of "hot block". Immediately place tip of a micropipet containing ca. 250 µL acetone (use the minimum volume needed to consistently clear the filter sections) into the inlet port of the PTFE cap on top of the "hot block" and inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 sec for the filter to clear, remove pipet and slide from their ports.
      CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous, frequent use of this device in an unventilated space may produce explosive acetone vapor concentrations.
   c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation. Avoid excess pressure and movement of the cover glass.
      NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.
   d. Glue the edges of the cover slip to the slide using lacquer or nail polish [14] Counting may proceed immediately after clearing and mounting are completed.
      NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturer's instructions. At least once daily use the telescope ocular (or Bertrand lens, for some microscopes) supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of calibrations and major servicings.
    a. Each time a sample is examined, do the following:
       (1) Adjust the light source for even illumination across the field of view at the condenser iris. Use Kohler illumination, if available. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contrast optics.
       (2) Focus on the particulate material to be examined.
       (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
    b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
       (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
       (2) Bring the blocks of grooved lines into focus in the graticule area.
           NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible

when centered in the graticule area. Blocks 4 or 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.

(3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.

11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis [15]. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field and PAT samples. The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.
    b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter s_r (step 21). Obtain separate values of relative standard deviation for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, >20 to 50 fibers in 100 graticule fields, >50 to 100 fibers in 100 graticule fields, and 100 fibers in less than 100 graticule fields. Maintain control charts for each of these data files.

    NOTE: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [16]

12. Prepare and count field blanks along with the field samples. Report counts on each field blank.

    NOTE 1: The identity of blank filters should be unknown to the counter until all counts have been completed.

    NOTE 2: If a field blank yields greater than 7 fibers per 100 graticule fields, report possible contamination of the samples.

13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the absolute value of the difference between the square roots of the two counts (in fiber/mm^2) exceeds 2.8 (X) s_r, where X = the average of the square roots of the two fiber counts (in fiber/mm^2) and s_r = one-half the intracounter relative standard deviation for the appropriate count range (in fibers) determined from step 11. For more complete discussions see reference [15].

    NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data [15].

    NOTE 2: If a pair of counts is rejected by this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.

14. The analyst is a critical part of this analytical procedure. Care must be taken to provide a non-stressful and comfortable environment for fiber counting. An ergonomically designed chair should be used, with the microscope eyepiece situated at a comfortable height for viewing. External lighting should be set at a level similar to the illumination level in the microscope to reduce eye fatigue. In addition, counters should take 10 to 20 minute breaks from the microscope every one or two hours to limit fatigue [17]. During these breaks, both eye and upper back/neck exercises should be performed to relieve strain.

15. All laboratories engaged in asbestos counting should participate in a proficiency testing program such as the AIHA-NIOSH Proficiency Analytical Testing (PAT) Program or the AIHA Asbestos Analyst Registry and routinely exchange field samples with other laboratories to compare performance of counters.

    NOTE: OSHA requires that each analyst performing this method take the NIOSH direct training course #582 or equivalent [1]. Instructors of equivalent courses should have attended the NIOSH #582 course at NIOSH within three years of presenting an equivalent course.

MEASUREMENT:

16. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.
17. Adjust the microscope (Step 10).
    NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm) [8].
18. Counting rules: (same as P&CAM 239 rules [3,7,9]; see APPENDIX B).
    a. Count only fibers longer than 5 µm. Measure length of curved fibers along the curve.
    b. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
    c. For fibers which cross the boundary of the graticule field:
       (1) Count any fiber longer than 5 µm which lies entirely within the graticule area.
       (2) Count as 1/2 fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rules a and b above.
       (3) Do not count any fiber which crosses the graticule boundary more than once.
       (4) Reject and do not count all other fibers.
    d. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
    e. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.
19. Start counting from the tip of the filter wedge and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

    NOTE 1: When counting a graticule field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 seconds per field is appropriate for accurate counting.

    NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report <u>total</u> fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters >1 µm), polarized light microscopy techniques may be used to identify and eliminate interfering non-crystalline fibers [18].

    NOTE 3: Under certain conditions, electrostatic charge may affect the sampling of fibers. These electrostatic effects are most likely to occur when the relative humidity is low (below 20%), and when sampling is performed near the source of aerosol. The result is that deposition of fibers on the filter is reduced, especially near the edge of the filter. If such a pattern is noted during fiber counting, choose fields as close to the center of the filter as possible [10].

CALCULATIONS AND REPORTING OF RESULTS:

20. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the average fiber count per graticule field, F/n_f, minus the mean field blank count per graticule field, B/n_b, by the graticule field area, A_f (approx. 0.00785 mm^2):

$$E = \frac{\left(\frac{F}{n_f} - \frac{B}{n_b}\right)}{A_f}, \text{ fibers/mm}^2.$$

NOTE: Fiber counts above 1300 fibers/mm^2 and fiber counts from samples with >50% of filter area covered with particulate should be reported as "uncountable" or "probably biased."

21. Calculate and report the concentration, C (fibers/cc), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (approx. 385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

22. Report intralaboratory and interlaboratory relative standard deviations (Step 11) with each set of results.

NOTE: Precision depends on the total number of fibers counted [7,19]. Relative standard deviation is documented in references [7,18,19,20] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Fig. 1).

EVALUATION OF METHOD:

A. This method is a revision of P&CAM 239 [3,7,9]. A summary of the revisions is as follows:

1. Sampling:
   The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [11].
2. Sample Preparation Technique:
   The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [6,8,9]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
3. Measurement:
   a. The Walton-Beckett graticule standardizes the area observed [21,22,23].
   b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [8,21].
   c. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). Lower levels generally result in an overestimate of the fiber count when compared to results in the recommended analytical range [25]. The recommended loadings should yield intracounter s_r in the range of 0.10 to 0.17 [7,24,26].

B. Interlaboratory comparability:
An international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [16]. The relative standard deviations (s_r) varied with sample type and laboratory. The ranges were:

	s_r		
	Intralaboratory	Interlaboratory	Overall
AIA (NIOSH Rules)*	0.12 to 0.40	0.27 to 0.85	0.46

*Under AIA rules, only fibers having a diameter less than 3 µm are counted and fibers attached to particles larger than 3 µm are not counted. NIOSH Rules are otherwise similar to the AIA rules.

A NIOSH study was conducted using field samples of asbestos [24]. This study indicated intralaboratory s_r in the range 0.17 to 0.25 and an interlaboratory s_r of 0.45. This agrees well with other recent studies [16,19,21].

At this time, there is no independent means for assessing the overall accuracy of this method. One measure of reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the interlaboratory variability, as well as showing how the results of this method relate to the theoretically attainable counting precision and to measured intra- and interlaboratory s_r. (NOTE: The following discussion does not include bias estimates and should not be taken to indicated that lightly loaded samples are as accurate as properly loaded ones).

Theoretically, the process of counting randomly-distributed (Poisson) fibers on a filter surface will give an s_r that depends on the number, N, of fibers counted:

$$s_r = 1/(N)^{1/2} \qquad (1)$$

Thus s_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual s_r found in a number of studies is greater than these theoretical numbers [16,19,20,21].

An additional component of variability comes primarily from subjective interlaboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [18] found this subjective component of intralaboratory s_r to be approximately 0.2 and estimated the overall s_r by the term:

$$\frac{(N + (0.2 \cdot N)^2)^{1/2}}{N} \qquad (2)$$

Ogden found that the 90% confidence interval of the individual intralaboratory counts in relation to the means were +2 s_r and - 1.5 s_r. In this program, one sample out of ten was a quality control sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of field sample results in 46 laboratories, the Asbestos Information Association also found that the variability had both a constant component and one that depended on the fiber count [21]. These results gave a subjective interlaboratory component of s_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [24]. This value falls slightly above the range of s_r (0.25 to 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH Proficiency Analytical Testing (PAT) program for laboratory-generated samples [20].

A number of factors influence s_r for a given laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an interlaboratory quality assurance program using field samples, the value for the subjective component of variability is estimated as 0.45. It is hoped that laboratories will carry out the recommended interlaboratory quality assurance programs to improve their performance and thus reduce the s_r.

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [19].

For example, if a sample yields a count of 24 fibers, Figure 1 indicates that the mean inter-laboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500-L volume, then the measured concentration is 0.02 fibers/mL (assuming 100 fields counted, 25-mm filter, 0.00785 mm^2 field counting area). If this same sample were counted by a group of laboratories, there is a 90% probability that the mean would fall between 0.01 and 0.08 fiber/mL. These limits should be reported in any comparison of results between laboratories.

Note that the s_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory s_r is smaller, then it is more correct to use that smaller s_r. However, the estimated s_r of 0.45 is to be used in the absence of such information. Note also that it has been found that s_r can be higher for certain types of samples, such as asbestos cement [16].

Quite often the estimated airborne concentration from an asbestos analysis is used to compare to a regulatory standard. For instance, if one is trying to show compliance with an 0.5 fiber/mL standard using a single sample on which 100 fibers have been counted, then Figure 1 indicates that the 0.5 fiber/mL standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fiber/mL (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/mL; i.e., $0.16 + 2.13 \times 0.16 = 0.5$.

It can be seen from Figure 1 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use +213% and −49% as the upper and lower confidence values of the mean for a 100-fiber count.

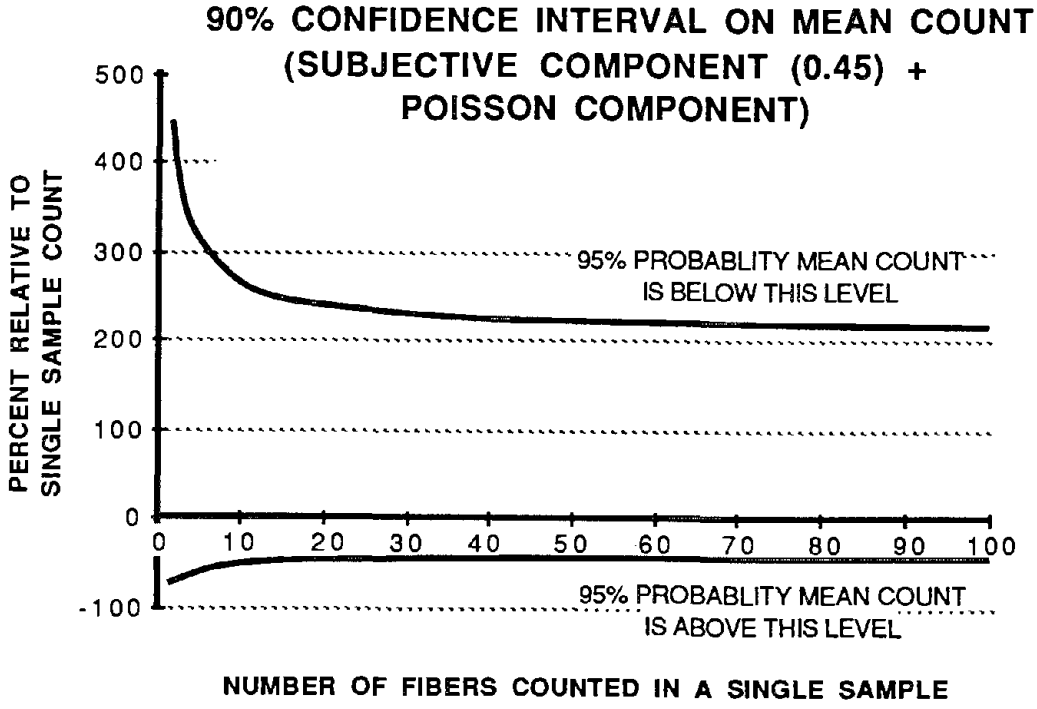

Figure 1. Inter-laboratory Precision of Fiber Counts

The curves in Figure 1 are defined by the following equations

$$UCL = \frac{2x + 2.25 + \sqrt{(2.25 + 2x)^2 - 4(1 - 2.25 s_r^2) x^2}}{2(1 - 2.25 s_r^2)} \quad (3)$$

$$LCL = \frac{2x + 4 - \sqrt{(4 + 2x)^2 - 4(1 - 4 s_r^2) x^2}}{2(1 - 4 s_r^2)} \quad (4)$$

where s_r = subjective inter-laboratory relative standard deviation, which is close to the total inter-laboratory s_r when approximately 100 fibers are counted.

x = total fibers counted on sample

LCL = lower 95% confidence limit

UCL = upper 95% confidence limit.

Note that the range between these two limits represents 90% of the total range.

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METHOD REVISED BY: Paul A. Baron, Ph.D.; NIOSH/DPSE.

APPENDIX A: CALIBRATION OF THE WALTON-BECKETT GRATICULE

Before ordering the Walton-Beckett graticule, the following calibration must be done to obtain a counting area (D) 100 µm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
3. Install the 40 to 45X phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (µm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

Example: If L_o = 112 µm, L_a = 4.5 mm and D = 100 µm, then d_c = 4.02 mm.

8. Check the field diameter, D (acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (acceptable range 0.00754 to 0.00817 mm^2).

APPENDIX B: EXAMPLES OF COUNTING RULES

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. The rules will be discussed as they apply to the labeled objects in the figure.

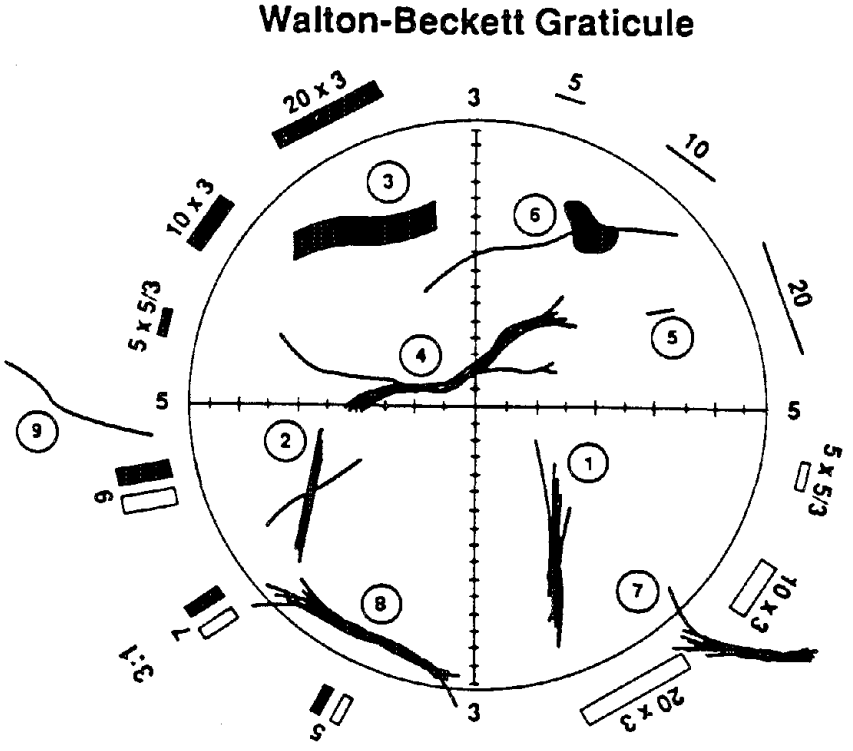

Figure 2. Walton-Beckett graticule with fibers.

FIBER COUNT		
Object	Count	DISCUSSION
1	1 fiber	Optically observable asbestos fibers are actually bundles of fine fibrils. If the fibrils seem to be from the same bundle the object is counted as a single fiber. Note, however, that all objects meeting length and aspect ratio criteria are counted whether or not they appear to be asbestos.
2	2 fiber	If fibers meeting the length and aspect ratio criteria (length >5 μm and length-to-width ratio >3 to 1) overlap, but do not seem to be part of the same bundle, they are counted as separate fibers.
3	1 fiber	Although the object has a relatively large diameter (>3 μm), it is counted as fiber under the rules. There is no upper limit on the fiber diameter in the counting rules. Note that fiber width is measured at the widest compact section of the object.
4	1 fiber	Although long fine fibrils may extend from the body of a fiber, these fibrils are considered part of the fiber if they seem to have originally been part of the bundle.
5	Do not count	If the object is ≤5 μm long, it is not counted.
6	1 fiber	A fiber partially obscured by a particle is counted as one fiber. If the fiber ends emanating from a particle do not seem to be from the same fiber and each end meets the length and aspect ratio criteria, they are counted as separate fibers.
7	1/2 fiber	A fiber which crosses into the graticule area one time is counted as 1/2 fiber.
8	Do not count	Ignore fibers that cross the graticule boundary more than once.
9	Do not count	Ignore fibers that lie outside the graticule boundary.

Appendix C. ALTERNATE COUNTING RULES

Other counting rules may be more appropriate for measurement of specific non-asbestos fiber types, such as fibrous glass. These include the "B" rules (from NIOSH Method 7400, Revision #2, dated 8/15/87), the World Health Organization reference method for man-made mineral fiber [27], and the NIOSH fibrous glass criteria document method [4]. The upper diameter limit in these methods prevents measurements of non-respirable fibers. It is important to note that the aspect ratio limits included in these methods vary. NIOSH recommends the use of the 3:1 aspect ratio in counting fibers.

It is emphasized that hybridization of different sets of counting rules is not permitted. Report specifically which set of counting rules are used with the analytical results.

"B" Counting Rules:

1. Count only ends of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2. Add split ends to the count as appropriate if the split fiber segment also meets the criteria of rules 1 and 2 above.
4. Count visibly free ends which meet rules 1 and 2 above when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 µm in diameter.
5. Count free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules 1 and 2 above.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 graticule fields. Stop at 100 gradicule fields, regardless of count.
7. Divide total end count by 2 to yield fiber count.

FORMULA: $H_2C=O$

M.W.: 30.03

FORMALDEHYDE

METHOD: 2541

ISSUED: 5/15/89

OSHA: 1 ppm; STEL 2 ppm
NIOSH: carcinogen; 0.016 ppm; C 0.1 [1]
ACGIH: 1 ppm; STEL 2 ppm; Suspected Human Carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.067 (air = 1); BP -19.5 °C; explosive range 7 to 73% v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 50% w/v HCHO); CAS #50-00-0.

SAMPLING

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

FLOW RATE: 0.01 to 0.10 L/min

VOL-MIN: 1 @ 3 ppm
-MAX: 36 L

SHIPMENT: routine

SAMPLE STABILITY: 3 weeks @ 25 °C [2]

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 10 per sample set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of formaldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

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

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C for 1 min; 15 °C; hold @ 240 °C for 10 min

CARRIER GAS: He, 1 to 2 mL/min; makeup flow 29 mL/min

COLUMN: capillary, 30 m x 0.32-mm ID, 0.5-µm film, DB-Wax or equivalent

CALIBRATION: formalin solution spiked on sorbent

RANGE: 3 to 200 µg per sample [3,4]

ESTIMATED LOD: 1 µg per sample [3]

PRECISION (s_r): 0.0052 @ 38 to 194 µg per sample [3]

APPLICABILITY: The working range is 0.24 to 16 ppm (0.3 to 20 mg/m^3) for a 10-L air sample. The method is suitable for the simultaneous determinations of acrolein and formaldehyde.

INTERFERENCES: None have been observed. Acid mists may inactivate the sorbent leading to inefficient collection of formaldehyde. A 15-m x 0.32-mm ID DB-1301 fused silica capillary column can also be used. This column will also separate the acetaldehyde and acrolein oxazolidines.

OTHER METHODS: OSHA Method 52 is similar but uses slightly larger sampling tubes [3]. This method has improved sample stability and ease of personal sampling compared to NIOSH Methods 2502 (which has been withdrawn), 3500 and 3501. However, Method 3500 (chromotropic acid) is the most sensitive.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas) or equivalent. Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Formalin solution, 37%*.
5. Formaldehyde* stock solution, 1 mg/mL (see APPENDIX A).
6. Sulfuric acid, 0.02 N.
7. Sodium hydroxide, 0.01 N.
8. Sodium sulfite (Na_2SO_3), 1.13 M. Prepare fresh immediately before use.
9. Water, deionized, distilled.
10. Hydrogen, prepurified.
11. Air, filtered.
12. Helium, purified.
13. Magnesium sulfate.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, with flame-sealed ends and plastic caps, containing two sections of 2-(hydroxymethyl)piperidine-coated XAD-2 (see APPENDIX B) (front = 120 mg; back = 60 mg)retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 Pa (5.7 mm Hg). Tubes are commercially available (Supelco ORBO-23 or equivalent).
2. Personal sampling pump, 0.01 to 0.10 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2541-1).
4. Ultrasonic water bath.
5. Vials, glass, 2-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Syringes, 10-mL (readable to 0.1 mL), 25-, and 50-mL.
9. File.
10. Beakers, 50-mL.
11. pH meter.
12. Magnetic stirrer.
13. Burets, 50-mL.
14. Flasks, round-bottomed, 100-mL.
15. Soxhlet extraction apparatus.
16. Vacuum oven.
17. Distillation apparatus.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen [1,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.10 L/min for a total sample size of 1 to 36 L.
   NOTE: Formaldehyde reacts with 2-(hydroxymethyl)piperidine to form an oxazolidine derivative in the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Sampling above 0.10 L/min may cause appreciable breakthrough due to incomplete reaction, possibly invalidating the sample.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file in front of the first sorbent section.
6. Break sampler at score line. Remove and place front glass wool plug and front sorbent section in a vial.
7. Transfer back section with remaining glass wool plugs to a second vial.
8. Add 1.0 mL toluene to each vial. Crimp cap tightly onto each vial.
   NOTE: An appropriate internal standard, such as 1 µL/mL dimethylformamide, may be added at this point [4].
9. Agitate vials in an ultrasonic water bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least five working standards, in duplicate, covering the range of interest.
    a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from ten unused samplers (media blanks).
    b. Inject aliquots of formaldehyde stock solution into the vials at five different levels and allow to sit overnight at room temperature. Use serial dilutions of the calibration stock solutions to spike the adsorbent in the range of interest.
    c. Desorb (steps 7 through 9) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (peak area or peak height) vs. µg of formaldehyde.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2541-1. Inject 1-µL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene, reanalyze, and apply the appropriate correction factor in calculations..
13. Measure peak area or peak height. For formaldehyde derivative t_r = 6.4 min and for 2-(hydroxymethyl)piperidine t_r = 9.4 min under these conditions.
    NOTE: If necessary, verify the identity of the formaldehyde oxazolidine by the analysis of an anthentic sample (see APPENDIX C).

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of oxazolidine derivative found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C (mg/m^3), of formaldehyde in the air volume sampled, v (L):

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

NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary. Report field blanks as samples.

EVALUATION OF METHOD:

This method is similar to OSHA Method 52 [3]; however, the OSHA samplers contained 20% more coated sorbent than the samplers used in this method. In a study by OSHA, 5% breakthrough occurred after 396 min at a flow rate of 0.1 L/min and a test atmosphere concentration of 5.3 mg/m^3. The relative humidity in the study was 49% at 24 °C. A storage study was done by NIOSH/MRSB [2] by spiking samplers at two concentrations, 10.0 and 61.0 µg/sample [2]. Three spikes at each concentration were stored at different temperatures for seven days. The storage conditions were as follows:

Sample set no.	Storage temp.	Storage time
1	20 °C	7 days
2 (a)	20 °C and 40 °C	1 day
(b)	20 °C	6 days
3	4 °C (refrigeration)	7 days

The recovery of formaldehyde was essentially 100% for all of the storage temperatures.

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METHOD WRITTEN BY: Eugene R. Kennedy, Ph.D., and Karen J. Williams, NIOSH/DPSE.

APPENDIX A: PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0(N_a \cdot V_a - N_b \cdot V_b)}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL).

APPENDIX B: SORBENT PREPARATION (optional if commercially-prepared tubes are used)

Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for ca. 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 12 and 13). No blank peak is expected for any aldehydes other than formaldehyde and possibly acetaldehyde.

APPENDIX C: SYNTHESIS OF FORMALDEHYDE OXAZOLIDINE

Place a solution of purified 2-(hydroxymethyl)piperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2-(hydroxymethyl)piperidine from the container used for weighing. Add magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 1 mL 37% aqueous formaldehyde in 10 mL toluene to the 2-(hydroxymethyl)piperidine solution dropwise with stirring over 1 h. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation.

FORMULA: $H_2C=O$

M.W. = 30.03

FORMALDEHYDE

METHOD: 3500
ISSUED: 2/15/84
REVISION #1: 5/15/89

OSHA: 1 ppm; STEL 2 ppm
NIOSH: carcinogen; 0.016 ppm; C 0.1 [1]
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; BP -19.5 °C; vapor density 1.067 (air = 1.00); explosive range 7 to 73 % v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v HCHO); CAS #50-00-0.

SAMPLING

SAMPLER: FILTER + IMPINGERS
(1-µm PTFE membrane and 2 impingers, each with 20 mL 1% sodium bisulfite solution)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 1 L @ 3 ppm
-MAX: 100 L

SHIPMENT: transfer samples to low-density polyethylene bottles before shipping

SAMPLE STABILITY: 30 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 1.25 to 7.5 mg/m^3 [3]
[80-L samples]

BIAS: none identified

OVERALL PRECISION (s_r): 0.09 [3]

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROMETRY

ANALYTE: formaldehyde

SAMPLE WORKUP: note liquid volume; remove 4-mL aliquot

COLOR DEVELOPMENT: chromotropic acid + sulfuric acid; absorbance @ 580 nm

CALIBRATION: standard solutions of formaldehyde in distilled water

RANGE: 2 to 40 µg per sample [2,3]

ESTIMATED LOD: 0.5 µg per sample [3,4]

PRECISION (s_r): 0.03 @ 1 to 20 µg per sample [4]

APPLICABILITY: The working range is 0.02 to 4 ppm (0.025 to 4.6 mg/m^3) for an 80-L air sample. This is the most sensitive formaldehyde method in the NIOSH Manual and is able to measure ceiling levels as low as 0.1 ppm (15-L sample). It is best suited for the determination of formaldehyde in area samples.

INTERFERENCES: Oxidizable organic materials may give a positive interference [3]. Phenols, in 8-fold excess over formaldehyde, produce a -10% to -20% bias [5]. A method for the removal of the phenol interference has been reported by Hakes et. al. [6]. Ethanol and higher molecular weight alcohols, olefins, aromatic hydrocarbons [7] and cyclohexanone also produce small negative interferences [5]. Little interference is seen from other aldehydes [5].

OTHER METHODS: This revises Method 3500 (dated 2/15/84). This method was originally adapted from the Intersociety Committee [8] and designated P&CAM 125 [5]. For personal samples or where interferences to this method are present, use Method 2541. Method 3501 uses collection in a bubbler followed by polarography. Ref. [9] is a recent review of formaldehyde methods.

REAGENTS:

1. Chromotropic acid,1%. Dilute 0.10 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 mL with distilled water. Filter. Store in brown bottle. Prepare fresh weekly.
2. Sulfuric acid (H_2SO_4), 96%.*
3. Formaldehyde stock solution, 1 mg/mL (See APPENDIX).
4. Formalin solution, 37%.*
5. Distilled, deionized water.
6. Sulfuric acid, 0.02 N, aqueous.
7. Sodium hydroxide, 0.01 N, aqueous.
8. Sodium sulfite, 1.13 M, aqueous. Prepare fresh immediately before use.
9. Sodium bisulfite ($NaHSO_3$), 1%. Dissolve 1 gin distilled water. Dilute to 100 mL. Prepare fresh weekly.
10. Magnesium sulfate.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm polytetrafluoroethylene (PTFE) membrane filter, 1- to 3-µm pore size followed by two midget impingers; inert, flexible tubing for cassette-to-impinger connection.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Bottles, screw-cap, low-density polyethylene (Nalgene CPE or equivalent), 50-mL.
   NOTE: Do not use bottles with "polycone" liners (see step 4)
4. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm.
5. Volumetric pipettes, 0.1-, 0.5-, 1-, 4-, 5-, 6- and 10-mL; 1-, 2- and 5-mL, graduated in 0.1-mL units, with pipet bulb.
6. Volumetric flasks, 10- and 100-mL, and 1-L.
7. Burets, 50-mL.
8. pH meter.
9. Flasks, glass-stoppered, 25-mL.
10. Graduated cylinder, 25-mL.
11. Waterbath at 95 °C.
12. Magnetic stirrer.
13. Beaker, 50-mL.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles. Formaldehyde is viewed as a potential carcinogen [1,10] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the two impingers for each sample with 20 mL 1% sodium bisulfite solution. Make cassette-to-impinger and impinger-to-sampling pump conections with flexible, inert tubing. Insert a second filter/cassette assembly in line between the sampler and sampling pump to trap any liquid which might splash over from the impingers during sampling.
   NOTE: The PTFE filter is necessary when sampling is to be conducted in a dusty environment, which could contribute either a positive or negative interferences to the method. The use of dual impingers in series is recommended to ensure efficient collection of formaldehyde.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 1 to 100 L.
4. Transfer the contents of the impingers to separate low-density polyethylene bottles for shipping.
   NOTE: Sample contamination may occur if glass or polyethylene scintillation vials with "polycone" plastic lined caps are used [11].

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Record volume of solution from front impinger, V_f (mL), backup impinger, V_b (mL), and blank impinger, V_B (mL).
6. Pipette a 4-mL aliquot from each sample solution into 25-mL glass-stoppered flasks.
   NOTE: Adjust aliquot size to contain between 2 and 20 µg formaldehyde for optimum absorbance. The calibration graph becomes non-linear above an absorbance of ca. 1.0.

CALIBRATION AND QUALITY CONTROL:

7. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL with 1% sodium bisulfite solution.
8. Pipet, e.g., 0, 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 mL calibration stock solution into 25-mL glass-stoppered flasks.
9. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL.
10. Analyze together with samples and blanks (steps 12 through 15).
11. Prepare calibration graph (absorbance vs. µg formaldehyde/mL).

MEASUREMENT:

12. Add 0.1 mL 1% chromotropic acid to each flask and mix.
    NOTE: This amount of chromotropic acid can react with ca. 40 µg of formaldehyde. Due to this fact, the range of the calibration curve should not exceed 36 µg (90% of theoretical).
13. Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution to mix.
    CAUTION: Mixing of the sample solution with concentrated sulfuric acid is highly exothermic.
14. Heat the solution to 95 °C for 15 min. Cool the solution to room temperature.
    NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure buildup within the flask.
15. Read sample absorbance at 580 nm in a 1-cm cuvette.
    NOTE: If absorbance is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 4 mL with 1% sodium bisulfite solution, and analyze (steps 12 through 15). For optimum results, all samples containing over 20 ug formaldehyde should be diluted and reanalyzed.

CALCULATIONS:

16. Calculate the mass, µg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and average blank impinger (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot/original volume from step 6) and the total sample volume noted in step 5.
    NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass found in the front impinger. Collection efficiency is ca. 95% for each impinger.
17. Calculate the concentration, C, of formaldehyde in the air volume sampled, V (L):

$$C = \frac{M_f + M_b - 2M_B}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard samples containing between 1 and 20 µg formaldehyde. The results agreed within ± 5% [8]. This method was independently compared with the 2,4,-dinitrophenylhydrozine-coated silica gel method of Beasley et al. [12] over the range of 0.8 to 2.2 ppm formaldehyde and was found to give approximately 25% lower concentrations.

In another study comparing the present method, P&CAM 318 [13], and the method of Beasley, et al., all three methods were found to be statistically equivalent for loadings from 8.2 to 22.4 µg formaldehyde per sample [14]. The method of Septon and Ku [15] was compared with this method . The slope of the correlation line was 1.09. The concentration range of the comparison was not given.

In a study comparing the pararosaniline method [16] and NIOSH P&CAM 125 over the range 0.021 to 0.5 ppm, the NIOSH method gave better collection efficiency and accuracy [17]. Precision for both methods was equivalent.

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METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0(N_a \cdot V_a - N_b \cdot V_b)}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL).

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FORMULA: $H_2C=O$

M.W. = 30.03

FORMALDEHYDE

METHOD: 3501
ISSUED: 2/15/84
REVISION #1: 5/15/89

OSHA: 1 ppm; STEL 2 ppm
NIOSH: carcinogen; 0.016 ppm; C 0.1 [1]
ACGIH: 1 ppm; STEL 2 ppm
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; BP -19.5 °C; vapor density 1.067 (air = 1); explosive range 7 to 73% v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 50% w/v HCHO); CAS #50-00-0.

SAMPLING

SAMPLER: LIQUID IN BUBBLER
(midget bubbler, 15 mL Girard T reagent)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 6 L @ 3 ppm
-MAX: 18 L

SHIPMENT: seal bubblers to prevent leakage before shipping

SAMPLE STABILITY: 1 week @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 1.8 to 7.4 mg/m^3 [3]
(18-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.052 (TWA) [3];
0.058 (Ceiling) [3]

MEASUREMENT

TECHNIQUE: POLAROGRAPHY

ANALYTE: formaldehyde-Girard T derivative

SAMPLE PREPARATION: note volume of sample; transfer to dry vessel with ca. 0.3 mL Hg

POLAGRAPHY: sampled DC; 1-sec drop time, scan; -0.7 to -1.3 V vs. saturated calomel electrode @ 5 mV/sec

CALIBRATION: standard solutions of formaldehyde in distilled water

RANGE: 20 to 220 µg per sample [3]

ESTIMATED LOD: 6 µg per sample

PRECISION (s_r): 0.021 [3] @ 33 to 133 µg per sample

APPLICABILITY: The working range is 1 to 10 ppm (1.1 to 12 mg/m^3) for an 18-L sample. In attempts at validation of P&CAM 125 [4], a sample stability problem was noted [3]. This method was found to overcome the problem. Being a bubbler method, it is best suited to area sampling. The method has sufficient sensitivity to make peak measurements over the range of 5 to 20 ppm.

INTERFERENCES: Other volatile aldehydes such as acrolein, crotonaldehyde and benzaldehyde and products diffusing out of polyvinyl chloride tubing may cause significant interference.

OTHER METHODS: This revises method S327 [2] and Method 3501 (dated 2/15/84). For personal samples or where interferences in this method are present, Method 2541 is preferred. Method 3500 (chromotropic acid) is more sensitive, although it is also cumbersome for personal samples.

REAGENTS:

1. Citric acid, reagent grade.
2. Disodium hydrogen phosphate, reagent grade.
3. Girard T reagent, reagent grade.
4. Buffered Girard T reagent (See APPENDIX).
5. Triton X-100, 0.075%. Dilute 0.75 mL Triton X-100 to 1 L with distilled water.
6. Formalin solution, 37%.*
7. Distilled, deionized water.
8. Sulfuric acid, 0.02 N.
9. Sodium hydroxide solution, 0.01 N.
10. Sodium sulfite solution, 1.13 M. Prepare fresh immediately before use.
11. Formaldehyde stock solution*, 6.6 mg/mL (See APPENDIX). Stable at least three months.
12. Magnesium, sulfate.
13. Nitrogen, compressed, oxygen-free.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget bubblers.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Volumetric flasks, 1-L, 100-mL.
4. China marker.
5. Burettes, 50-mL.
6. Polarograph, capable of DC or sampled DC polarography with reference to a saturated colomel electrode.
7. Syringes, volumetric, 1-, 10-, 25- and 50-µL.
8. Pipets, volumetric, 0.3-, 0.75-, 1-, 2-, 5-, 10-, 15- and 20-mL, graduated in 0.1-mL increments.
9. pH meter.
10. Graduated cylinder, 25-mL.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen [1,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the bubbler with 15 mL buffered Girard T reagent solution using a 15-mL pipet. Mark the initial liquid level in the bubbler.
3. Make bubbler-to-sampling pump conections with flexible inert tubing. Insert a glass wool trap between bubbler and personal sampling pump to prevent splashover.
4. Sample at 0.2 L/min for 30 min (6 L) for peak measurements or at, e.g., 0.1 L/min for 1 to 3 hrs (6 to 18 L) for TWA measurements. Do not exceed a sample volume of 18 L, in order to maintain an 80-fold molar excess of the Girard T reagent over the total amount of formaldehyde sampled.

SAMPLE PREPARATION:

5. Tap the bubbler stem lightly against the bubbler body to drain the contents into the body. If necessary, bring samples up to the 15-mL mark with distilled water. Swirl the bubbler to mix.
6. Transfer solution to a clean, dry polarographic cell which contains a small amount (0.3 mL) of mercury.

CALIBRATION AND QUALITY CONTROL:

7. Add aliquots of standardized formaldehyde stock solution to 15-mL volumetric flasks using volumetric syringes and bring to volume with buffered Girard T reagent. Prepare six working standards to cover the range of 6 to 220 µg per sample.
8. Analyze these standards as directed in steps 6, and 10 through 13.
9. Prepare calibration graph (µg formaldehyde/15 mL vs. diffusion current).

MEASUREMENT:

10. Place the cell on the polarograph and purge the sample for 5 min with oxygen-free nitrogen at a flow rate of 200 mL/min.
11. Analyze the sample with sampled DC polarography using conditions given on page 3501-1.

12. Rinse electrodes with distilled water between samples.
13. Measure diffusion current from the reduction of the formaldehyde-Girard T reagent derivative.
    NOTE: The half-wave potential of the formaldehyde- Girard T reagent derivative is -0.99 V vs. saturated calomel electrode.

CALCULATIONS:

14. Read the mass (µg) formaldehyde/15 mL of Girard T reagent found in the sample (W) and the average blank (B) from the calibration graph.
15. Calculate the concentration of formaldehyde in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S327 was validated under the joint NIOSH/OSHA Standards Completion Program September 2, 1977 [3,6,7] over the range 1.8 to 7.4 mg/m^3 using an 18-L 8-hour time weighted average air sample and a 5.5-liter, 30-minute peak air sample. Air samples were collected from dynamically generated test atmospheres. The collection efficiency tests conducted at 7.9 mg/m^3 concentration of formaldehyde and a flow rate of 0.185 L/min was close to 1.0. The precisions for the total sampling and measurement for the 8-hour time weighted average and peak standards were 0.052 and 0.058 respectively. The measurement precision in the concentration range 33 to 133 µg per sample was 0.021. Samples were stable for at least 1 week when stored at room temperature.

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METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE; S327 validated under NIOSH Contract 210-76-0123.

APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL formaldehyde stock solution. The pH should now be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid = 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0(N_a \cdot V_a - N_b \cdot V_b)}{V_s}$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL).

BUFFERED GIRARD T REAGENT:
Dissolve 13.3 g disodium hydrogen phosphate, 10.8 g citric acid, 3.93 g Girard T reagent in a 1-L volumetric flask. Add 6.6 mL Triton X-100 soluton and dilute to 1 L with distilled water. The pH of the resulting solution should be 4.5.

FORMULA: $C_4H_3OCH_2OH$; $C_5H_6O_2$

M.W.: 98.10

FURFURYL ALCOHOL

METHOD: 2505

ISSUED: 5/15/89

OSHA: 10 ppm; STEL 15 ppm (skin)
NIOSH: 10 ppm; STEL 15 ppm (skin) [1]
ACGIH: 10 ppm, STEL 15 ppm (skin)
(1 ppm = 4.01 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.13 g/ml @ 20 °C; BP 170 °C; VP 0.13 kPa (1 mm Hg) @ 31.8 °C; explosive range 1.8% to 16.3% (v/v) in air

SYNONYMS: 2-furyl carbinol; 2-(hydroxymethyl)furan; 2-furanmethanol; CAS #98-00-0.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Porapak Q, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 3 L @ 10 ppm
-MAX: 25 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 118 to 478 mg/m^3 [2]
(6-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.072 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: furfuryl alcohol

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5.0 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 225 °C
-COLUMN: 200 °C

CARRIER GAS: He or N_2, 50 mL/min

COLUMN: stainless steel, 1 m x 3-mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of furfuryl alcohol in acetone

RANGE: 0.12 to 3.6 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION (s_r): 0.031 @ 0.6 to 2.4 mg per sample [2]

APPLICABILITY: The working range is 4 to 150 ppm (20 to 600 mg/m^3) for a 6-L air sample.

INTERFERENCES: None identified. The method was used in epoxy spray paint operations with no apparent interference from ethylene chloride, toluene, xylene, perchloroethylene and Freon 113 [3]. Alternative columns for this method are 5% FFAP on Chromosorb T (40/60 mesh) packed on stainless steel [3] and a WCOT OV-101 (0.25-µm film thickness) glass capillary [4].

OTHER METHODS: This revises NIOSH Method S365 [5].

REAGENTS:

1. Furfuryl alcohol* (purify as in APPENDIX A).
2. Acetone, distilled in glass.
3. Benzene,* distilled in glass.
4. DE stock solution, 0.1 mg/μL. Dilute 1.0 g furfuryl alcohol to 10 mL with benzene.
   NOTE: Acetone may be substitued for benzene if desorption efficiency is adequate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, flame-sealed with plastic caps, 8.5 cm long, 6-mm OD, 4-mm ID; two sections of 50/80 mesh pre-extracted Porapak Q (front = 150 mg; back = 75 mg) separated by a 2-mm section of urethane foam and held in place with plugs of silanized glass wool. (See APPENDIX B for sorbent clean-up procedure). Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ioniztion detector, integrator and column (page 2505-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10- to 50-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL and other convenient sizes.
7. Pipets, TD, 1.0-mL and other convenient sizes.
8. Balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Furfuryl alcohol is toxic and reacts violently with acids [6]. Benzene is a suspected human carcinogen [6]. Perform all work with this solvent in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 3 to 25 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL acetone to each vial. Cap each vial.
7. Allow to stand 15 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 3.6 mg furfuryl alcohol per sample.
   a. Add known amounts of pure furfuryl alcohol to acetone in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions to prepare the lower concentrations.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg furfuryl alcohol).
9. Determine desorption efficiency (DE) at least once for each lot of Porapak Q used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of DE stock solution or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg furfuryl alcohol recovered.
10. Analyze three quality control blind spikes and three analyst spikes to 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 2505-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with acetone, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

This method was validated over the range 118 to 478 mg/m^3 on February 18, 1977 using test atmospheres generated dynamically by the vapor pressure saturation/air dilution technique at 765 torr and 22 °C [2,5,7]. At a challenge concentration of 105 ppm (418 mg/m^3), furfuryl alcohol in humidified air (RH >80%) and a flowrate of 0.044 L/min, there was no breakthrough of the front sorbent bed after sampling for 7 hrs. The mean desorption efficiency over the range 0.59 to 2.36 mg per sample was 0.96. Recovery of analyte collected (in a 6-L sample) from synthetic atmospheres over the range 118 to 478 mg/m^3 averaged 98.4%. The recovery of the collected analyte (1.2 mg per sample), stored at ambient temperatures for 1 week, was 97%.

REFERENCES:

[1] NIOSH Testimony of the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
[2] Backup Data Report for Furfuryl Alcohol, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 2," Order No. PB-271-464 from NTIS, Springfield, VA 22161.
[3] NIOSH Health Hazard Evaluation Report HHE 80-154-1027, (unpublished, 1981).
[4] Holt, J. UBTL Inc., personal communication to NIOSH (1983).
[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S365, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402
[7] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Robert Glaser, NIOSH/DPSE; S365 originally validated under NIOSH Contract 210-76-0123

APPENDIX A:

PURIFICATION OF NEAT STANDARD:
Pure furfuryl alcohol is a clear viscous liquid; however, it decomposes upon standing for extended periods. If the furfuryl alcohol as received is dark-colored, distill it at 170 °C prior to use. Store the purified material in a dark bottle in a refrigerator at 0 °C.

APPENDIX B:

PREPARATION OF SORBENT AND SAMPLE TUBES:
Prior to use, wash the Porapak Q with acetone in a Soxhlet apparatus to remove any contaminants present. Place several grams of the sorbent in the thimble sample container and secure the sorbent in the thimble with glass wool. Extract the sorbent with acetone for 4 hrs. After the extraction, remove the liquid acetone via filtration through a sintered filter fitted to a vacuum flask. Remove the solvent residue by transferring the sorbent to an evaporating dish and drying at 120 °C in a clean vacuum oven under reduced pressure (25 torr) for 4 hrs. Allow to cool in a clean dessicator.

Avoid excessive agitation of the sorbent during handling. A static charge can be induced in the material which is not readily dissipated; the individual particles will agglomerate, making the tubes difficult to pack. Wash the glass sampling tubes with acetone and allow them to air-dry prior to packing with Porapak Q in order to prevent the sorbent from adhering to the walls. The pressure drop across the sampling tubes must be less than 10 torr at 0.05 L/min [4].

FORMULA: $O=CH(CH_2)_3CH=O$; $C_5H_8O_2$

GLUTARALDEHYDE

METHOD: 2531

M.W.: 100.12

ISSUED: 5/15/89

OSHA: C 0.2 ppm
NIOSH: C 0.2 ppm [1]
ACGIH: C 0.2 ppm
(1 ppm = 4.09 mg/m^3 @ NTP)

PROPERTIES: oil; d 0.72 g/mL @ 20 °C ;BP 188 °C;
MP −14 °C; VP 2.2 kPa (17 mm Hg) @ 20 °C

SYNONYMS: glutaric dialdehyde; 1,5-pentanedial; CAS #111-30-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg: Supelco ORBO-23 or equivalent)

FLOW RATE: 0.01 to 0.08 L/min, or 0.2 L/min for 20 min

VOL-MIN: 4 L @ 0.2 ppm
-MAX: 39 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 weeks @ 25 °C [2]

FIELD BLANKS: 10% of samples
MEDIA BLANKS: 10 per set

ACCURACY

RANGE STUDIED: 0.8 to 9 mg/m^3 [2]
(22-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.087 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of glutaraldehyde

DESORPTION: 2 mL toluene; 60 min ultrasonic

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

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 20 °C/min; hold 2 min @ 290 °C

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

COLUMN: capillary, 10 m x 0.25 mm, 5% phenyl, 95% methyl polysiloxane (DB-5 or equivalent)

CALIBRATION: standard glutaraldehyde solutions spiked on sorbent

RANGE: 3 to 180 µg per sample [2]

ESTIMATED LOD: 1 µg per sample [3]

PRECISION (s_r): 0.091 [2] @ 5 to 50 µg per sample

APPLICABILITY: The working range is 0.03 to 2 ppm (0.14 to 8 mg/m^3) for a 22-L air sample; the method is sensitive enough for ceiling determinations. The method is suitable for the simultaneous determination of furfural and glutaraldehyde.

INTERFERENCES: None have been observed.

OTHER METHODS: This is a new method. A wide-bore 10-m capillary column is an alternate chromatographic column.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas) or equivalent. Extract 4 hrs in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Glutaraldehyde,* 25% (w/v) solution in water.
5. Glutaraldehyde stock solution, 10 µg/µL (see APPENDIX A).
6. Glutaraldehyde oxazolidine (see APPENDIX B) stock solution, 2 mg/mL. Add 20 mg to toluene and dilute to 10 mL.
7. Sulfuric acid, 0.02 N.
8. Sodium hydroxide, 0.01 N.
9. Sodium sulfite, 1.13 M. Prepare fresh immediately before use.
10. Water, deionized, then distilled.
11. Hydrogen, prepurified.
12. Air, filtered.
13. Helium, purified.
14. Magnesium sulfate.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

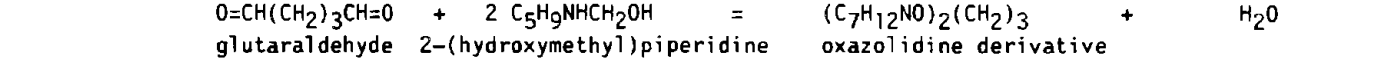
1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, flame-sealed ends and plastic caps, containing two sections of 40/60 mesh 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX C). Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 Pa (5.7 mm Hg). Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Personal sampling pump, 0.01 to 0.08 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2531-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, TD, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-µL (readable to 0.1 µL), 25-, and 50-µL.
10. File.
11. Beakers, 50-mL.
12. pH meter.
13. Magnetic stirrer.
14. Burets, 50-mL.
15. Flasks, round-bottomed, 100-mL.
16. Soxhlet extraction apparatus.
17. Vacuum oven.
18. Distillation apparatus.

SPECIAL PRECAUTIONS: Glutaraldehyde can irritate the mucous membranes and act on the central nervous system [4]. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break 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 0.08 L/min for a total sample size of 4 to 39 L. For ceiling determination, sample at 0.2 L/min for 20 min.

   NOTE: The aldehyde reacts with the 2-(hydroxymethyl)piperidine to form an oxazolidine derivative in the sorbent bed during sampling (see equation below). Sampling rate is limited by the speed of this reaction. Sampling rates above 0.1 L/min for extended periods may cause breakthrough due to incomplete reaction, possibly invalidating the sample.



SAMPLE PREPARATION:

4. Score each sampler with a file in back of the back sorbent section.
5. Break sampler at score line. Remove and place back glass wool plug and back sorbent section in a vial.
6. Transfer front section with remaining glass wool plugs to a second vial.
7. Add 2.0 mL toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials in an ultrasonic bath for 60 min.
   NOTE: Desorption efficiency is affected by the amount of time that the vials are allowed to spend in the ultrasonic bath. A minimum of 60 min residence time in the ultrasonic bath is required to ensure adequate desorption.

CALIBRATION AND QUALITY CONTROL:

9. Prepare glutaraldehyde oxazolidine standard solutions.
   a. Add known amounts of glutaraldehyde oxazolidine stock solution (equivalent to the range of the samples) to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with at least five working standards covering the range of the samples.
   a. Weigh 120-mg portions of unused sorbent from media blanks into vials.
   b. Add aliquots of glutaraldehyde stock solution or dilutions thereof. Cap vials and allow them to stand overnight at room temperature.
   c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
   d. Prepare calibration graph (combined peak area vs. µg glutaraldehyde).
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary. Check desorption efficiency occasionally in the range of interest (see APPENDIX D).
11. Analyze three quality control blind spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2531-1. Inject 1-µL sample aliquot.
   NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene and apply the appropriate dilution factor in calculations.
13. Measure total peak area of the two analyte peaks.
   NOTE: On the recommended column, the oxazolidine derivative gives two peaks, since the diastereoisomers are resolved. t_r for the glutaraldehyde derivative = 9.4 and 9.7 min; and t_r for 2-(hydroxymethyl)piperidine = 2.6 min for these conditions.

CALCULATIONS:

14. Determine the mass, µg, of glutaraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
   NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of glutaraldehyde in the air volume sampled, V (L):

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

EVALUATION OF METHOD:
Atmospheres were generated by injection of an aqueous solution of glutaraldehyde by syringe pump into a heated block injector and flash vaporization into a stream of air flowing at a fixed rate [2]. Relative humidity during generation was controlled at 80% ± 5%. The generator and sampling manifold system have been described previously [5]. Concentration of glutaraldehyde vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [6]. No bias with dynamically-generated atmospheres was observed with the method over the range 0.8 to 8 mg/m^3 using 22-L air samples. Desorption efficiencies on statically-spiked samples averaged 87% in the range 5 to 50 µg/sample. Recovery averaged 1.10 with s_r = 0.043 for twelve tubes spiked with 67 µg glutaraldehyde [7].

REFERENCES:
[1] NIOSH Testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
[2] Kennedy, E. R., Y.T. Gagnon, J.R. Okenfuss and A. W. Teass. "The Determination in Air of Selected Low-Molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography", Appl. Ind. Hyg., 3:274-279 (1988).
[3] NIOSH Sequence Reports 5827 (Nov. 13, 1987) and 6565-J (Feb. 27, 1989) (unpublished).
[4] The Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
[5] Kennedy, E. R. and R. H. Hill, Jr. "Determination of Formadehyde in Air as an Oxazolidine Derivative by Capillary Gas Chromatography," Anal. Chem., 54, 1739-1741 (1982).
[6] Lipari, F. and S. J. Swarin. "Determination of Formaldehyde and other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method", J. Chromatog., 247, 297-306, (1982).
[7] DataChem Inc., UserCheck, NIOSH Seq. #6565-M (Unpublished, June 13, 1989).

METHOD WRITTEN BY: Julie R. Okenfuss and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

A. PREPARATION AND STANDARDIZATION OF GLUTARALDEHYDE STOCK SOLUTION (ca. 10 µg/µL):

Dilute 1 mL 25% aqueous glutaraldehyde to 25 mL with distilled, deionized water. Put 10.0 mL 1.13 M sodium sulfite solution in a beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 1.0 mL glutaraldehyde stock solution. The pH should be about 12. Titrate the solution back to its original pH with 0.02 N sulfuric acid. If the endpoint pH is overrun, back-titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (µg/µL), of the glutaraldehyde stock solution:

$$C_s = \frac{50.06\ [(N_a \cdot V_a) - (N_b \cdot V_b)]}{V_s}.$$

where: 50.06 = equivalent weight of glutaraldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_s = volume of glutaraldehyde stock solution (1.0 mL).

B. SYNTHESIS OF GLUTARALDEHYDE OXAZOLIDINE:

Place a solution of purified 2-hydroxymethylpiperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Several 2-mL portions of toluene can be used to rinse residual 2-(hydroxymethyl)piperidine from the container used for weighing. Add magnesium sulfate (2.5 g) to the round-bottomed flask to dry the glutaraldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 1 mL of 25% aqueous glutaraldehyde (0.25 g, 2.5 mmol) in 10 mL of toluene to the 2-hydroxymethylpiperidine solution dropwise with stirring over 1 hr. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation. The product is a yellow viscous oil, ca. 90 to 95% pure.

NOTE: Exact amounts of reagent are required for this synthesis since excess glutaraldehyde can cause appreciable formation of the mono-oxazolidine derivative of glutaraldehyde.

C. SORBENT PREPARATION (optional if commercially prepared tubes are used):

Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 hr. To determine the amount of background for each batch, extract several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for glutaraldehyde.

D. DESORPTION EFFICIENCY:

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10. If desired, the following procedure can be used to determine DE:

a. Prepare and analyze a set of glutaraldehyde oxazolidine standard solutions (step 9.a) and a set of working standards (step 10), including media blanks.

b. Treating the working standards as unknowns, read the mass (µg) of oxazolidine found in each working standard (W), and in the average media blank (B).

c. Using the mass of glutaraldehyde, µg, spiked onto the working standard (W_o) and the stoichiometric conversion factor between glutaraldehyde and glutaraldehyde oxazolidine (2.94), calculate the desorption efficiency:

$$DE = \frac{W - B}{W_o \cdot 2.94} .$$

d. Prepare a graph of DE vs. µg glutaraldehyde recovered per sample [(W - B)/2.94].

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FORMULA: HCN

M.W.: 27.03

HYDROGEN CYANIDE
METHOD: 6010
ISSUED: 5/15/89

OSHA: STEL 4.7 ppm
NIOSH: STEL 4.7 ppm [1]
ACGIH: 10 ppm/10 min (skin)
(1 ppm = 1.11 mg/m^3 @ NTP)

PROPERTIES: gas; d 0.94 (air = 1.00) g/L @ 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

SAMPLER: SOLID SORBENT TUBE
(soda lime, 600 mg/200 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 0.6 L @ 5 ppm
-MAX: 90 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 2 to 15 mg/m^3 [2]
(3-L samples)

BIAS: Not significant [2]

OVERALL PRECISION (s_r): 0.076 [2]

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: cyanide ion complex

DESORPTION: 10 mL deionized water; stand 60 min

COLOR DEVELOPMENT: N-chlorosuccinimide/ succinimide oxidizing agent and barbituric acid/pyridine coupling agent; absorption @ 580 nm in 1-cm cuvette

CALIBRATION: standard solutions of KCN in 0.1 N NaOH

RANGE: 3 to 300 µg CN^- per sample [2]

ESTIMATED LOD: 1 µg CN^- per sample [2]

PRECISION (s_r): 0.041 @ 10 to 50 µg per sample [2]

APPLICABILITY: The working range is 1 to 333 mg/m^3 (0.9 to 300 ppm) for a 3-L air sample. 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: None found.

OTHER METHODS: This is based on the method of Lambert, et al. [4]. NIOSH Method 7904 uses an ion specific electrode for measurement.

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 plugs, with a 5-mm diameter glass fiber filter placed before the plug on inlet side.
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.

*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 [4]. Soda lime is very caustic [5]. Workers should be aware of the latest laboratory safety procedures. 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 soda lime sampler immediately before sampling. Attach soda lime 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 plug.
   NOTE: Particulate cyanides will be trapped on the glass fiber plug. An estimate of their concentration may be obtained by carrying the glass fiber plug through the following procedure. However, no evaluation data are available for particulate cyanides determined in this manner.
6. Transfer front and back sorbent sections to separate vials.
7. Add 10.0 mL deionized distilled water to each vial. Cap each vial.
8. Allow to stand 60 minutes, with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 3 to 300 µg per sample.
   a. Prepare a calibration working standard solution, 1.00 µg CN^-/mL, by diluting 100 µL of calibration stock solution to 100 mL with 0.1 N NaOH.
   b. Pipet 0.5-, 1.00-, 1.50-, 2.00- and 2.50-mL of the calibration working standard solution into 25-mL volumetric flasks to make 0.50, 1.00, 1.50, 2.00 and 2.50 µg CN^- standards.
   c. Analyze together with field samples and blanks (steps 12 through 19).
   d. Prepare calibration graph (absorbance vs. µg CN^-).
10. Determine desorption efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
   (a) Remove and discard back sorbent section of a blank sampler.
   (b) Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
   (c) Cap, and allow to stand overnight.
   (d) Desorb (steps 5 through 8) and analyze together with working standards (steps 12 through 19).
   (e) Prepare a graph of DE vs. µg CN^- recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Pipet a sample aliquot estimated to contain 0.50 to 2.50 µg 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.
16. Immediately add 1.0 mL N-chlorosuccinimide/succinimide oxidizing reagent. Mix and let stand.
17. After at least 5 min. standing (but not longer than 15 min), starting with the reagent blank, add 1.0-mL barbituric acid-pyridine coupling reagent. Mix.
18. Adjust sample volume to 25 mL with deionized-distilled water and allow to stand at least 12 min (but not longer than 30 min) for color development.
19. Read absorbance at 580 nm in a 1-cm light path cuvette on a spectrophotometer. If sample absorbance is outside the range of the calibration standards, take an aliquot, re-analyze (steps 12 through 19), and apply the appropriate aliquot factor in calculations.

CALCULATIONS:

20. Calculate the mass, µg, of CN^- in aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, µg, of CN^- in the original 10 mL solution.
21. Determine the mass, µg CN^- (corrected for DE), found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections. If $W_b > W_f/10$, report breakthrough and possible sample loss.
22. Calculate concentration, C, of HCN in the air volume sampled, V(L).

$$C = \frac{(W_f + W_b - B_f - B_b) \times 1.039}{V}, \text{ mg/m}^3$$

where 1.039 = conversion factor, CN^- to HCN

EVALUATION OF METHOD:

The method was evaluated by sampling the 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_r 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) on HCN; Sequence NIOSH/MRSB-6366A, Unpubl. NIOSH, (1988).
[4] Lambert, J. L., Ramasamy, J., and J. V. Paukstelis, "Stable Reagents for the Colorimetric Determination of Cyanide by Modified Konig Reactions," Analyt. Chem., 47, 916-918 (1975).
[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.

FORMULA: TDI: $CH_3C_6H_3(NCO)_2$
MDI: $CH_2(C_6H_4NCO)_2$
HDI: $OCN(CH_2)_6NCO$
M.W.: TDI 174.16; MDI 250.26; HDI 168.20

ISOCYANATES
METHOD: 5521
ISSUED: 5/15/89

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

SAMPLER: IMPINGER
(solution of 1-(2-methoxyphenyl)-piperazine in toluene)

FLOW RATE: 1 L/min

VOL-MIN: 5 L @ 35 µg TDI/m^3
-MAX: 500 L

SHIPMENT: ship in screw-cap vial
refrigerated @ 4 °C or lower

SAMPLE STABILITY: may be unstable; perform steps 8 & 9 as soon as possible

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not known

OVERALL PRECISION (s_r): not known

MEASUREMENT

TECHNIQUE: HPLC, ELECTROCHEMICAL and UV DETECTION

ANALYTE: urea derivatives of isocyanates

SAMPLE PREP: acetylate excess reagent, evaporate toluene, redissolve in 5 mL CH_3OH

INJECTION VOLUME: 10 µL

MOBILE PHASE: acetonitrile (20% to 40%)/pH 6.0 methanolic buffer (80% to 60%); 1 mL/min; ambient temperature

COLUMN: Supelcosil, LC-8-DB, 3-µm particle size, 7.5 cm x 4.6 mm; 2-cm guard column, 10-µm particle size

DETECTORS: UV, 242 nm; ECHD, + 0.80 V vs. Ag/AgCl

CALIBRATION: standard solutions of ureas in methanol

RANGE: 2,4-TDI: 0.5 to 8 µg per sample
2,6-TDI: 0.7 to 10 µg per sample
MDI: 0.3 to 4 µg per sample
HDI: 1 to 15 µg per sample

ESTIMATED LOD: ca. 0.1 µg diisocyanate per sample

PRECISION (s_r): not determined

APPLICABILITY: The working range is from 5 µg/m^3 2,4-TDI, 7 µg/m^3 2,6-TDI, 3 µg/m^3 MDI, and 1 µg/m^3 HDI to more than 1 mg/m^3 for 100-L air samples. This method determines the air concentration of specific diisocyanates. The method is only qualitative for polyisocyanates, as it gave low evaluation results with both polyisocyanates used. The method has been applied to samples from general foaming, spray- or dip-painting industries [1].

INTERFERENCES: Any substance which elutes with the ureas and absorbs ultraviolet light or is electroactive will interfere with the analysis. Mobile phase conditions can be adjusted to separate most co-eluting peaks, however, ureas of HDI and TDI are difficult to separate.

OTHER METHODS: This method is a modification of Method MDHS 25 published by the Health and Safety Executive of Great Britain [2,3]. Method 2535 is an alternate method for TDI vapor, employing collection on glass wool impregnated with N-(4-nitrophenylmethyl)propylamine.

REAGENTS:

1. 1-(2-Methoxyphenyl)piperazine*, 98%.
2. Acetic anhydride, reagent grade.
3. Methanol, HPLC grade.
4. Acetonitrile, HPLC grade.
5. Water, deionized, distilled.
6. Sodium acetate, anhydrous.
7. Acetic acid, glacial.
8. Nitrogen, 99.995%.
9. Toluene, HPLC grade.
10. Sampling medium, 1-(2-methoxyphenyl)piperazine in toluene, 43 mg/L.
11. Ureas derived from the isocyanate. (See APPENDIX).
12. Dimethyl sulfoxide, reagent grade.
13. Mobile phase, acetonitrile and buffer solution to achieve appropriate mobile phase.
14. Buffer solution. Dissolve 15 g anhydrous sodium acetate in 1 L distilled-deionized water. Add 1 L methanol. Add glacial acetic acid to bring pH to 6.0.
15. Urea calibration stock solution, 0.01 µg/µL urea in methanol.
16. Reagent calibration stock solution, 1.0 µg/µL 1-(2-methoxyphenyl)-piperazine in methanol.
17. Helium, prepurified.

*See SPECIAL PRECAUTIONS

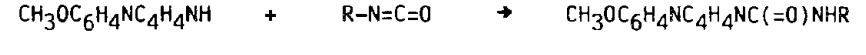
EQUIPMENT:

1. Sampler: Midget impinger, 25-mL.
2. Personal sampling pump, 1.0 L/min, with flexible connecting tubing free of phthalate plasticizer.
   NOTE: Avoid collection of plasticizer in the toluene during sampling. Fluran™ tubing is an acceptable tubing.
3. Liquid chromatograph (HPLC) with ultraviolet (UV) detector (242 nm) and electrochemical (ECHD) detector (+ 0.80 V vs. Ag/AgCl), recorder, integrator and column (page 5521-1).
4. Ultrasonic water bath.
5. Vials, 4-mL glass, with screw caps and 20-mL glass, screw caps with cone-shaped polyethylene liner and shrinkable sealing bands.
6. Pasteur pipets, 7-cm glass, disposable.
7. Flasks, volumetric, glass, 10-mL.
8. Syringes, sizes appropriate for preparing standard solutions.
9. Pipets, 5- and 15-mL glass, delivery, with pipet bulb.
10. Hot plate, spark free, 60 °C.
11. Evaporator, Mini-Vap, 6-port or equivalent.
12. pH meter.
13. Vacuum oven.
14. Buchner funnel, fritted glass, medium porosity, 100-mL.
15. Vacuum pump.
16. Flask, filtration, 500-mL.

SPECIAL PRECAUTIONS: Preparation of urea derivatives, samples, and standards should be done in hood to avoid exposure to isocyanate and solvent vapors. Isocyanates are known respiratory irritants. Toxicity of 1-(2-methoxyphenyl)piperazine is unknown.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL sampling medium to an impinger.
3. Connect the assembled impinger to a sampling pump.
4. Sample 5 to 500 L of air at 1.0 L/min.
   NOTE 1: Toluene evaporates during sampling; when level of solution drops below 10 mL, restore volume to 15 mL with toluene.
   NOTE 2: The reagent in the sampling medium reacts with isocyanates to form ureas:



$$CH_3OC_6H_4NC_4H_4NH + R\text{-}N{=}C{=}O \rightarrow CH_3OC_6H_4NC_4H_4NC(=O)NHR$$

5. Prepare blank samples by transferring 15 mL sampling medium to 20-mL vials.
6. Transfer the sample solution to a 20-mL vial for shipment. Rinse both impinger parts with 2 to 3 mL toluene and add rinsings to the sample. Secure vial's screw cap with sealing band. Refrigerate samples as soon as possible. If samples are to be shipped, carefully pack the vials to avoid breakage or spillage of sample.

7. Obtain a bulk sample (1 to 2 mL) of and the material safety data sheet for any polyisocyanate used at the worksite. Analysis of samples prepared from this bulk material will be useful for identifying ureas derived from the polyisocyanate.

SAMPLE PREPARATION:

8. Add 25 µL acetic anhydride to acetylate the excess 1-(2-methoxyphenyl)piperazine remaining in the sample solution, to provide for efficient chromatography.
   NOTE: The acetylation reaction is:

$$CH_3OC_6H_4NC_4H_4NH + CH_3C(=O)OC(=O)CH_3 \rightarrow CH_3OC_6H_4NC_4H_4NC(=O)CH_3 + CH_3C(=O)OH$$

9. Evaporate the acetylated sample to dryness under a gentle stream of nitrogen while warming to 60 °C on a hotplate.
10. Redissolve the residue in 5.0 mL methanol, while agitating the sample in an ultrasonic water bath for 15 min.

CALIBRATION AND QUALITY CONTROL:

11. Prepare working standards containing 0.01 to 4.0 µg/mL of the appropriate urea(s) (TDIU, HDIU, and/or MDIU) and 100 µg/mL of 1-(2-methoxyphenyl)piperazine by adding aliquots of calibration stock solutions to 2 mL methanol in a 10-mL volumetric flask. Add 10 µL acetic anhydride to each standard. Mix and dilute to the mark with methanol.
    NOTE: The standard solutions need include only ureas derived from the diisocyanates expected in the air samples and, if polyisocyanates are of interest, ureas derived from the diisocyanates structurally most similar to the polyisocyanates.
12. Analyze working standards together with samples and blanks (steps 15 through 17). Prepare a calibration graph for the urea in terms of quantity of isocyanate group, M (ECHD area vs. µmol of isocyanate group per sample). Molecular weights of typical ureas are: TDIU = 558.7 g/mol; MDIU = 634.8 g/mol; HDIU = 552.7 g/mol).

$$M = \frac{(C)\bullet(N)\bullet(5)}{MW}, \ \mu mol/sample$$

Where: M is the quantity of isocyanate group per sample (µmol)
C is the concentration of urea in the standard solution (µg/mL)
N is the number of isocyanate groups per molecule (eg, 2 for a diisocyanate)
5 is the liquid volume of a sample (mL)
MW is the molecular weight of the urea

13. Prepare control samples by adding 0.1, 1.0 and 10.0 µg of urea to 15 mL sampling medium. Prepare these samples for analysis (steps 8 through 10).
14. Prepare qualitative samples from bulk polyisocyanate. Using information from the container or the material safety data sheet, add enough polyisocyanate to react with approximately 1/10 to 1/3 of the reagent in 15 mL of sampling medium. Prepare samples for analysis (in steps 8 through 10) and analyze. Use the chromatographic data for aid in indentifying peaks of ureas derived from polyisocyanates.

MEASUREMENT:

15. Set up the HPLC system according to manufacturer's recommendations and to the conditions given on page 5521-1.
16. Inject a 10-µL aliquot of the sample solution from step 10. Capcity factors for the urea derivatives are:

Isocyanate	Mobile Phase: Acetonitrile	Mobile Phase: Buffer Solution	Capacity Factor (k')[a]
2,4-TDI	30%	70%	2
MDI	35%	65%	4
PMPPI[b]	35%	65%	10
2,4-TDI	40%	60%	3
HDI	40%	60%	3
HDI-Biuret[c]	40%	60%	6
$(HDI)_3$ [d]	40%	60%	8

[a] $k' = (t_r - t_0) / t_0$, where t_r is the retention time of the urea and t_0 is the retention time of an unretained compound.
[b] One or several oligomers of polymethylenepolyphenyl isocyanate.
[c] 1,3,5-Tris(6-isocyanatohexyl)biuret.
[d] 1,3,5-Tris(6-isocyanatohexyl)hexahydro-1,3,5-triazin-2,4,6-trione.

17. Measure peak area with both detectors.
    NOTE 1: Use ECHD response for quantitation of ureas.
    NOTE 2: The ureas from the polyisocyanates are identified (step 19) by the ratio of their response to electrochemical and ultraviolet detection. These ratios are similiar in value to the ratio of the urea from the diisocyanate to which the polyisocyanate is structurally related.

CALCULATIONS:

18. Calculate the ratio of the electrochemical detector response to the ultraviolet detector response for all peaks in the chromatogram.
19. Identify as a polyisocyanate-derived urea any peak in the samples for which the ratio is between 0.75 and 1.5 times the average ratio given by the urea of the structurally similar diisocyanate in calibration standards.
20. Read from calibration graph the quantity, M (µmol per sample), of isocyanate group for the urea from the isocyanate of interest.
21. Calculate the concentration of the specific isocyanate of interest, C_M ($\mu g/m^3$), in the air volume sampled, V (L):

$$C_M = M \bullet MW \bullet 10^3 / N \bullet V, \quad \mu g/m^3$$

Where: MW is the molecular weight of isocyanate
N is the number of isocyanate groups per molecule

EVALUATION OF METHOD:

The stability of 2,4-TDIU in toluene was investigated using groups of six samples stored at room temperature for up to two weeks or at 4 °C for 1 week with the following results:

Quantity (µg)	Storage Period (days)	Storage Temperature	Percent Recovery, 95% Confidence Interval
1.9	0	room	99 ± 11
3.8	0	room	98 ± 4
1.9	7	room	78 ± 7
1.9	7	4 °C	88 ± 7
3.8	7	room	67 ± 6
3.8	14	room	70 ± 11

The data demonstrate sample instability at room temperature (about 22 °C) and suggest that the samples are somewhat unstable even at 4 °C.

Estimates of the limits of quantitation (LOQs) (expressed in terms of the quantity of diisocyanate per sample) were made from the electrochemical-detector calibration curves used for the analysis of field samples or control samples: 2,4-TDI, 0.5 µg [1, Sequence 6043]; 2,6-TDI, 0.7 µg [1, Sequence 6043]; MDI, 0.3 µg [1, Sequence 6019]; HDI, 1 µg [4]. The corresponding limits of detection (LODs) were: 2,4-TDI, 0.2 µg; 2,6-TDI, 0.2 µg; MDI, 0.09 µg; HDI, 0.3 µg. Because the polyisocyanates for which authentic standards are not available must be identified by the ratio of the electrochemical-detector and UV-detector responses, the detection limits for these substances depend upon the less sensitive UV detector and, thus, will be higher.

The use of the ratio of detector responses to identify ureas formed from polyisocyanates and the estimation of polyisocyanate concentration by comparing to diisocyanate standards were evaluated using samples of commercial isocyanates, which were MDI- or HDI-based polyisocyanates, reagent grade HDI, and a solution of 80% 2,4-TDI and 20% 2,6-TDI. The MDI-based commericial product, MF184, was reported to be 50% polymethylenepolyphenyl isocyanate and 50% MDI. The HDI-based commercial product was reported to be 44% of the trimer, 1,3,5-tris(6-isocyanatohexyl)hexahydro-1,3,5-triazin-2,4,6-trione [$(HDI)_3$], with no HDI present. Fifty-six samples were prepared and analyzed for isocyanate, 15 from MF184, 12 from $(HDI)_3$, 11 from HDI, and 18 from TDI. The range of isocyanate group present was 0.078 - 1.7 µmol per sample as determined from the measurement of the isocyanate by weight or volume. The average recoveries for these samples using the procedure described in the method were 61% for MF184, 54% for $(HDI)_3$, 123% for HDI, and 90% for TDI.

The precision of the average ratio of the response of the electrochemical detector to the response of the ultraviolet detector was determined from the standard-curve data for the two detectors. The relative standard deviations were 21%, 12%, and 14% for 2,4-TDIU, MDIU, and HDIU, respectively. The average values of the ratios vary with the HPLC mobile phase conditions used for analysis.

REFERENCES:

[1] NIOSH - Measurement Research Support Branch Analytical Report, Sequences #6019, 6043, 6100, and 6354 (NIOSH, unpublished, 1988).

[2] "MDHS 25: Methods for the Determination of Hazardous Substances, Organic Isocyanates in Air. Laboratory Method Using 1-(2-Methoxyphenyl)piperazine Solution and High Performance Liquid Chromatography," Occupational Medicine and Hygiene Laboratory, Health and Safety Executive, London, U.K. (1987).

[3] Bagon, D. A., C. J. Warwick, and R. H. Brown, Am. Ind. Hyg. Assoc. J. 45: 39-43(1984).

[4] User check, DataChem Inc., NIOSH analytical seq. #6543 (unpublished, Feb. 24, 1989).

METHOD WRITTEN BY: M. J. Seymour and A. W. Teass, NIOSH/DPSE

Table 1: Synonyms, exposure limits, and properties

Compounds (Synonyms)	Exposure Limits, µg/m³*			Properties
	(OSHA)	(NIOSH)	(ACGIH)	
2,4-TDI (2,4-TDI; 2,4-Toluene diisocyanate; CAS # 584-84-9)	40	40** 150 STEL	40	liquid; d 1.224 g/mL @ 20 °C; BP 251 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C; MP 19.5 - 21.5 °C
2,6-TDI (2,6-TDI; CAS # 91-08-7)	None	40** 150 STEL	None	liquid; d 1.22 g/mL @ 20 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C
MDI (4,4'-methylenediphenyl isocyanate; diphenylmethane-4,4'-diisocyanate; methylenebis(phenyl isocyanate); CAS # 101-68-8)	200 (ceiling)	50 200 (ceiling)	200 (ceiling)	solid (fused); d 1.198 g/mL @ 70 °C; MP 37.2 °C; VP 0.04 Pa @ 24 °C
HDI (Hexamethylene diisocyanate; CAS # 822-06-0)	None	35 140 (ceiling)	35	liquid; d 1.04 g/mL @ 20 °C; BP 255 °C
Polyisocyanates (Prepolymers; the biuret derived from HDI; cyclic trimer of HDI; isocyanate-bearing polyurethanes)	None	None	None	refer to material safety data sheet

* 1 ppm = 7100 µg/m³ TDI; 10208 µg/m³ MDI; 7350 µg/m³ HDI; **Carcinogen

APPENDIX: PREPARATION OF UREA DERIVATIVE

Dissolve 0.005 mole (1 g) of 1-(2-methoxyphenyl)piperazine in 25 mL dimethyl sulfoxide. Dissolve 0.002 mole (350-500 mg) of isocyanate in 25 mL dimethyl sulfoxide. Over a period of 1-2 min, gradually add the isocyanate solution to the stirred derivatizing reagent solution. Warm the resulting solution to 60-90 °C and continue to stir for at least 30 min. Discontinue heating of the solution and add 300 mL deionized water. The urea will precipitate as a white solid. Stop stirring after addition of water. Collect the urea in a fritted-glass Buchner funnel by suction filtration. Dry the compound in a vacuum oven at 75 °C to remove water. Recrystallize until a constant melting point is obtained.

To recrystallize urea, add toluene (150 mL) to dried urea and warm mixture to 60 °C. Slowly and very carefully add just enough methanol (BP 65 °C) to completely dissolve the urea. Remove from heat and allow to cool. Collect the crystals by suction filtration and dry them in vacuum oven at 35 °C. The urea derivatives and their melting points are as follows:

Diisocyanates	Urea Derivatives	MP (°C)
2,4-TDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-2,4-toluenediamine (2,4-TDIU)	212-213 (platelets)
2,6-TDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-2,6-toluenediamine (2,6-TDIU)	231-233 (platelets)
MDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-4,4'-methylenedianiline (MDIU)	209-210 (needles)
HDI	N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-hexamethylenediamine (HDIU)	199-200 (needles)

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FORMULA: Table 1

M.W.: Table 1

KETONES I

METHOD: 1300

ISSUED: 2/15/84

REVISION #1: 5/15/89

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS: (Synonyms: Table 1)
acetone
cyclohexanone
diisobutyl ketone
2-hexanone
methyl isobutyl ketone
2-pentanone

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

	acetone	others
VOL-MIN:	0.5 L	1 L
-MAX:	3 L	10 L

SHIPMENT: MIBK must be refrigerated [1]

SAMPLE STABILITY: unknown

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED, BIAS and
OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

COLUMN: glass (3.5 m x 6 mm), packed with 10% SP-2100 0.1% Carbowax 1500 on Chromosorb WHP

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 50 °C to 170 °C @ 10°/min

CARRIER GAS: N_2 or He, 30 mL/min

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 0.06 to 10 mg per sample [2]

ESTIMATED LOD: 0.02 mg per sample

PRECISION (s_r): see EVALUATION OF METHOD

APPLICABILITY: This is intended as a general method for the ketones listed above. If only certain compounds are of interest, the instrumental conditions can be changed to maximize instrument response for these compounds.

INTERFERENCES: None reported. Alternate columns, e.g., 10% SP-2100 or DB-1 fused silica capillary, can be used.

OTHER METHODS: This method combines and replaces Methods S1, S18, S19 and S20 [3], S178 and S358 [4], and 1300 (dated 2/15/84).

REAGENTS:

1. Carbon disulfide (CS_2)GC grade.*
2. Analytes, reagent grade.
3. Nitrogen, prepurified.
4. Hydrogen, dry.
5. Air, filtered, dry.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph equipped with FID, integrator and column (page 1300-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, TD, 1-mL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 3 L for acetone or 1 to 10 L for the other analytes.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 10 mg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of analyte or of a standard solution of analyte in CS_2 directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to 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 1300-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

The methods were validated under NIOSH Contract CDC-99-74-45 [5]. Desorption efficiency was checked by spiking known amounts of the compounds (either neat or in solutions with CS_2) on coconut shell charcoal. Samples were generated for acetone, cyclohexanone, 2-pentanone, and methyl isobutyl ketone by heating a quantity of the liquid to just below its boiling point in a 3-necked, 500-mL round bottom flask. The compound was carried through a fixed-temperature condenser to the concentrations. Samples were generated for diisobutyl ketone and 2-hexanone using a syringe pump which delivered the compounds to a heated glass-lined inlet which was swept with nitrogen, carrying the vapor to the mixing chamber. Results were as follows:

Compound	Method [2-5]	Overall Range, mg/m^3 (s_r)	Breakthrough[1] (L)	Measurement Range, mg/sample (s_r)	DE[2]
Acetone	S1,127	1200 to 4500 (0.082)	4.3	2.4 to 14.2 (0.024)	0.86
Cyclohexanone	S19	98 to 392 (0.062)	65	3.8 to 18.0 (0.025)	0.82
Diisobutyl ketone	S358	145 to 582 (0.070)	44	1.8 to 7.0 (0.032)	0.97
2-Hexanone	S178	188 to 790 (0.053)	>45	1.5 to 8.1 (0.018)	0.81
MIBK	S18	208 to 836 (0.064)	17	2.1 to 8.3 (0.008)	0.91
2-Pentanone	S20	395 to 1570 (0.063)	19	3.5 to 14.0 (0.011)	0.90

[1]5% breakthrough, 0.2 L/min at high end of concentration range in dry air.
[2]Averaged over mass range shown.

Low-level desorption efficiency checks showed the DEs to be 70% and 76% for 0.024 and 0.096 mg/sample respectively for cyclohexanone and 87% for 0.052 mg/sample of MIBK [2].

REFERENCES:
[1] UBTL Report, Sequence #5528-J (NIOSH, unpublished, Oct. 2, 1986).
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METHOD REVISED BY: Edward J. Slick, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General Information

Compound (Synonyms)	Formula (M.W.)	Properties*	Exposure Limits, ppm OSHA / NIOSH / ACGIH	mg/m³/ ppm @ NTP
Acetone 2-Propanone; CAS #67-64-1)	CH_3COCH_3 (58.08)	liquid; BP 56 °C; d 0.791 g/mL; VP 35.5 kPa (266 mm Hg)	750; STEL 1000 250 750; STEL 1000	2.37
Cyclohexanone (CAS #108-94-1)	$C_6H_{10}O$ (98.15)	liquid; BP 155 °C; d 0.947 g/mL; VP 0.3 kPa (2 mm Hg)	25 (skin) 25 (skin) 25 (skin)	4.01
Diisobutyl ketone (2,6,-dimethyl- 4-heptanone; CAS #108-83-8)	$((CH_3)_2CHCH_2)_2CO$ (142.24)	liquid; BP 169 °C; d 0.847 g/mL; VP 0.23 kPa (1.7 mm Hg)	25 25 25	5.82
2-Hexanone (methyl n-butyl ketone; MBK; CAS #591-78-6)	$CH_3(CH_2)_3COCH_3$ (100.16)	liquid; BP 127 °C; d 0.812 g/mL; VP 0.4 kPa (3 mm Hg)	5 1 5	4.09
Methyl isobutyl ketone (MIBK; hexone; isopropyl acetone; 4-methyl- 2-pentanone; CAS #108-10-1)	$(CH_3)_2CHCH_2COCH_3$ (100.16)	liquid; BP 117 °C; d 0.800 g/mL; VP 2.0 kPa (15 mm Hg)	50; STEL 75 50; STEL 75 50; STEL 75	4.09
2-Pentanone (methyl propyl ketone; CAS #107-87-9)	$CH_3CH_2CH_2COCH_3$ (86.13)	liquid; BP 100 °C; d 0.812 g/mL, VP 3.6 kPa (27 mm Hg)	200; STEL 250 150 200; STEL 250	3.52

*Density @ 25 °C; VP @ 20 °C.

FORMULA: Hg

M.W.: 200.59

MERCURY

METHOD: 6009
ISSUED: 5/15/89

OSHA: 0.05 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin) [1]
ACGIH: 0.05 mg/m^3

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; MP -39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C

SYNONYMS: quicksilver; CAS# 7439-97-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Hydrar in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.05 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [2]

FIELD BLANKS: 10% of samples
MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [3]
(10-L samples)

BIAS: not significant [2,3]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{++} in 1% HNO_3

RANGE: 0.1 to 1.2 µg per sample

ESTIMATED LOD: 0.03 µg per sample

PRECISION (s_r): 0.042 @ 0.9 to 3 µg per sample [4]

APPLICABILITY: The working range is 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [4].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [5,6,7]. This method is based on the method of Rathje and Marcero [8] and is similar to the OSHA method ID 145H [3].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg++, 1000 µg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloricacid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 µg/mL. Place 0.1 mL 1000 µg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v).

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hydrar held in place by glass wool plugs (commercially available from SKC, Inc., Cat. #226-17-1).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the Hydrar may be used if particulate mercury isto be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-µL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

*See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and intact skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.15 to 0.25 L/min for a sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hydrar sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 hour or until the black Hydrar sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series of working standards covering the range 0.01 to 0.5 µg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height from the recorder vs. solution concentration, µg/sample).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 µg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
    a. Remove the bubbler from the BOD bottle.
    b. Rinse the bubbler with deionized water.
    c. Allow the recorder tracing to establish a stable baseline.
    d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
    e. Quickly add 5 mL 10% stannous chloride solution.
    f. Quickly place the bubbler into the BOD bottle.
    g. Allow the spectrophotometer to attain maximum absorbance.
    h. Vent the mercury vapor from the system.
    i. Rinse the bubbler using deionized water.
    i. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
    j. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot (W,µg) from the calibration graph.
18. Calculate the concentration C (mg/m^3), of mercury in the air volume sampled, V (L):

$$C = [W \bullet (Vs/Va) - B]/V$$

Where:
Vs = original sample volume (step 8; normally 50 mL)
Va = aliquot volume (step 9; normally 20 mL)
B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [8]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [9]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m^3 and an adsorbent tube loading of 1 to 7 µg was used. The Hydrar material used in the present method is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [10]. OSHA also validated a method for mercury using Hydrar [3]. An average 99% recovery, with $s_r = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 µg) of mercury added (as $Hg(NO_3)_2$) [11]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at -15 °C; longer storage times were not investigated [11].

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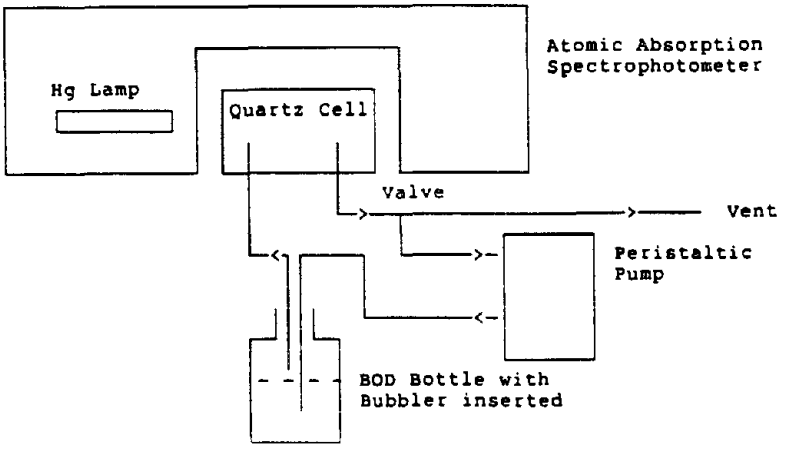
METHOD WRITTEN BY: Keith R. Nicholson and Michael R. Steele, Data Chem, Inc., Salt Lake City, Utah. under NIOSH contract No. 200-87-2533.

APPENDIX: Cold Vapor Mercury Analysis System



1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hydrar tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow which will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination due to adsorption of mercury.

FORMULA: $C_5H_8O_2$; $H_2C=C(CH_3)COOCH_3$

M.W.: 100.12

METHYL METHACRYLATE

METHOD: 2537

ISSUED: 5/15/89

OSHA: 100 ppm
NIOSH: 100 ppm
ACGIH: 100 ppm
(1 ppm = 4.10 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.944 g/mL @ 20 °C; BP 100 °C; VP 4.7 kPa (35 mm Hg) @ 20 °C; explosive range 1.7 to 8.2% v/v in air

SYNONYMS: methacrylic acid methyl ester; CAS #80-62-6.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(XAD-2, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 8 L

SHIPMENT: in dry ice

SAMPLE STABILITY: ≥7 days @ 25 °C [1];
≥32 days @ 4 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 193 to 725 mg/m^3
(3-L samples) [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.063 [3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl methacrylate

DESORPTION: 2 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 100 °C

CARRIER GAS: He, 1 mL/min, makeup 20 mL/min

COLUMN: 30 m x 0.25-mm ID DB-1; 1-µm film fused silica capillary [2]

CALIBRATION: standard solutions of methyl methacrylate in CS_2

RANGE: 0.03 to 1 mg per sample [2,3]

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION (s_r): 0.007 @ .56 to 2.35 mg per sample [1]

APPLICABILITY: The working range is 10 to 1100 mg/m^3 (2.4 to 270 ppm) for a 3-L air sample. Because of the similarity in the chemical structures and properties of methyl methacrylate and ethyl methacrylate and the available stability and desorption efficiency data this method may also be useful for determining ethyl methacrylate in air [4].

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises NIOSH Method S43 [5], which utilized a 20-ft. x 1/8-inch stainless steel column, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport with nitrogen as carrier gas at 30 mL/min.

REAGENTS:

1. Methyl methacrylate, chromatographic quality.
2. Carbon disulfide, reagent grade.*
3. Undecane, 99%
4. Eluent: carbon disulfide, containing 0.1% (v/v) undecane or other suitable internal standard.
5. Calibration stock solution, 94.4 mg/mL. Dilute 1.0 mL methyl methacrylate to 10 mL with eluent.
6. Helium, pre-purified.
7. Hydrogen, pre-purified.
8. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections (front = 400 mg; back = 200 mg) of XAD-2 resin (20/50 mesh), contained and separated by plugs of silylated glass wool. Tubes are commercially available (SKC ST 226-30-06 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (see page 2537-1).
4. Syringes, microliter, 10-µL, readable to 0.1µL.
5. Pipets, various sizes to prepare standards.
6. Flasks, volumetric, 10-mL.
7. Vials, 2-mL and 5-mL, glass with PTFE-lined screw caps.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (has flash point = -30 °C); work with it only in a hood. Methyl methacrylate may cause irritation of the nose, throat, skin and eyes [6].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of 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 sample size of 1 to 8 L.
4. Cap the samplers. Pack securely for shipment in a cold container at 4 °C or lower.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections in separate 5-mL vials. Discard plugs.
6. Add 2.0 mL eluent to each vial. Cap each vial.
7. Allow to stand 30 min. with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of analyte or calibration stock solution to eluent in 10-mL volumetric flasks and dilute to mark. Use serial dilutions as needed to obtain methyl methacrylate concentrations in the range 0.005 to 0.5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of XAD-2 used. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of calibration stock solution directly into front sorbent section with a microliter syringe.
   c. Cap the tubes and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2537-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.
12. Measure peak area. Divide the peak area of the analyte by the peak area of the internal standard on the same chromatogram.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Method S43 was issued on July 6, 1979, and validated with generated atmospheres over the concentration range 193 to 725 mg/m^3 [3,7]. Average recovery was 98.1% (18 samples) in the range 0.56 to 2.35 mg/sample. Overall precision (s_r) was estimated to be 0.063. Breakthrough volume was 6.46 L for 786 mg/m^3 methyl methacrylate in air with 90% relative humidity. In order to achieve greater sensitivity, analytical modifications in the method were made [2]. Desorption efficiency was checked by spiking 0.56 to 2.4 mg per sample onto XAD-2 tube; DE found was in the range 0.96 to 1.0. Storage studies over 32 days at 4 °C showed an average recovery of 97.3% [2].

A storage and stability study for ethyl methacrylate was performed on XAD-2 using 0.14 to 1.4 mg of analyte per sample at 20 °C and also at 4 °C for 23 days. The results of the study indicated an average recovery in the range 95 to 107%.

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

METHOD REVISED BY: James F. Tanguay, Ph.D., NIOSH/DPSE; S43 originally validated under NIOSH Contract NO. 210-76-0123.

FORMULA: Table 1

M.W.: Table 1

NITROSAMINES

METHOD: 2522

ISSUED: 5/15/89

OSHA: no PELs; N-nitrosodimethylamine is a carcinogen
NIOSH: no recommended exposure limits
ACGIH: no TLVs

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Thermosorb/N™ air sampler)

FLOW RATE: 0.2 to 2 L/min

VOL-MIN: 15 L @ 10 μg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 weeks @ 20 °C [1,2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

!TECHNIQUE: GAS CHROMATOGRAPHY, TEA [1]
!
!ANALYTE: nitrosamines (Table 1)
!
!DESORPTION: 2 mL 1/3 (v/v) methanol dichloromethane, stand 30 min
!
!INJECTION VOLUME: 5 μL
!
!COLUMN: stainless steel (10 in x 1/8 in); 10% Carbowax 20M + 2% KOH on Chromosorb W-AW
!
!TEMPERATURE: -INJECTION: 200 °C
! -DETECTOR: 550 °C to 600 °C
! -COLUMN: 110 °C to 200 °C programmed @ 5°/min;
!
!GASES: N_2 carrier, 25mL/min; oxygen, 5 mL/min; ozone, 0.2 mL/min
!
!CALIBRATION: standard solution of analytes in methanol/dichloromethane
!
!RANGE: 0.15 to 0.5 μg per sample [2]
!
!ESTIMATED LOD: 0.05 μg per sample [2]
!
!PRECISION (s_r): 0.014 @ 0.05 to 0.4 μg per sample [2]
!

APPLICABILITY: The working range is 0.003 to 10 mg/m^3 for a 50-L air sample. If high ambient concentrations of nitrosamines are expected another Thermosorb/N tube should be used as a back-up in sampling.

INTERFERENCES: When the thermal energy analyzer (TEA) is operated in the nitrosamine mode, it is highly specific, for N-nitroso compounds. Because of the TEA's selectivity and sensitivity, it is possible to chromatograph and quantitate N-nitroso compounds, even in the presence of other co-eluting compounds. Therefore, there is little or no interference from other compounds.

OTHER METHODS: This replaces NIOSH methods P&CAM 252 [3] and P&CAM 299 [4].

REAGENTS:

1. Dichloromethane, reagent grade.
2. Methanol, reagent grade.
3. Nitrogen, purified.
4. Oxygen, purified 99.99%.
5. Standard solution of N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodipropylamine, N-nitrosodibutylamine, N-nitrosomorpholine, N-nitrosopiperidine, N-nitrosopyrrolidine.
6. Eluent, 1/3 (v/v) dichloromethane/methanol.
7. Air, filtered, compressed.
8. Ozone, purified 99.99%.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Commercially available Thermosorb/N Tubes (Thermoelectron Corp., Waltham, MA; Cat. # 6533).
2. Personal sampling pump, 0.2 to 2 L/min, with flexible tubing.
3. Gas chromatograph equipped with thermal energy analyzer (TEA), integrator and column (page 2522-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Pipets, various sizes for preparing standards.
6. Syringes, 1-, 5-, 10-, 25-, and 100-µl readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Gloves for safe handling of toxic chemicals.
9. Syringe, glass, 5.0-mL, with male luer adapter.
10. Needle, industrial blunt, 20-gauge with female luer adapters.

SPECIAL PRECAUTIONS: N-nitrosodimethylamine is an OSHA-regulated carcinogen. Other nitrosamines are suspected carcinogens and are very toxic. Handle samples and standards in a well-ventilated hood or glove box.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the Thermosorb/N tube from the foil pouch. Save the pouch.
3. Remove the red end caps from the inlet and outlet ports. Store red caps on the Thermosorb/N tube in the brackets under the "AIR IN" sign.
4. Label the Thermosorb/N tube with the peel-off "AIR SAMPLER" label provided on the foil pouch.
5. Attach the Thermosorb/N tube to the sampling pump with flexible tubing.
6. Sample at an accurately known flow rate between 0.2 and 2 L/min for a total sample size of 15 to 1000 L.
7. After sampling, detach the sampler from the pump.
8. Replace the red end-caps on the inlet and outlet ports of the sampler.
9. Replace the Thermosorb/N tube in the foil pouch. Fold the pouch and seal it with the clip provided and pack securely for shipment.

SAMPLE PREPARATION:

10. Remove the sampler from the foil pouch.
11. Label analysis vial with the label from the Thermosorb/N air sampler.
12. Remove the red end-caps, store them in the bracket provided with the tube.
13. Attach a syringe needle to the male luer fitting of the Thermosorb/N tube.
14. Attach a syringe barrel containing eluent to the female luer fitting of the Thermosorb/N tube.
15. Elute by "backflushing" the Thermosorb/N tube with 2.0 mL of eluent. Collect the effluent in the labeled vial.
    NOTE: The optimum elution rate is 0.5 ml/min.

CALIBRATION AND QUALITY CONTROL:

16. Calibrate daily with at least five working standards over the range of 0.05 to 0.5 µg of analyte per sample (0.025 to 0.25 µg/mL).
    a. Add known amounts of the nitrosamines standard solution to eluent in 10-ml volumetric flasks and dilute to mark.
    b. Analyze together with samples.
    c. Prepare calibration graph (peak area of analyte vs. µg analyte).
17. Determine desorption efficiency (DE) at least once for each batch of Thermosorb/N tubes used.
    a. Inject a known amount of nitrosamine standard solution directly onto the Thermosorb/N tube with a microliter syringe.
    b. Cap the tube. Allow to stand overnight.
    c. Desorb (steps 12 through 15) and analyze together with working standards (steps 19 through 22).
    d. Prepare a graph of DE vs. ug analyte recovered.
18. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

19. Set gas chromatograph and TEA to the conditions listed on page 2522-1.
20. Inject sample aliquot manually, using solvent flush technique or with an autosampler.
21. Approximate retention times of the seven nitrosamines at indicated column temperatures are:

COMPOUND	COLUMN TEMP. °C	RETENTION TIME (MIN)
N-nitrosodimethylamine	120	2.23
N-nitrosodiethylamine	125	3.07
N-nitrosodipropylamine	142	6.25
N-nitrosodibutylamine	145	7.41
N-nitrosomorpholine	178	13.23
N-nitrosopiperidine	169	11.97
N-nitrosopyrrolidine	166	11.23

22. Measure peak area.

CALCULATIONS:

23. Determine the mass, µg (corrected for DE) of analyte found in the sample (W).
24. Calculate concentration, C, analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

The method was evaluated over the range 0.05 to 0.5 µg of the seven nitrosamines per sample. Desorption efficiency was checked by spiking known amounts of the compounds on Thermosorb/N tubes and was found to be nearly 100% for all nitrosamines studied. The sampling device is small and interferences are minimal; large concentrations can be sampled (up to 1500 µg loading) with no breakthrough. Samples can be stored at room temperature for long periods of time (>6 weeks). Some field samples were also used for evaluation of this method [2].

REFERENCES:
[1] Roundbehler, D. and Fajen J. N-Nitroso Compounds in the Factory Environment, NIOSH contract #210-77-0100 (1977).
[2] Foley, D. NIOSH/MRSB Method Development Efforts, Backup Data Report and Analysis for Nitrosamines, (NIOSH, Unplublished, (1983-1988).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 252 U.S. Department of Health Education and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Ibid., V.5, P&CAM 299, NIOSH Publ. 79-141 (1979).

METHOD WRITTEN BY: G. David Foley, NIOSH/DPSE.

Table 1: General Information

Compounds (Synonyms)	Formula	MW	Properties
N-nitrosodimethylamine (N-Methyl-N-nitrosomethanamine; dimethylnitrosamine; DMN; DMNA; CAS #62-75-9)	$(CH_3)_2N-N=O$	74.1	liquid; d 1.01 g/mL @ 20 °C; BP 150 °C; VP 0.36 kPa (2.7 mm Hg @ 20 °C)
N-nitrosodiethylamine (N-Ethyl-N-nitrosoethanamine; diethylnitrosamine; DEN; DENA; CAS #55-18-5)	$(C_2H_5)_2N-N=O$	102.1	liquid, d 0.94 g/mL @ 20 °C; BP 175 °C; VP 0.1 kPa (0.86 mm Hg @ 20 °C)
N-nitrosodipropylamine (N-Propyl-N-nitrosopropylamine DPN; DPNA; CAS #621-64-7)	$(C_3H_7)_2N-N=O$	130.2	liquid; d 0.916 g mL/@ 20 °C; BP 194.5 °C; VP 11 Pa (0.085 mm Hg @ 20 °C)
N-nitrosodibutylamine (N-Butyl-N-nitrosobutylamine; dibutylnitrosamine; CAS #924-16-3)	$(C_4H_9)_2N-N=O$	158.2	liquid; d 9.901 g/mL @ 20 °C; BP 116 °C @ 14 mm Hg, VP 4 Pa (0.03 mm Hg @ 20 °C)
N-nitrosomorpholine (NMOR; 4-Nitrosomorpholine; MORNA; CAS #59-89-2)	$O=C_4H_8N-N=O$	116.1	liquid/crystals; d unknown; BP 225 °C; MP 29 °C; VP unknown
N-nitrosopiperidine (N-NPIP; PIPNA; NPIP; CAS #100-75-4)	$(CH_2)_5N-N=O$	114.2	liquid; d 1.063 @ 19 °C; BP 217 °C @ 720 mm Hg; @ 20 °C VP unknown
N-nitrosopyrrolidine (N-NPyr; NPYR, PYRNA; 1-Nitrosopynolodine; CAS #930-55-2)	$C_4H_8N-N=O$	100.1	liquid; d 109 g/mL @ 20 °C; BP 214 °C; VP 10 Pa (0.072 mm Hg @ 20 °C)

FORMULA: C_6Cl_5OH

M.W.: 266.35

PENTACHLOROPHENOL

METHOD: 5512
ISSUED: 5/15/89

OSHA: 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin)
ACGIH: 0.5 mg/m^3; STEL 1.5 mg/m^3 (skin)
(1 ppm = 10.8 mg/m^3 @ NTP)

PROPERTIES: solid; MP 190 °C; d 1.978 @ 22 °C;
VP 0.016 kPa (0.12 mm Hg) @ 100 °C

SYNONYMS: penta; PCP; CAS #87-86-5.

SAMPLING

SAMPLER: FILTER + BUBBLER
(mixed cellulose ester membrane with stainless steel backup screen/ ethylene glycol)

FLOW RATE: 0.5 to 1.0 L/min

VOL-MIN: 48 L @ 0.5 mg/m^3
-MAX: 480 L

SHIPMENT: place filter in bubbler containing 15 mL ethylene glycol after sampling

SAMPLE STABILITY: at least 8 days @ 25 °C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.265 to 1.130 mg/m^3 [1]
(180-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.072 [1]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: pentachlorophenol

EXTRACTION: 10 mL methanol

INJECTION VOLUME: 20 µL

MOBILE PHASE: 60% methanol/40% water, 1.5 mL/min

COLUMN: µ-Bondapak C_{18}, 10-µm particle size, 30 cm x 3.9 mm ID

DETECTOR: UV @ 254 nm

CALIBRATION: standard solutions of pentachlorophenol in ethylene glycol and methanol

RANGE: 24 to 270 µg per sample [1]

ESTIMATED LOD: 8 µg per sample [2]

PRECISION (s_r): 0.051 @ 45 to 180 µg per sample [1]

APPLICABILITY: The working range is 0.13 to 11 mg/m^3 for a 180-L air sample. This method is also applicable to STEL measurements using a 15-L sample. The method has been used to sample for pentachlorophenol in the presence of 2,3,4,6-tetrachlorophenol at a lumber yard [3].

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S297 [2]. An independent analytical method provided by Vulcan Materials Co. [4] using a sampling train consisting of Zefluor filter and silica gel tube and HPLC analysis was used by a NIOSH contractor [5] for analyzing samples containing pentachlorophenol.

REAGENTS:

1. Pentachlorophenol*, ACS reagent grade.
2. Ethylene glycol, ACS reagent grade.
3. Methanol, distilled in glass.
4. Isopropanol, distilled in glass.
5. Water, deionized and distilled.
6. Calibration stock solution, 5 mg/mL. Dissolve 50 mg pentachlorophenol in 10 mL isopropanol.

*See Special Precautions.

EQUIPMENT:

1. Sampler: 37-mm cellulose ester membrane filter (0.8-µm pore size) supported by stainless steel screen in three-piece filter holder followed by a 25-mL bubbler with 15 mL ethylene glycol.
2. Personal sampling pump, 1.5 mL/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 20-mL with PTFE-lined caps.
5. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5512-1).
6. Tweezers.
7. Syringes, 50- and 100-µL.
8. Volumetric flasks, 25-mL.
9. Pipets, 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 25-mL.

SPECIAL PRECAUTIONS: Pentachlorophenol can irritate the eyes, can be absorbed through the skin, and can cause liver damage [6].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL ethylene glycol to a bubbler.
3. Attach outlet of filter holder to inlet arm of bubbler. Connect outlet arm of bubbler to a second empty bubbler and then to the sampling pump.
4. Sample 48 to 480 L (15 L for STEL) of air at an accurately known rate between 0.5 and 1.0 L/min.
5. Transfer filter carefully using tweezers to the bubbler. Seal bubbler for shipment in a suitable container in order to prevent damage during transit. Seal the inlet and outlet of the bubbler stem by connecting a piece of PTFE tubing between them or by inserting PTFE plugs in the inlet and outlet.
6. Collect a bulk sample (ca.1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Transfer the liquid from the bubbler, quantitatively, to a graduated cylinder.
8. Bring volume to 15 mL with ethylene glycol. (If volume is greater than 15 mL, as would be the case when H_2O is scrubbed from humid air, record the volume and make an appropriate correction in the final calculations.)
9. Just before analysis, add 10 mL methanol and mix gently but thoroughly.

CALIBRATION AND QUALITY CONTROL:

10. Prepare working standards (8 to 270 µg/25 mL) by adding appropriate aliquots of calibration stock solution to a 60/40 (v/v) mixture of ethylene glycol and methanol.
11. Analyze working standards together with samples and blanks (steps 14 through 16). Prepare a calibration graph of area vs. amount (µg) of pentachlorophenol per 25 mL of sample.

12. Determine recovery for each lot of filters used for sampling in the concentration range of interest. Prepare four filters at each of five levels plus three media blanks.
    a. Spike aliquot of calibration solution onto each filter.
    b. After air-drying, extract filters in 15 mL ethylene glycol.
    c. Just before analysis, add 10 mL methanol and analyze (steps 14 through 16).
    d. Prepare graph of recovery vs. µg pentachlorophenol.
13. Check recovery at two levels for each sample set. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

14. Set liquid chromatograph to conditions given on page 5512-1.
15. Inject 20-µL sample aliquot.
16. Measure peak area.

CALCULATIONS:

17. Read mass, µg (corrected for recovery), of pentachlorophenol (W) found in the sample from the calibration graph.
18. Calculate concentration of pentachlorophenol in the actual air volume, V (L), at the sampling site:

$$C = \frac{W \cdot 10^3}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was validated in 1977, over the range of 0.265 to 1.131 mg/m^3 at 24 °C and pressure of 761 mm Hg using 180-L samples [1,2]. Overall sampling and measurement precision, s_r, was 0.072, with average recovery of 105%, representing a non-significant bias. The concentration of pentachlorophenol was independently verified by direct UV analysis of sample solutions. Recovery of pentachlorophenol from filters was 101% in the range 45 to 180 µg per sample. Sample stability during storage was evaluated at a sample concentration of 100 µg pentachlorophenol per sample. Samples showed a recovery of 95.3% after eight days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S297, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Analysis of NIOSH Samples for Pentachlorophenol and Tetrachlorophenol, NIOSH/MRSB Sequence #4492, Utah Biomedical Research Laboratory, Salt Lake City, UT (1984).
[4] Vulcan Materials Co. Analytical Backup Report #1. Determination of Pentachlorophenol in Air, Birmingham, AL 35255 (1982).
[5] Analysis of NIOSH samples for Pentachlorophenol, NIOSH/MRSB Sequence #4065, Southern Research Institute, Birmingham, AL 35255, (1984).
[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY: M. J. Seymour, NIOSH/DPSE.

FORMULA: SiO_2

M.W.: 60.08

QUARTZ in coal mine dust, respirable

METHOD: 7603

ISSUED: 5/15/89

OSHA: 10 mg/m^3/(%SiO_2 + 2)
NIOSH: 0.05 mg/m^3 [1]
ACGIH: 0.1 mg/m^3

PROPERTIES: solid; d 2.65 g/mL @ 0 °C; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to crystobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide; CAS #1480-60-7.

SAMPLING

SAMPLER: CYCLONE + PREWEIGHED FILTER (cyclone, 10-mm + PVC filter, 37-mm, 5-µm)

FLOW RATE: 2.0 L/min

VOL-MIN: 300 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

BULK SAMPLE: required for OSHA standard calculations; area respirable or settled dust

ACCURACY

RANGE STUDIED: 25 to 160 µg/sample [2] (2 mg quartz/m^3 atmosphere)

BIAS: none

OVERALL PRECISION (s_r): 0.13 to 0.22 (varies with sample loading and matrix) [2]

MEASUREMENT

TECHNIQUE: INFRARED SPECTROPHOTOMETRY (IR)

ANALYTE: quartz

WEIGH: dust cassette

ASH: muffle furnace or RF plasma asher

REDEPOSIT: 0.45-µm acrylic copolymer membrane filter

IR: scan, 1000 to 650 cm^{-1}, absorbance mode with blank filter in reference beam

CALIBRATION: standard suspension of quartz in 2-propanol

RANGE: 30 to 250 µg per sample [2]

ESTIMATED LOD: 10 µg quartz per sample [2]

PRECISION (s_r): 0.05 to 0.10 (varies with sample matrix) @ 100 to 500 µg per sample [2,3]

APPLICABILITY: The working range is 0.03 to 2 mg/m^3 for a 1000-L sample. The method was specifically developed for respirable coal mine dust samples. [3]

INTERFERENCES: Calcite is used as a dusting agent in coal mines and interferes by reacting with quartz during muffle furnace treatment resulting in low quartz assay. Kaolinite is sometimes present in coal dust and interferes by absorbing radiation at the quartz analytical wavelength of 800 cm^{-1}. These interference are corrected by procedures given in this method. Muscovite does not interfere. Cristobalite, tridymite and amorphous silica all have absorbance peaks at 800 cm^{-1} but none of these have been detected in coal mine dust.

OTHER METHODS: Quartz can also be determined by NIOSH Methods 7500 (XRD), 7602 (IR), and 7601 (UV-VIS) and MSHA Method P7.

REAGENTS:

1. Quartz (SRM 1878, available from Office of Standard Reference Materials, B311 Chemistry Building, Washington, DC 20234).*
2. 2-Propanol, reagent grade.
3. Calibration stock solution, 15 µg/mL. Suspend 7.5 mg of quartz in 2-propanol in a 500-mL volumetric flask and dilute the suspension to the mark with 2-propanol (See CALIBRATION AND QUALITY CONTROL).
4. Kaolinite (Hydrite UF from Georgia Kaolin), for standard samples, 100 µg/mL. Suspend 50 mg of dried kaolinite in a 500-mL volumetric flask with 2-propanol and dilute the suspension to the mark with 2-propanol.
   NOTE: This is not required if muffle furnace is used to ash samples (see step 5).
5. Hydrochloric acid solution. 25% v/v conc. HCl in distilled water. Required if calcite is present and samples are ashed with a muffle furnace.
6. Dessicant (Drierite).
7. Oxygen, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone; 37-mm, 5-µm preweighed polyvinyl chloride (PVC) membrane filter, filter cassette.
2. Personal sampling pump: 2.0 L/min with flexible connecting tubing.
3. Filters for standards and redeposition, 47-mm diameter, 0.45-µm pore size, vinyl chloride-acrylonitrile copolymer membrane (DM-450 Gelman Instrument Co., Ann Arbor, MI 48106, or equivalent).
4. Glass fiber filters, 25-mm diameter, for backup during filtration.
5. Filtration apparatus for redepositing sample after ashing, consisting of fritted support (Millipore XX1002502), side-arm vacuum flask and special funnel similar to Millipore XX1002514 but with an internal diameter of 1.0 cm. This can be made of glass with a bakelite base and should seal to the fritted support to make the fit liquid-tight.**
6. Funnel for treating filters to remove calcite (required only if using a muffle furnace). This consists of Millipore XX1002514 with apparatus in item 5 above except with funnel internal diameter ca. 1.6 cm. This step requires 0.5-µm pore size PVC filters, 37-mm diameter to recollect residue.**
7. Double-beam infrared spectrophotometer, with sample holders for infrared instrument: metal (preferably steel) plates with a center hole to match the diameter of the sample deposit (1 cm), and small ring magnets to hold the filter in position on the plate.
8. Low-temperature radio frequency asher (LTA) or muffle furnace.
9. Ultrasonic bath.
10. Porcelain crucibles with covers, 10-mL.**
11. Beakers, 50-mL.**
12. Analytical balance, 0.01-mg; dessicator cabinet;
13. Magnetic stirrer with thermally insulated top, and stirring bars.
14. Reagent bottles with ground glass stoppers, 500-mL, and volumetric flasks, 500-mL.**
15. Tweezers.
16. Petri dishes, plastic, for 47-mm diameter filters.
17. Polyethylene wash bottles; metal spatulas;
18. Serological pipets, various sizes as required.
19. Lighted viewing box (optional).

** Glassware should be detergent-washed, rinsed thoroughly with distilled or deionized water, and then with 2-propanol, and dried in a dust-free area.

SPECIAL PRECAUTIONS: Avoid inhaling quartz dust [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Preweigh each filter to the nearest 0.01 mg.
3. Sample at 2.0 L/min for a total sample size of 300 to 1000 L. Avoid overloading the filter (maximum ca. 2 mg dust loading on the filter).
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

4. Reweigh the filters under conditions identical to those for preweighing. The difference is the sample weight, W (mg).
5. Ash sample and blank filters by one of the following methods:
   a. Low-temperature ashing.
      Using forceps, transfer filter to a 50-mL beaker. Ash 2 hrs at 300 watts RF power and oxygen flow rate of 75 mL/min using techniques recommended in the instrument manual. After ashing, add 15 mL 2-propanol to each beaker.
   b. Muffle furnace ashing.
      (1) If the samples contain calcite in concentrations greater than 20% of the total dust loading, wash the filters with acid using the filtration apparatus with the 1.6-cm ID glass funnel. Place a 25-mm glass fiber filter over the frit area, then place a 0.5-µm, 37-mm PVC filter over the glass fiber filter. Clamp down the filter funnel. Add 5 mL 2-propanol and check for leakage. Remove the sample filter from the cassette. Fold it in half with the collection surface inside, then in quarters. Place the folded filter into the funnel. If necessary, push the filter to the bottom half of the funnel with a glass rod. Add 10 mL HCl solution, then 5 mL 2-propanol. Continue suction until all of the liquid has been removed. Press the folded sample filter onto the surface of the collecting filter if necessary to remove all the liquid. Remove both filters and place in a porcelain crucible. Allow filters to air-dry.
      (2) If acid wash was not required, transfer filter samples and blanks to porcelain crucibles.
      (3) Loosely cover the crucibles and place in a muffle furnace. Hold for 2 hrs at 600 °C. After ashing, add several mL 2-propanol to the ash, scrape the crucible to loosen all particles and transfer to a 50-mL beaker. Wash the crucible several times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to ca. 15 mL.
6. Redeposit the sample residue as follows using the filtration apparatus with the 1.0-cm funnel. With a slight vacuum applied, place a 25-mm glass fiber filter on the fritted base. Cut a 47-mm DM-450 filter in half. Superimpose one half over the other, glossy sides down, and place on the glass fiber filter. (The lower half of the DM-450 filter serves as a blank and is used in the reference beam of the infrared spectrometer). Position filter funnel, apply clamp and turn off vacuum. Add several mL 2-propanol to the funnel. Check that the funnel is securely and uniformly clamped. Place beakers into ultrasonic bath for at least 30 sec to ensure homogeneous dispersion. Remove a beaker, wipe excess water from the outside, transfer slurry to the filtration funnel and reapply vacuum. During filtration, rinse the beaker twice with 2-propanol to remove all dust and add rinsings to funnel. Control the filtration rate to keep the liquid near the funnel top during rinsing to avoid disturbing the deposit. When the depth of liquid in the funnel reaches ca. 4 cm above the filter, gently rinse the inside of funnel with 2-propanol and complete filtration. Remove the clamp and lift off the funnel, taking care not to disturb and deposit. Release the vacuum. Define the deposit area by marking around the circumference using a pencil or scriber. This is especially important for standards or light-colored samples. Place the DM-450 filter halves in petri dishes and allow to air-dry.

CALIBRATION AND QUALITY CONTROL:

7. Prepare and analyze standard quartz filters.
   a. Place the flask containing the calibration stock solution in an ultrasonic bath for 30 to 45 min.
   b. Move the flask to a magnetic stirrer and stir slowly while the flask cools to room temperature. Continue to stir slowly while preparing standards.
   c. Mount a DM-450 filter in the filtration apparatus in the same manner used to redeposit the samples. Add 5 mL 2-propanol to the funnel. Withdraw an aliquot of the quartz suspension from the center of the flask. Draw liquid to the mark but do not attempt to adjust volume by draining pipet. Carefully wipe the outside of the pipet, then drain the suspension into the filter funnel. Rinse down the inside wall of the pipet with a few mL of 2-propanol, draining the washings into the filter funnel. Apply vacuum to complete the filtration. Prepare quartz standards to cover the range 10 to 250 µg per filter.
   d. Carry an additional set of these standards and media blanks through steps 5 and 6 to monitor for contamination and losses.

   NOTE: Accuracy depends on obtaining uniform deposition of samples and standards across the filter surface and obtaining reproducible aliquots from the quartz suspension. This requires some skill. The quartz calibration curve should be prepared before analyzing samples as a check on the analyst's ability to prepare uniform deposits. Repeatability should be <10% on replicate standards with more than 40 µg quartz.

8. Perform an IR scan for each standard filter using the other half of the filter in the reference beam (steps 10 through 12). Construct a standard curve of absorbance at 800 cm^{-1} vs. µg quartz per filter. This curve should be linear and pass through the origin.
9. (Only for samples ashed in LTA). Prepare suspensions of at least 5 kaolinite standards in the range 100 to 600 µg per filter. Perform an IR scan of the kaolinite standards from 1000 to 650 cm^{-1}. Draw baselines as described in step 12 and measure the height of the absorbance bands at both 915 and 800 cm^{-1}. Prepare a graph with absorbance at 915 cm^{-1} as ordinate vs. absorbance at 800 cm^{-1} as abscissa. Plot a point for each standard. If possible, generate the correction curve data on the same day that coal mine dust samples are analyzed since curve parameters may vary somewhat from day to day. A curve through the points should be linear but will not pass through the origin since the peak at 915 cm^{-1} is more intense than the peak at 800 cm^{-1} and small amounts of kaolinite do not interfere with the quartz analysis.

   NOTE: Kaolinite correction calibration curve is required when samples are ashed in an LTA since kaolinite is not destroyed under these circumstances and has an interfering peak at 800 cm^{-1} for which a correction must be performed.

MEASUREMENT:

10. Set appropriate instrument conditions for quantitative analysis.
11. Place the dry DM-450 filter-half containing the dust deposit on a holder. Center the deposit over the hole in the holder and secure the filter with a magnet. (A lighted viewing box facilitates this procedure). Insert the sample into the sample beam of the spectrophotometer. Place the other half of the DM-450 filter on another holder, secure with a magnet and insert it into the reference beam.

    NOTE: For best precision, the reference filter should be half of the same DM 450 filter which contains the redeposit. However, for routine analysis, the same 2-propanol-treated blank can be used for all filters with the same lot number.

12. Run an infrared scan, in linear absorbance mode from 1000 to 650 cm^{-1}. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from ca. 820 to 670 cm^{-1}. Measure and record the absorbance at 800 cm^{-1}, baseline to maximum. If the sample was ashed in an LTA, the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw a baseline under this band from ca. 960 cm^{-1} to 860 cm^{-1}. Measure and record the absorbance at 915 cm^{-1}, baseline to maximum.

13. Analyze blanks. Check results for contamination.

CALCULATIONS:

14. Correct for kaolinite, if required. Using the sample absorbance at 915 cm^{-1}, refer to the kaolinite curve to find the absorbance at 800 cm^{-1} due to kaolinite. Subtract this amount from the sample absorbance at 800 cm^{-1}. Use this corrected value to calculate µg quartz in the sample.
15. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} determined in step 12. Determine the weight of quartz, w (µg), from the quartz standard curve. Since the deposition area for samples and standards is the same, it is not necessary to correct for area.
16. Calculate the percent quartz by dividing the weight of quartz, w (µg), by the total sample weight, W (mg). Multiply by 10^{-1} to obtain % units.

$$\% \text{ quartz} = \frac{w\ (\mu g)}{W\ (mg)} \cdot 10^{-1}.$$

EVALUATION OF METHOD:

This method is based on a previously unpublished Bureau of Mines method which was collaboratively tested [2]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher, amount of calcite or kaolinite on the sample, ashing time, pH of solvent to remove calcite, shipment of samples and others. None of these factors was found to have an effect. Results obtained by this method are equivalent to those obtained by Method 7500. A collaborative study of the ruggedized method was performed with 15 laboratories participating [2]. The total errors and interlaboratory and intralaboratory errors were found to be dependent on the type of samples. For samples collected from laboratory-generated aerosols, using a set of matched-flow orifices, the lower and upper limits of the relative standard deviation over the range 60 to 150 µg quartz were:

	Lower	Upper
Total error (RSD)	0.13	0.22
Intralaboratory error	0.07	0.10
Interlaboratory error	0.08	0.14

The lower limit applies to samples containing up to 1 mg coal mine dust with less than 2% kaolinite; the upper limit was found for samples with 2 mg coal mine dust or a lower amount of coal mine dust with more than a few percent kaolinite. The total error increased to 0.36 to 0.40 (lower and upper range) when personal sampling pumps were used to collect the samples. The pump error increased the interlaboratory error. Precision for pure quartz samples is ca. 0.05 in the 100 to 500 µg range [3]. Precision for actual samples is not as good and depends on sample size and ashing technique.

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METHOD WRITTEN BY: Michele Bolyard, NIOSH/DPSE.

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FORMULA: $C_8H_{12}N_4O_5$

M.W.: 244.21

RIBAVIRIN

METHOD: 5027

ISSUED: 5/15/89

OSHA: no standard
NIOSH: no recommended exposure limit
ACGIH: no TLV

PROPERTIES: solid; MP 170 °C; VP negligible; sol. (water): 142 mg/mL @ 25 °C

SYNONYMS: 1-β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide; Virazole; ICN 1229; CAS #36791-04-5

SAMPLING	MEASUREMENT
SAMPLER: FILTER (1-µm, 37-mm glass fiber)	TECHNIQUE: HPLC, UV DETECTION
FLOW RATE: 1 to 4 L/min	ANALYTE: Ribavirin
VOL-MIN: 5 L @ 0.4 mg/m^3 -MAX: 1000 L	EXTRACTION: 3 mL H_2SO_4 (pH = 2.5), ultrasonic
SHIPMENT: routine	COLUMN: 30 cm x 7.8 mm, cation exchange resin
SAMPLE STABILITY: stable in dark at room temperature [1]	INJECTION VOLUME: 30 µL
FIELD BLANKS: 10% of samples	MOBILE PHASE: H_2SO_4, (pH = 2.5), isocratic
	TEMPERATURE: 65 °C
	FLOW RATE: 0.6 mL/min
	DETECTOR: UV, 210 nm
ACCURACY	CALIBRATION: standard solutions of Ribavirin in H_2SO_4 (pH = 2.5)
RANGE STUDIED: not studied	RANGE: 2 µg to 2000 µg per sample [1, 2]
BIAS: unknown	ESTIMATED LOD: 0.7 µg per sample [1, 2]
OVERALL PRECISION (s_r): unknown	PRECISION (s_r): 0.057 @ 19 to 112 µg per sample [1, 2]

APPLICABILITY: The working range is 0.04 to 40 mg/m^3 for a 50-L air sample.

INTERFERENCES: none known.

OTHER METHODS: This method is a modification of a bulk assay procedure developed by Eastman Kodak Company [3].

REAGENTS:

1. Ribavirin,* reagent grade.
2. H_2SO_4,* conc.
3. Mobile phase: add conc. H_2SO_4,* to deionized, distilled water until pH is 2.5 +/- 0.1 as measured by a pH meter.
4. Calibration stock solution: dilute 5 mg Ribavirin to 10 mL in a volumetric flask using mobile phase as solvent. Prepare fresh daily.
5. Standard buffer solutions (pH 7.00 and 3.00) for calibrating pH meter.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 1-µm, 37-mm glass fiber filter (Type A/E; Cat. No. 61652, Gelman Sciences, Inc., Ann Arbor, MI 48106, or equivalent) with a cellulose backup pad in a 2-piece cassette.
2. Personal sampling pump capable of operating for 8 hours at 1 to 4 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph, isocratic, with water jacket (or equivalent) to maintain column temperature at 65 °C; UV detector (210 nm); peak integrator; and cation exchange resin column (Cat. No. HPX-87H, Bio-Rad Laboratories, Richmond, CA 94804 or equivalent).
4. Vials, 10 mL, glass with PTFE-lined cap.
5. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
6. Syringe filters, disposable 0.45-µm pore size, for filtering samples.
7. Pipets, 1- to 10-mL.
8. Volumetric flasks, 10-mL.
9. Forceps.
10. Ultrasonic bath.
11. pH meter.

SPECIAL PRECAUTIONS:

Ribavirin has been found to be teratogenic in animals. [4, 5] Use protective gloves when handling. Work only in a fume hood. Women of childbearing age should exercise extreme caution. Avoid skin contact with concentrated sulfuric acid.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line. Attach sampler to personal sampling pump with flexible tubing.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 5 to 1000 L. Avoid overloading the filter (ca. 2 mg total dust maximum loading).
3. Seal the samplers and pack securely for shipment.
4. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

5. Carefully remove the filter from the cassette. Use forceps to fold the filter in half, and insert into a culture tube. Discard the backup pad.
6. Add 3 mL mobile phase. Seal tightly with screw cap and agitate samples in an ultrasonic bath for 15 minutes.
   NOTE: Although Ribavirin is stable as a solid, it degrades after 12 hours in the mobile phase necessitating daily preparation of standards and prompt analysis of extracted samples. [3]
7. Filter the sample solution through a syringe filter.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.2 to 700 µg/mL.
   a. Add known amounts of calibration stock solution to mobile phase in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 through 13).
   c. Prepare calibration graph (peak area vs. µg Ribavirin).
9. Determine recovery (R) at least once for each lot of filters used for sampling in the range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of Ribavirin onto the filter. Allow filters to air dry.
   b. Store samples overnight in the dark.
   c. Prepare (steps 5 through 7) and analyze with working standards.
   d. Prepare a graph of R vs. µg Ribavirin spiked.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

11. Set up liquid chromatograph system according to manufacturer's recommendations and to the conditions given on page 5027-1.
12. Inject sample aliquot using syringe, fixed volume sample loop or autosampler.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, µg (corrected for R) of Ribavirin found in the sample (W), and in the average media blank (B), from the calibration graph.
15. Calculate concentration, C, of Ribavirin in the air volume sampled, V (L):

$$C = \frac{(W-B)*10^3}{V}, \ \mu g/m^3$$

EVALUATION OF METHOD:

This method is a modification of a bulk assay procedure developed by Eastman Kodak Company [3]. Measurement precision, s_r, was 0.057 with average recovery of 100% representing no bias, based on 16 samples ranging from 19.2 to 112 µg per filter. Sampling precision was not determined. The calibration curve was shown to be linear between 0.63 and 666 µg of Ribavirin/mL of extraction solution. A least-squares fit of the calibration curve yielded a Hubaux-Vos limit of detection of 0.7 µg per filter and a limit of quantitation of 2 µg per filter [1,2].

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METHOD WRITTEN BY:

Barry R. Belinky and G. David Foley, NIOSH/DPSE

FORMULA: SiO_2

M.W.: 60.08

SILICA, crystalline, respirable

METHOD: 7500
ISSUED: 2/15/84
REVISION #1: 5/15/89

OSHA: quartz (respirable), 10 mg/m^3/(%SiO_2+2)
NIOSH: 0.05 mg/m^3 [1]
ACGIH: quartz 0.1 mg/m^3; cristobalite and tridymite (respirable), 0.05 mg/m^3

PROPERTIES: solid; d 2.65 g/cm^3 @ 0 °C; Crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide; CAS #14808-60-7 (quartz), CAS #14464-46-1 (cristobalite), CAS #15468-32-3 (tridymite).

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone + 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 400 L @ 0.05 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

BULK SAMPLE: high-volume respirable (preferred) or settled dust; to identify interferences

ACCURACY

RANGE STUDIED: 25 to 2500 µg/m^3 [2] (800-L sampler)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.09 (50 to 200 µg) [2]

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: crystalline SiO_2

ASH: muffle furnace or RF plasma asher or dissolve in tetrahydrofuran

REDEPOSIT: on 0.45-µm Ag membrane filter

XRD: Cu target X-ray tube, graphite monochromator
Optimize for intensity; 1° slit
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: suspensions of silica in 2-propanol

RANGE: 0.02 to 2 mg per sample [3]

ESTIMATED LOD: 0.005 mg per sample [3]

PRECISION (s_r): 0.08 @ 0.05 to 0.2 mg per sample [2]

APPLICABILITY: The working range is 0.025 to 2.5 mg/m^3 for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This revises Method 7500 (dated 2/15/84) and P&CAM 259 [4] which has been collaboratively tested [2]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. Colorimetry (Method 7601 [10]) is an alternate measurement procedure, as is IR spectrometry (Methods 7602 and 7609).

REAGENTS:

1. Silica standards. Wet-sieve (10-µm sieve) all standards, with 2-propanol [11]. Air-dry, then dry 4 hr at 110 °C, store in desiccator.
   a. Quartz* (SRM 1878) and Cristobalite* (SRM 1879), available from Office of Standard Reference Materials, B311 Chemistry Building, National Institute of Standards and Technology (NIST) Gaithersburg, MD 20899.
   NOTE: Min-U-Sil 5 may also be used as a quartz standard.
   b. Tridymite*, available from NIOSH, DPSE, MRB, 4676 Columbia Parkway, Cincinnati, OH 45226.
2. 2-Propanol, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. Optional (if calcite present): 25% v/v concentrated hydrochloric acid (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone; polyvinyl chloride (PVC) membrane filters, 37-mm diameter, 5-µm pore size; two-piece filter cassette.
   NOTE: Gelman VM-1 filters are unacceptable because of high ash and background. Gelman GLA-5000 and FWS-B filters (MSA) are suitable if THF dissolution is used.
2. Personal sampling pump, 1.7 L/min, with flexible connecting tubing.
3. High-volume sampler: 0.5-inch HASL cyclone; PVC membrane filters, 37-mm diameter, 5-µm pore size; three-piece filter cassette; with high-volume pump, 9 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size (Selas Flotronics, Dresher, PA 19006).
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher or muffle furnace.
8. Membrane filtration apparatus and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm, for wet sieving.
10. Analytical balance (0.01 mg); magnetic stirrer with thermally-insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1]. THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump for 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 L/min for a total sample size of 400 to 1000 L. Avoid overloading the filter (ca. 2 mg maximum load on the filter).
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.
3. Take a high-volume respirable dust sample (e.g., 4 m^3 at 9 L/min).

SAMPLE PREPARATION:

4. Prepare the high-volume respirable dust or settled dust sample for qualitative analysis. The respirable dust sample need only be transferred to a filter and XRD sample holder by: (1) ashing and redepositing as described below for personal samples, or (2) removing part of the dust from a thickly-coated sample and redepositing it, or, (3) by simply mounting all or part of the collection filter on the holder. The settled dust may be ground and/or wet-sieved to best match the airborne dust exposure. Wet-sieving is done with a 10-µm sieve, 2-propanol, and an ultrasonic bath [12], followed by evaporation

of excess alcohol, drying in an oven for 2 hours, and overnight storage in a dessicator. The end product can be deposited on a filter or packed in a conventional XRD powder holder.

NOTE: 1. For quantitative determination of percent silica, weigh out, in triplicate, 2 mg of the respirable or sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.

NOTE: 2. In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be treated in hot phosphoric acid in a carefully controlled way [13] in order to dissolve the interfering compound(s) and avoid the losses of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD and LOQ in the bulk.

5. Use one of the following methods to ash filter samples and blanks:
   a. Low Temperature Ashing: Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or
   b. Muffle Furnace Ashing:
      1. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of $CaSiO_3$. Remove the calcite by the following procedure: Place a 0.5-µm, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and 5 mL 2-propanol to the filter funnel and allow to sit for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
      2. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 hrs at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or
   c. Filter Dissolution: Place the filter in a 40-mL wide-mouth centrifuge tube with 10 mL THF. Place the centrifuge tube in an ultrasonic bath for 10 min. The filter should dissolve almost instantaneously. Continue with the procedure given below at step 6 substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
8. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze standard filters.
   a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.

b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar. Cool to room temperature before withdrawing aliquots.

c. Mount a silver filter on the filtration apparatus. Place several mL 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.

d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.

e. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Transfer the silver filter to the diffractometer sample mount. Prepare working standard filters, in triplicate, by this technique, at e.g., 20, 30, 50, 100, 200 and 500 µg.

f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x^0 and are then normalized (step 12.e) to obtain $\hat{I}_x^0$. Correct the intensities of working standards >200 µg for matrix absorption (steps 12.f and 13).

g. Prepare a calibration graph ($\hat{I}_x^0$, vs. µg of each standard).
NOTE: Poor repeatability (>10% above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.

h. Determine the slope, m, of the calibration graph in counts/µg. The intercept, b, on the abscissa should be within ± 5 µg of zero.
NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.

10. Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}^0$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 degrees 2-theta) of the high-volume respirable sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The expected diffraction peaks are:

	Peak (2-Theta Degrees)		
Mineral	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

12. Perform the following for each sample, working standard, and blank filter:

a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (s_r <0.01) measured.

b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min. (longer scan times will lower the limit of detection).

c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
e. Calculate and record the normalized intensity, $\hat{I}_x$, for the sample peak on each sample, field blank and standard:

$$\hat{I}_x = \frac{I_x}{I_r} \bullet N.$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

f. Determine the normalized count, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
g. Scan each field blank over the same 2-θ range used for the analyte and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

13. Calculate the concentration of silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \bullet f(T) - b}{m \bullet V}, \ mg/m^3$$

where:

$\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration graph ($\hat{I}^0_x$ vs. W)
m = slope of calibration graph, counts/µg
$f(t) = \frac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)
$R = \sin(\theta_{Ag})/\sin(\theta_x)$
$T = \hat{I}_{Ag}/(\text{average } \hat{I}^0_{Ag})$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}^0_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [14] through [19].

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [2]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and sonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [10] and when all standards and samples were Min-U-Sil 5. The relative standard deviations for intralaboratory, total measurement and overall (including sampling) variability are:

Measurement Precision, s_r:

Intralaboratory:	50 to 200 µg	-- 0.08 [1]
	20 µg	-- 0.20 [5]
	10 µg	-- 0.28 [20]
Total (intra- and interlaboratory):	50 to 200 µg	-- 0.17 [1]

Overall (Sampling & Measurement) Precision, s_r:

Total (intra- and interlaboratory):	50 to 200 µg	-- 0.29 [2]

The use of THF for dissolving the collection filter is not a well-established technique for silica, but preliminary data are available on samples from the NIOSH Proficiency Analytical Testing (PAT) Program. On 40 such samples analyzed over a period of one year, results averaged 95% of the geometric mean of all the participating laboratories. The precision for three analysts using THF approximated the total measurement error given above [20].

Microscopic particle size examination of SRM 1878 quartz material indicated that it contained particles larger than 10 µm; these particles are considered non-respirable. Removal of all particles larger than 10 µm from the SRM 1878 will result in more accurate results when the "cleaned" SRM 1878 material is used to prepare XRD standards to be compared to respirable samples. Wet-sieved SRM 1878 was used to prepare XRD calibration standards, in replicate experiments, and compared to non-sieved SRM 1878 calibration standards. Results indicated 10 to 12% lower results in the field samples using the non-sieved SRM 1878 calibration curves [11].

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METHOD REVISED BY: M. T. Abell; D. D. Dollberg, Ph.D.; J. Palassis; B. A. Lange, Ph.D., NIOSH/DPSE; and C. C. Anderson, SRI International.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations.

		f(T) (at indicated degrees 2-θ)							
Transmittance	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
1.00		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99		1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98		1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97		1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96		1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95		1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94		1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0635
0.93		1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92		1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91		1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90		1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89		1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88		1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87		1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86		1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85		1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84		1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83		1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82		1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81		1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80		1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79		1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78		1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77		1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76		1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75		1.2175	1.2535	1.2822	1.3297	1.2672	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3465	1.2806	1.3278	1.2849	1.3328
0.73		1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72		1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71		1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70		1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69		1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68		1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67		1.3103	1.3628	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66		1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65		1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64		1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63		1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62		1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61		1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60		1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995

		f(T) (at indicated degrees 2-θ)							
Transmittance	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
0.59		1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58		1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57		1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56		1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55		1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54		1.4991	1.6858	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53		1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52		1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51		1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50		1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531

APPENDIX:

INTERFERENCES

Interferences include micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase and lead sulfide.

The patterns for three forms of aluminum phosphate (JCPDS 10-423, 11-500, 20-44) are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite, if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-Williams [18] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

FORMULA: SO_2

M.W.: 64.06

SULFUR DIOXIDE

METHOD: 6004
ISSUED: 8/15/87
REVISION #1: 5/15/89

OSHA: 2 ppm; 5 ppm STEL
NIOSH: 2 ppm; 5 ppm STEL [1,2];
Group I Pesticide [3]
ACGIH: 4 ppm
(1 ppm = 2.62 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 2.26 (air = 1);
BP -10 °C; MP -75.5 °C;
nonflammable

SYNONYMS: CAS #7446-09-5.

SAMPLING

SAMPLER: FILTER
(cellulose + KOH; preceded by
0.8-µm cellulose ester membrane)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 40 L @ 0.5 ppm
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

!TECHNIQUE: ION CHROMATOGRAPHY
!
!ANALYTE: sulfite and sulfate ions
!
!DESORPTION: 10 mL 3 mM $NaHCO_3$/2.4 mM Na_2CO_3
!
!INJECTION LOOP VOLUME: 100 µL
!
!ELUENT: 3 mM $NaHCO_3$/2.4 mM Na_2CO_3, 2 to
! 3 mL/min @ ambient temperature
!
!COLUMNS: anion precolumn, fast run, anion
! separator, fast run; anion suppressor
!
!CONDUCTIVITY SETTING: 10 µS full scale
!
!CALIBRATION: standard solutions of $SO_3^=$
! and $SO_4^=$ in eluent
!
!RANGE: 0.05 to 0.2 mg SO_2 per sample
!
!ESTIMATED LOD: 0.02 mg SO_2 per sample [4]
!
!PRECISION (s_r): 0.05 @ 0.05 to 1 mg SO_2 per
! sample [5]
!

APPLICABILITY: The working range is 0.2 to 8 ppm (0.5 to 20 mg/m^3) for a 100-L air sample. SO_2 is collected on the back (treated) filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and may be quantitated as total particulate sulfate and sulfite.

INTERFERENCES: Bromide has the same retention time as sulfite on these columns. Sulfur trioxide gas, if present in dry atmospheres, may give a positive interference for SO_2.

OTHER METHODS: This revises P&CAM 268 [5] and Method 6004 (dated 8/15/87). P&CAM 146 [6], P&CAM 163 [7], and S308 [8] use 0.3 N H_2O_2 for sampling, followed by titration with NaOH or barium perchlorate. P&CAM 160 [9] uses tetrachloromercurate solution and visible spectrophotometry. P&CAM 204 [10] uses a solid sorbent (molecular sieve 5A), thermal desorption, and mass spectrometry.

REAGENTS:

1. Water, deionized, filtered, specific conductance ≤10 µS/cm.
2. Filter-impregnating solution. Dissolve 20 g KOH in about 50 mL deionized water. Add 10 mL glycerol and dilute with deionized water to 100 mL.
3. Eluent: 3 mM $NaHCO_3$/2.4 mM Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in 4 L filtered deionized water.
4. Formaldehyde, 0.5% (w/v) in deionized, filtered water.
5. Calibration stock solutions, 1 mg/mL (as the anion). Prepare in duplicate.
   a. Sulfite: dissolve 0.1575 g Na_2SO_3 in 0.5% (w/v) formaldehyde in water. Dilute to 100 mL.
   b. Sulfate: dissolve 0.1479 g Na_2SO_4 in deionized water; Dilute to 100 mL.
6. Hydrogen peroxide (H_2O_2), 30% (w/v).*

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two 37-mm diameter cassette filter holders (connected in series by a M-M Luer adapter, e.g., Millipore XX1102503, or a short piece of plastic tubing) containing:
   a. (Front cassette) cellulose ester membrane filter, 0.8-µm pore size, supported by a backup pad.
   b. (Back cassette) cellulose filter (Whatman 40 or equivalent) which has been saturated with filter-impregnating solution and dried 20 to 30 min at 100 °C, supported by a cellulose backup pad.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Vials, glass, 20-mL, screw-cap, such as scintillation vials.**
4. Ion chromatograph, fast-run anion separator and precolumn, anion suppressor column, conductivity detector, and strip chart recorder. (Optional: integrator.)
5. Syringes, 10-mL, polyethylene, with luer tip.**
6. Filters, luer tip holder with membrane filter, 13- or 25-mm, 0.45-µm pore size.
7. Micropipets, 50- to 1000-µL, with disposable tips.**
8. Volumetric flasks, 50- and 100-mL.**
9. Pipet, 10-mL.**
10. Polyethylene bottles, 250-mL.**

**Clean by rinsing thoroughly with deionized water.

SPECIAL PRECAUTIONS: H_2O_2 is a strong oxidizer and can be explosive. Avoid contact with skin. Should contact occur, flush immediately with water.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove end caps of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 40 to 200 L. Do not exceed a total particulate loading of 2 mg on the front filter.
4. Seal the sampler and pack securely for shipment.

   NOTE 1: If determination of sulfuric acid is required, transfer the front (membrane) filter to a clean vial within 4 hrs to avoid low recovery of sulfate. Handle the filter with tweezers to avoid contamination.

   NOTE 2: If particulate sulfite analysis is desired or if particulate sulfite is present and its interference with particulate sulfate is to be prevented, transfer the front (membrane) filter to a vial containing 10.0 mL 0.5% formaldehyde solution immediately after sampling.

SAMPLE PREPARATION:

5. Put the two filters from the sampler into separate, clean vials. Discard the backup pads. Add 10.0 mL eluent to each vial and let stand, with occasional vigorous shaking, for 30 min.
6. Add one drop of 30% H_2O_2 to oxidize sulfite to sulfate.

   NOTE 1: Do not add H_2O_2 to the front filter if particulate sulfite is to be determined.

NOTE 2: The SO_2 collected on the treated (back) filter is present as sulfite, which oxidizes in air slowly (over several weeks) to sulfate. This H_2O_2 oxidation step may be omitted for the back filter, in which case the contributions of sulfite and sulfate found on the back filter must be summed, with appropriate stoichiometric factors applied, to give the SO_2 concentration.

7. Pour each sample into a syringe fitted with an in-line filter.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known aliquots of sulfate calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to produce solutions containing 0.001 to 0.02 mg/mL $SO_4^=$. Prepare sulfite standards in the same range in 0.5% formaldehyde solution [11].
   b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
   c. Analyze working standards with samples and blanks (steps 9 through 11).
   d. Prepare a calibration graph for each anion [peak height (mm or μS) vs. mg sulfite or sulfate].
   NOTE: If any samples have been treated with 0.5% formaldehyde solution, prepare two or three sulfate standards in this solution to verify that this matrix does not affect detector response. If an effect is noted, prepare a calibration graph in this matrix.

MEASUREMENT:

9. Set ion chromatograph to conditions given on page 6004-1, according to manufacturer's instructions.
10. Inject sample aliquot. For manual operation, inject 2 mL of sample from syringe to ensure complete rinse of sample loop.
    NOTE: All samples, eluents, and water flowing through the ion chromatograph must be filtered to avoid plugging system valves or columns.
11. Measure peak height.
    NOTE: If peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, mg, of sulfate found on the front (W_f) and back (W_b) filters and in the corresponding average media blanks (B_f and B_b).
13. Calculate the concentration, C_1, of sulfur dioxide:

$$C_1 = \frac{(W_b - B_b)}{V} \cdot 667, \text{ mg/m}^3$$

14. Calculate the concentration, C_2, of particulate sulfate (including sulfuric acid) in the air volume sampled, V (L):

$$C_2 = \frac{(W_f - B_f) \cdot 10^3}{V}, \text{ mg/m}^3$$

15. If step 6 was omitted for the front filter, determine the mass, mg, of sulfite on the front filter (W_s) and in the average media blank (B_s). Calculate the concentration, C_3, of particulate sulfite:

$$C_3 = \frac{(W_s - B_s) \cdot 10^3}{V}, \text{mg/m}^3$$

NOTE: Under these chromatographic conditions, $SO_3^=$ and Br^- coelute. If Br^- is present, $SO_3^=$ cannot be quantitated unless different conditions are used.

EVALUATION OF METHOD:

The sampler was adapted from that of Pate, et al. [12]. In experiments in which SO_2 was generated by permeation tube and collected in impingers containing H_2O_2, untreated 0.8-µm cellulose ester membrane filters were shown to allow complete passage of SO_2 [13]. In subsequent sampling of an atmosphere containing ca. 10 ppm SO_2 at 1 L/min for 30 min, two treated filters were placed in series following a cellulose ester membrane filter. Recoveries were: 0.667 mg SO_2 from the first treated filter, 0.02 mg SO_2 from the second treated filter, and less than 0.003 mg SO_2 in the backup impinger containing 0.3 N H_2O_2 [14].

Three 0.8-µm pore size mixed cellulose ester filters were spiked with 0.2 mg H_2SO_4 and gave the following recoveries: 83.5% using H_2O extraction, 98.5% using hot H_2O extraction, and 82.5% using 0.01 M HCl for extraction. One filter was spiked with 0.2 mg sulfate from K_2SO_4 and gave 109.5% recovery with water extraction. Two filters were spiked with 0.1 mg sulfate from $(NH_4)_2SO_4$ and $CuSO_4$ solutions and gave recoveries of 109 and 110%, respectively, when extracted with water.

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METHOD REVISED BY: Peter M. Eller, Ph.D, CIH, NIOSH/DPSE.

FORMULA: $CH_3C_6H_3(NH_2)_2$; $C_7H_{10}N_2$

M.W.: 122.17

2,4- AND 2,6-TOLUENEDIAMINE
(in the presence of isocyanates)

METHOD: 5516
ISSUED: 5/15/89

OSHA: no standard
NIOSH: no recommended exposure limits
ACGIH: no TLV

PROPERTIES: 2,4-: solid; MP 99 °C
2,6-: solid; MP 106 °C; VP 0.13 kPa (1 mm Hg @ 106 °C)

SYNONYMS: 2,4-: 4-methyl-1,3-benzenediamine; 2,4-diaminotoluene; CAS #95-80-7;
2,6-: 2-methyl-1,3-benzenediamine; 2,6-diaminotoluene; CAS #823-40-5.

SAMPLING

SAMPLER: IMPINGER
(solution of 1-(2-methoxyphenyl)-piperazine in toluene, 15 mL)

FLOW RATE: 1 L/min

VOL-MIN: 30 L @ 10 µg/m³
-MAX: 500 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C in the dark [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTES: 2,4- and 2,6-bisacetamidotoluene

PREPARATION: acetylate 4 hour, evaporate, redissolve in 1.5 mL methanol

INJECTION VOLUME: 10 µL

MOBILE PHASE: programmed; sodium acetate in acetonitrile/water at pH 6.0; 1.0 mL/min; ca. 20 °C

COLUMN: 10 cm x 8 mm octadecylsilylated silica (C_{18}), 5-µm particle size, in Waters RCM-100 radial compression module

CALIBRATION: standard solutions of analytes in methanol

RANGE: 0.3 to 3 µg per sample [1]

ESTIMATED LOD: 0.1 µg per sample [1]

PRECISION (s_r): 0.06 [1] @ 0.74 to 0.89 µg per sample

APPLICABILITY: The working range is 3 to 30 µg/m³ for a 100-L air sample. This method, based on that of Warwick et al. for isocyanates [2], determines 2,4- and 2,6-toluenediamine in air in the presence of isocyanates. Samples from polyurethane foam plants were analyzed simultaneously for 2,4- and 2,6-toluenediamine and 2,4- and 2,6-toluene diisocyanate [1].

INTERFERENCES: m-Phenylenediamine interferes in the determination of 2,4-toluenediamine.

OTHER METHODS: Holdren et al. [3] reported a similar method using N-(4-nitrobenzyl)propylamine in toluene for sampling and HPLC with electrochemical detection. Other methods are: (a) absorb on Tenax GC, desorb in toluene, GC [4]; (b) absorb on silica gel, desorb in 2-butanone, GC [5]; (c) sample in aqueous acid, work up, GC of free amines [6] or bis(heptafluorobutyryl)amides [7,8], (d) sample in ethanolic KOH, workup, LC of free amine [9,10] or GC of bis(pentafluoropropionyl)amides [11]; (e) sample with sulfuric acid-coated filter, work up, GC of bis(heptafluorobutyryl)amides [12]. Some of these methods [3,9-11] can be used for the simultaneous determination of toluenediamines and toluene diisocyanates.

REAGENTS:

1. Toluene, reagent grade.
2. 1-(2-Methoxyphenyl)piperazine, purified (see APPENDIX A).
3. Sampling medium: 43 µg/mL 1-(2-methoxyphenyl)piperazine in toluene.
4. 2,4-Toluenediamine*, reagent grade.
5. 2,6-Toluenediamine*, reagent grade.
6. Acetic anhydride, reagent grade.
7. Methanol, reagent grade.
8. Mobile phase A: Dissolve 60 mg anhydrous sodium acetate in 1 L of 12% acetonitrile in distilled water. Add 17% (V/V) aqueous acetic acid. Bring pH to 6.0.
9. Mobile phase B: Acetonitrile, chromatographic quality.
10. Water, distilled deionized.
11. Sodium acetate, anhydrous.
12. 2,4-Bisacetamidotoluene, (See APPENDIX B).
13. 2,6-Bisacetamidotoluene (See APPENDIX B).
14. Calibration stock solution, 0.5 µg/µL. Dissolve 5 mg each of 2,4- and 2,6-bisacetamidotoluene in methanol. Dilute to 10 mL.
15. Nitrogen, prepurified.
16. Pentane*, purified.

EQUIPMENT:

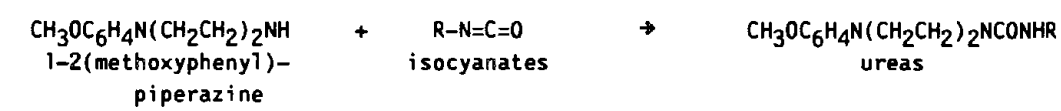
1. Sampler: midget impinger, 25-mL.
2. Personal sampling pump, 1 L/min, with flexible connecting tubing.
3. Liquid chromatograph (HPLC) with 229-nm UV detector, recorder, integrator, and column (page 5516-1).
4. Vials, 4-mL and 20-mL, glass, with PTFE-lined caps.
5. Pipets, Pasteur, 14.6-cm, glass disposable.
6. Volumetric flasks, 10-mL.
7. Syringes, 10- and 100-µL, readable to 0.1 µL.
8. Pipets, 2- (graduated) and 15-mL, glass, with pipet bulb.
9. Water bath.
10. Hotplate, spark-free, 35 to 50 °C.
11. Evaporator, Mini-Vap, six-port, or equivalent.
12. pH meter.
13. Beakers, 250-mL.
14. Flask, filtration, 500-mL.
15. Funnel, Buchner, fritted glass, 100-mL.
16. Vacuum pump.
17. Vacuum desiccator.
18. Watchglass.

*See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: 2,4-Toluenediamine is a cancer suspect agent [13]; 2,6-Toluenediamine may be mutagenic [14]. Handle these chemicals carefully in a hood or glove box, and avoid working-surface contamination which might occur by spillage or by dissipation of fine powder from opening of containers or making transfers.
Pentane is highly volatile and flammable. Take adequate precautions while handling pentane.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15.0 mL sampling medium to an impinger.
3. Connect the assembled impinger to a sampling pump.
4. Sample 30 to 500 L of air at an accurately measured sampling rate in the range around 1 L/min. When it is necessary to add solvent for proper impinger operation during sampling, add only toluene.
   NOTE: The reagent in the sampling medium reacts with isocyanates present to form ureas, thus preventing reaction of the isocyanate with the toluenediamines.



5. Transfer sample solution, including condensed water, to a 20-mL vial for shipment. Rinse impinger with 1 to 2 mL toluene. Add rinsings to sample solution.

SAMPLE PREPARATION:

6. Add 25 µL acetic anhydride to acetylate the 2,4- and 2,6-toluenediamine and excess 1-(2-methoxyphenyl)piperazine. Allow 4 hours for completion of reactions. Evaporate sample to dryness under a gentle stream of nitrogen while warming to 40 to 50 °C on a hotplate. Redissolve residue in 1.5 mL methanol.
NOTE: The acetylation reaction for 2,4-toluenediamine to produce 2,4-bisacetamidotoluene is:

$$\underset{\text{2,4-toluenediamine}}{CH_3C_6H_3(NH_2)_2} + \underset{\text{acetic anhydride}}{2CH_3COOCOCH_3} \rightarrow \underset{\text{2,4-bisacetamidotoluene}}{CH_3C_6H_3(NHCOCH_3)_2} + \underset{\text{acetic acid}}{2\ CH_3COOH}.$$

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards.
   a. Using aliquots of calibration stock solution, prepare working standards of 2,4- and 2,6-bisacetamidotoluene in methanol covering the range 0.1 to 3 µg/mL each.
   b. Analyze these with the unknown and blank samples (steps 9 through 11).
   c. Prepare calibration graphs (peak height vs. µg 2,4- and 2,6-toluenediamine per sample). Multiply the concentration of bisacetamidotoluene by 0.889 mL [122.17 x 1.5 mL ÷ 206.25], where 122.17 and 206.25 are formula weights of toluenediamine and bisacetamidotoluene, respectively, to obtain the quantity of toluenediamine per sample.
8. Prepare three quality control samples by adding known quantities of 2,4- and 2,6-toluenediamine to 15 mL of sampling medium and analyze (steps 9 through 11).

MEASUREMENT:

9. Set up the HPLC system according to the manufacturer's recommendations and to the conditions given on page 5516-1. The mobile phase program is:
   a. Linear gradient 100% A to 90% A over t = 0 to 8 min.
   b. 90% A to 40% A over t = 8 to 19 min following the convex gradient $\%\ A = 90 - 31\ (t - 8)^{1/5}$.
   c. Hold at 40% A for 1 min, or as long as necessary to clear the column.
   d. Return to 100% A and hold for 7 min before the next run.
   NOTE: If only 2,4- and 2,6-toluenediamine are to be quantified, the mobile phase program may be modified to hasten elution of the ureas derived from the isocyanates.
10. Inject a 10-µL aliquot of solution from step 6 or step 7b.
11. Measure the peak heights. Adjusted retention times for some compounds of interest are:

2,6-bisacetamidotoluene	5.2 min
1,4-bisacetamidobenzene	7.8 min
1,3-bisacetamidobenzene	9.4 min
2,4-bisacetamidotoluene	9.7 min
1-acetyl-4-(2-methoxyphenyl)piperazine	14.3 min
urea derivative of 2,6-toluene diisocyanate	17.0 min
urea derivative of 2,4-toluene diisocyanate	18.3 min

CALCULATIONS:

12. Using the calibration graphs, determine the mass, µg, of 2,4- and of 2,6-toluenediamine in each sample (W) and in the average media blank (B).

13. Calculate the concentration, C, of 2,4- and of 2,6-toluenediamine in the air volume sampled, V (L):

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

EVALUATION OF METHOD: [1]

The relationship of peak height and concentration of 2,4- and 2,6-bisacetamidotoluene in methanol was found to be essentially linear over the ranges 0.05 to 141 µg/mL and 0.14 to 84 µg/mL, respectively. The time required for completion of the acetylation reaction was determined using samples equivalent to 0.7 µg of 2,4-toluenediamine and 0.9 µg of 2,6-toluenediamine in 15 mL of sampling medium. Aliquots (2 mL) were treated with 10 µL of acetic anhydride and allowed to stand 0.25 to 6 hrs before further workup and analysis. The acetylation of 2,6-toluenediamine was the slower reaction, but it appeared complete after 4 h. Sample stability was studied using solutions of 2,4- and 2,6-toluenediamine in sampling medium at levels corresponding to 0.89 and 0.74 µg per sample, respectively. The recoveries, ranging from 97% to 106%, suggested the samples were stable under the conditions of storage -- 1, 7, and 14 days at room temperature in the dark. The potential for interference from isocyanates was investigated by drawing air containing 7.3 µg each of 2,4- and 2,6-toluene diisocyanate through samples of 0.9 µg each of 2,4- and 2,6-toluenediamine in 15 mL of sampling medium. The recoveries from these samples, averaging 95%, suggested that, when compared to identical samples not treated with toluene diisocyanate, a small but statistically significant negative bias was caused by the isocyanate. Using the data from all of the recovery experiments, the relative standard deviation (s_r) for 2,4-toluenediamine (0.74 and 0.83 µg per sample) ranged from 0.01 to 0.08 with a pooled average of 0.05 and for 2,6-toluenediamine (0.89 µg per sample) ranged from 0.02 to 0.14 with a pooled average of 0.06.

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METHOD WRITTEN BY: James E. Arnold and Alexander W. Teass, Ph.D., NIOSH/DPSE.

APPENDIX A:

PURIFICATION OF 1-(2-METHOXYPHENYL)PIPERAZINE:

Place 25 g 1-(2-methoxyphenyl)piperazine (yellowish white solid) in a 250-mL beaker. Add ca. 125 mL pentane. Bring to a boil (CAUTION: Pentane is FLAMMABLE) on a water bath and allow to boil until all but a small amount of yellow oil is in solution. The 1-(2-methoxyphenyl)piperazine will melt as it is warmed in the pentane. Decant the solution into a clean beaker, cover with a watchglass, and cool in the freezer for 2 to 3 h. Collect the resulting white needles in a Buchner funnel using suction filtration and dry them in a vacuum desiccator. The crystals are hygroscopic and melt at 26 to 29 °C. Store them in an airtight container in a refrigerator.

APPENDIX B:

SYNTHESIS OF 2,4- AND 2,6-BISACETAMIDOTOLUENE:

Place 0.5 g of 2,4- or 2,6-toluenediamine in a 250-mL beaker. Add ca. 100 mL of distilled water and warm to dissolve the compound. Filter the solution, if necessary. Chill the solution in an ice bath, then slowly add 5 mL acetic anhydride and stir. After keeping the mixture at least 1 h in the ice bath, collect the solid product by suction filtration. Recrystallize the product from water by dissolving it in boiling water, filtering the hot solution, chilling the filtrate in a refrigerator, and collecting the precipitate by suction filtration. Dry the precipitate in a vacuum desiccator.

2,4-Bisacetamidotoluene recrystallizes as white needles and melts at 230 °C.

2,6-Bisacetamidotoluene recrystallizes as brownish needles and melts at ca. 318 °C.

FORMULA: $CH_3(CH_2)_3CH=O$; $C_5H_{10}O$

M.W.: 86.13

VALERALDEHYDE

METHOD: 2536

ISSUED: 5/15/89

OSHA: 50 ppm
NIOSH: no recommended exposure limit
ACGIH: 50 ppm
(1 ppm = 3.52 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.810 g/mL @ 20 °C; BP 103 °C; flash point = 12.2 °C

SYNONYMS: pentanal; CAS #110-62-3.

SAMPLING

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

FLOW RATE: 0.01 to 0.04 L/min

VOL-MIN: 0.5 L @ 50 ppm
-MAX: 10 L

SHIPMENT: routine

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

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 18 per set

ACCURACY

RANGE STUDIED: 9 to 374 mg/m^3 [1]
(12-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r): 0.073 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: valeraldehyde oxazolidine (9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane)

DESORPTION: 2 mL toluene, 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 0.5 min @ 70°C; 50 °C/min to 120°C, hold 4 min; 20°C/min to 170°C, hold 7 min

CARRIER GAS: He, 27 cm/sec linear velocity
makeup flow 29 mL/min

COLUMN: capillary, 15-m x 0.32-mm, 5% phenyl, 95% methyl polysiloxane, 1-µm film (DB-5 or equivalent)

CALIBRATION: standard solutions of valeraldehyde on sorbent

RANGE: 4 to 3900 µg per sample [1]

ESTIMATED LOD: 2 µg per sample [1]

PRECISION (s_r): 0.066 @ 2 to 508 µg per sample [1]

APPLICABILITY: The working range is 0.11 to 110 ppm (0.4 to 390 mg/m^3) for a 10-L air sample. The method is also suitable for determination of furfural and glutaraldehyde in a mixture [2].

INTERFERENCES: None have been observed; an alternate glass capillary column, 15-m x 0.32-mm cyanopropylphenyl dimethylpolysiloxane, 1-µm film (DB-1301) can be used.

OTHER METHODS: The method of Lipari and Swarin [3] uses 2,4-dinitrophenylhydrazine for the collection of valeraldehyde.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas or equivalent). Extract 4 hrs in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Valeraldehyde,* 99% purity
5. Valeraldehyde stock solution, 40 µg/µL (see APPENDIX). Add 400 mg valeraldehyde to toluene and dilute to 10 mL.
6. Valeraldehyde oxazolidine (APPENDIX A) stock solution, 10 mg/mL. Add 0.10 g 9-butyl-1-aza-8-oxabicyclo-[4.3.0]noname to toluene and dilute to 10 mL.
7. Hydrogen, prepurified.
8. Air, filtered, compressed
9. Helium, purified.
10. Magnesium sulfate, anhydrous.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

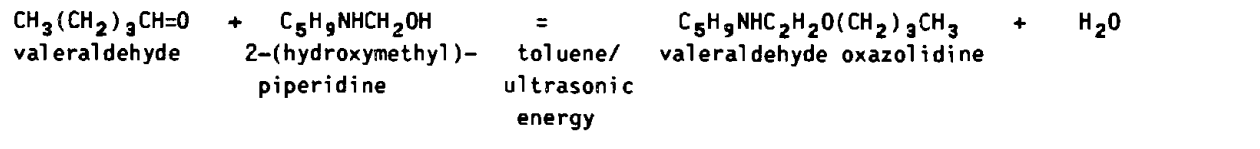
1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, flame-sealed ends and plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (front = 120 mg, back = 60 mg) (APPENDIX B). Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.1 L/min must be less than 760 Pa (5.7 mm Hg). Tubes are commercially available (Supelco Inc., ORBO 23 or equivalent).
2. Personal sampling pump, 0.01 to 0.04 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2536-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-µL (readable to 0.1 µL), 25-, and 50-µL.
10. Syringe pump
11. Block injector
12. File.
13. Beakers, 50-mL.
14. Magnetic stirrer.
15. Flasks, round-bottomed, 100-mL.
16. Soxhlet extraction apparatus.
17. Vacuum oven.
18. Distillation apparatus.

SPECIAL PRECAUTIONS: Valeraldehyde can irritate the mucous membranes [4]. It is flammable, a dangerous fire risk. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.04 L/min for a total sample size of 0.5 to 10 L.

   NOTE: Sampling rate is limited by the speed of the following reaction. Rates above 0.04 L/min may cause appreciable breakthrough due to incomplete reaction, possibly invalidating the sample.



SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

9. Identification of analytical peaks.
   a. Add known amounts of valeraldehyde oxazolidine stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with at least five working standards prepared in triplicate covering the range 2 to 3900 µg valeraldehyde per sample.
    a. Weigh 120-mg portions of unused sorbent from media blanks into vials.
    b. Add aliquots (1 to 10 µL) of valeraldehyde stock solution or dilutions thereof to the sorbent. Cap vials and allow to stand overnight at room temperature.
    c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (combined peak area vs. µg valeraldehyde).
    NOTE: Because the standard samples are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary. Check desorption efficiency in the range of interest and at least once over the entire range of the method with each lot of sorbent used. (APPENDIX C).
11. Analyze three quality control blind spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2536-1. Inject 1-µL sample aliquot.
    NOTE: If the amount of valeraldehyde oxazolidine in the aliquot exceeds the capacity of the column, dilute with toluene, reanalyze and apply the appropriate dilution factor in calculations. The upper limit for the column on (page 2536-1) is equivalent to ca. 260 µg valeraldehyde per sample.
13. Measure total peak area of the two analyte peaks.
    NOTE: On the recommended column, valeraldehyde oxazolidine gives two peaks, since the diastereoisomers are resolved with retention times 5.4 and 6.3 min. Retention time for 2-(hydroxymethyl)piperidine equals 2.2 min for these conditions.

CALCULATIONS:

14. Determine the mass, µg, of valeraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of valeraldehyde in the air volume sampled, V (L):

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

EVALUATION OF METHOD:
Atmospheres were generated by injection of valeraldehyde by syringe pump into a heated block injector and flash vaporizer into a stream of air at 80% ± 5% RH flowing at a fixed rate. The generator and sampling manifold system have been described previously [5]. Concentration of valeraldehyde vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [3] or by monitoring with an AID Model 590 organic vapor monitor. Breakthrough studies of valeraldehyde at 100 ppm, conducted at 75 and 50 mL/min flow rates, gave 5% breakthrough at 170 min and 280 min, respectively.

The method was evaluated over the range of 9 to 374 mg/m^3 using 12-L samples. Desorption efficiencies from statically-spiked samples averaged 102.5% (89.2-126.6%) for the range 2 to 508 µg/sample. No bias with dynamically-generated samples was observed with the method when samples were collected at 40 mL/min and below. When samples were collected at ca. 60 mL/min, a negative bias of approximately 20-30% was observed. Samples were found to be stable for at least 4 weeks when stored at room temperature.

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METHOD WRITTEN BY: Yvonne T. Gagnon, Eugene R. Kennedy, Ph.D. and Julia R. Okenfuss, NIOSH/DPSE.

APPENDIX A: SYNTHESIS OF 9-BUTYL-1-AZA-8-OXABICYCLO[4.3.0]NONANE:

Place a solution of purified 2-hydroxymethylpiperidine (1.15 g, 10 mmol) in 20 mL of toluene in a 100-mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2-(hydroxymethyl)piperidine from the container used for weighing. Add anhydrous magnesium sulfate (2.0 g) to the flask to dry the valeraldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 0.947 g valeraldehyde (11 mmole) in 20 mL of toluene to the 2-hydroxymethylpiperidine solution dropwise with stirring over 1 hour. (NOTE: Excess aldehyde was added to ensure complete conversion of 2-hydroxymethylpiperidine to oxazolidine.) Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure (1 mm Hg) by rotary evaporation. The product is a pale yellow viscous oil, ca. 90 to 95% pure by gas chromatography. Store the oxazolidine at 0 °C to prevent decomposition.

Mass spectral data for 9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane: m/e with relative intensities in parenthesis, 182 (7.0%), 152 (4.6%), 126 (100%), 110 (11.3%), 98 (37%). IR data (Vapor phase @ 280 °C) for this compound in cm^{-1} with relative intensity in parenthesis are: 2945 (s), 2874 (m), 2781 (m), 1455 (w), 1383 (w), 1339 (w), 1265 (w), 1203 (w), 1133 (m), 1075 (w), 1028 (m).