FIRST SUPPLEMENT

to

NIOSH Manual of Analytical Methods (NMAM™)

Fourth Edition

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TRANSMITTAL NOTICE

This is the First Supplement to the NIOSH Manual of Analytical Methods (NMAM), 4th edition (printed August 15, 1994). This supplement is dated May 15, 1996, and includes 15 methods, three new chapters, and updated Contents, Method Finder, and indexes, as well as errata replacement pages.

INSTRUCTIONS FOR INSERTING FIRST SUPPLEMENT INTO YOUR MANUAL

Table of Contents
Remove Contents pages vi to xiii. Replace with new Contents.

Method Finder
Remove old pages MF-1 to MF-14. Replace with new MF-1 to MF-17.

Using NMAM (Blue pages)
Remove pp. 32 to 63. Replace with pp. 32 to 96.

Indexes (Yellow pages - end of 3rd volume)
Remove pp. A-11 through A-56. Replace with A-11 to A-59.

Methods
Insert methods alphabetically in NMAM.

Ammonia by IC, 6016
n-Butyl Mercaptan, 2525
Capsaicin and Dihydrocapsaicin, 5041
Carbon Monoxide, 6604
Chromium (VI) in Settled Dust Samples, 9101
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Lead in Air by Chemical Spot Test, 7700
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Methyl Bromide, 2520
Methyl Ethyl Ketone, 2500 - Remove existing version, and replace.
Oil Mists, Mineral, 5026 - Remove existing version, and replace.
Terpenes, 1552
Volatile Organic Compounds (Screening), 2549

Errata
Only the pages that contained errors are being replaced. In general, complete methods have not been supplied, except where page content has changed because of additions or deletions. Remove old pages and replace with corresponding pages.

ACKNOWLEDGMENTS

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

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

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

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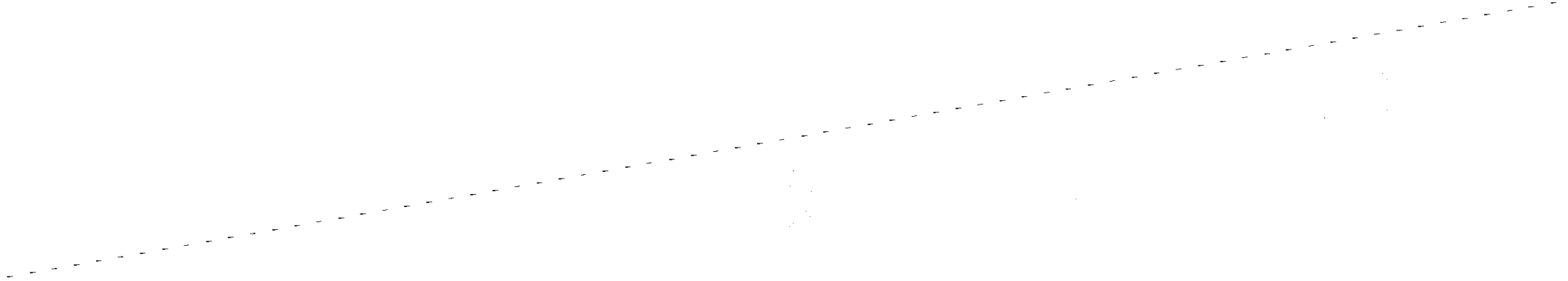

METHOD FINDER (Key on page MF-17)

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Acenaphthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Acenaphthylene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Acetaldehyde	2538	ACETALDEHYDE	U	0.01-0.05	1	12	GC-FID	XAD-2/HMP
Acetaldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD2/HMP
Acetaldehyde	3507	ACETALDEHYDE	F	0.1-0.5	6	60	HPLC-UV	BuB
Acetic acid	1603	ACETIC ACID	F	0.01-0.1	20	300	GC-FID	CCT
Acetic anhydride	3506	ACETIC ANHYDRIDE	F	0.2-1.0	25	100	VIS	BuB
Acetone	1300	KETONES I	F	0.01-0.2	0.5	3	GC-FID	CCT
Acetone	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Acetone cyanohydrin	2506	ACETONE CYANOHYDRIN	P	0.2	0.3	12	GC-NPD	Por QS
Acetonitrile	1606	ACETONITRILE	P	0.01-0.2	3	25	GC-FID	CCT
Acetylene dichloride	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.2	5	GC-FID	CCT
Acetylene tetrabromide	2003	1,1,2,2-TETRABROMOETHANE	P	0.2-1.0	50	100	GC-FID	SG
Acetylene tetrachloride	1019	1,1,2,2-TETRACHLOROETHANE	P	0.01-0.2	3.0	30	GC-FID	PCT
Acids, inorganic	7903	ACIDS, INORGANIC	F	0.2-0.5	3.0	100	IC	SG (washed)
Acrolein	2501	ACROLEIN	P	0.01-0.1	1.5	48	GC-NPD	XAD-2/HMP
Acrolein	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Acrylonitrile	1604	ACRYLONITRILE	F	0.01-0.2	3.5	20	GC-FID	CCT
Aldehydes, screening	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2
Aldrin	5502	ALDRIN & LINDANE	F	0.2-1.0	18	240	GC-ECN	GFF & BuB
Alkaline dusts	7401	ALKALINE DUSTS	F	1 - 4	70	1000	Titration	PTFE
Allyl alcohol	1402	ALCOHOLS III	P	0.01-0.2	1	10	GC-FID	CCT
Allyl chloride	1000	ALLYL CHLORIDE	F	0.01-1.0	16	100	GC-FID	CCT
Allyl glycidyl ether	2545	ALLYL GLYCIDYL ETHER	F	0.01-0.2	1.5	8	GC-FID	Tenax
Allyl trichloride	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	2	60	GC-FID	CCT
Alumina	0500	PARTICULATES N.O.R.	F	1 - 2	7	133	Grav	PVC, tared
Aluminum	7300	ELEMENTS by ICP	P	1 - 4	5	100	ICP-AES	MCEF
Aluminum	7013	ALUMINUM & CPDS, as Al	P	1 - 3	10	400	FAAS	MCEF
Amines, aliphatic	2010	AMINES, ALIPHATIC	P	0.01-1.0	3	30	GC-FID	SG
Amines, aromatic	2002	AMINES, AROMATIC	F	0.2-1.0	30	150	GC-FID	SG
Aminobenzene	2002	AMINES, AROMATIC	F	0.2-1.0	30	150	GC-FID	SG
2-Aminoethanol	2007	AMINOETHANOL COMPOUNDS I	P	0.01-0.2	4	24	GC-FID	SG
2-Aminoethanol	3509	AMINOETHANOL COMPOUNDS II	P	0.5-1.0	5	300	IC	IMP
p-Aminophenylarsonic acid	5022	ARSENIC, ORGANO-	F	1 - 3	50	1000	IC-HYAAS	PTFE
2-Aminotoluene	2002	AMINES, AROMATIC	F	0.02-1.0	10	150	GC-FID	SG
Ammonia	6015	AMMONIA by VIS	P	0.1-0.2	0.1	90	VIS-Auto	SG + H_2SO_4
Ammonia	6016	AMMONIA by IC	f	0.1-0.5	0.1	96	IC	SG + H_2SO_4

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
n- and *sec*-Amyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Amyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Aniline	2002	AMINES, AROMATIC	F	0.02-0.2	5	30	GC-FID	SG
Anisidine	2514	ANISIDINE	F	0.5-1.0	24	320	HPLC-UV	XAD-2
Anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
p-Arsanilic acid	5022	ARSENIC, organo-	F	1 - 3	50	1000	IC-HYAAS	PTFE
Arsenic	7900	ARSENIC & compounds, as As	P	1 - 3	30	1000	FAAS	MCEF
Arsenic	7300	ELEMENTS by ICP	P	1 - 4	5	2000	ICP-AES	MCEF
Arsenic trioxide	7901	ARSENIC TRIOXIDE, as As	F	1 - 3	30	1000	GFAAS	MCEF
Arsine	6001	ARSINE	F	0.01-0.2	0.1	10	GFAAS	CCT
Asbestos	7400	ASBESTOS FIBERS by PCM	F	0.5-16	400	Var	PCM	MCEF-open
Asbestos	7402	ASBESTOS FIBERS by TEM	P	0.5-16	400	Var	TEM	MCEF-open
Asbestos	9000	ASBESTOS, CHRYSOTILE by XRD	F	NA	NA	NA	XRD	bulk
Asbestos	9002	ASBESTOS (bulk) by PLM	P	NA	NA	NA	PLM	bulk
Aspartame	5031	ASPARTAME	P	1 - 3	70	1200	HPLC-UV	PTFE
Azelaic acid	5019	AZELAIC ACID	P	1 - 3	200	1000	GC-FID	PVC
Azinphos methyl	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1.0	12	240	GC-FPD	OVS-2
B[a]P	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Barium	7056	BARIUM, SOLUBLE COMPOUNDS	F	1 - 4	50	2000	FAAS	MCEF
Benzaldehyde	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Benz(a)anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Benzene	3700	BENZENE by portable GC	P	> 0.02	NA	80% vol	GC	air bag
Benzene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	5	30	GC-FID	CCT
Benzene	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	2	30	GC-FID	CCT
Benzidine Dyes	5013	DYES	P	1 - 3	150	500	HPLC-UV	PTFE
Benzidine	5509	BENZIDINE and 3,3'-DICHLORO-BENZIDINE	F	0.2	20	100	HPLC-UV	GFF
Benzo(a)pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzo(b)fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Benzo(e)pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzo(k)fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzo(ghi)perylene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-ID	PTFE & XAD-2
Benzoyl peroxide	5009	BENZOYL PEROXIDE	F	1 - 3	40	400	HPLC-UV	MCEF
Benzyl chloride	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	6	50	GC-FID	CCT
Beryllium	7300	ELEMENTS by ICP	P	1 - 4	1250	2000	ICP-AES	MCEF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Beryllium & compounds	7102	BERYLLIUM and cpds, as Be	F	1 - 4	25	1000	HGAAS	MCEF
Biphenyl	2530	DIPHENYL	F	0.01-0.5	15	30	GC-FID	Tenax GC
Boron carbide	7506	BORON CARBIDE	P	1.7 or 2.2	100	1000	XRD	CYC & PVC
Boron oxide	0500	PARTICULATES N.O.R.	F	1.5-2.0	25	133	Grav	PVC
Bromine	6011	CHLORINE and BROMINE	F	0.3-1.0	8	360	IC	Ag F
Bromoform	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	4	70	GC-FID	CCT
Bromotrifluoromethane	1017	TRIFLUOROBROMOMETHANE	P	0.01-0.05	0.3	1.0	GC-FID	2 CCT
Bromoxynil	5010	BROMOXYNIL and B'OCTANOATE	P	1 - 3	2	400	HPLC-UV	PTFE
Bromoxynil octanoate	5010	BROMOXYNIL and B'OCTANOATE	P	1 - 3	90	400	HPLC-UV	PTFE
1,3-Butadiene	1024	1,3-BUTADIENE	F	0.01-0.5	5	25	GC-FID	CCT
2-Butanone	2500	METHYL ETHYL KETONE	F	0.01-0.2	1	12	GC-FID	Carbon beads
2-Butanone	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
2-Butoxyethyanol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
2-Butoxyethanol	1403	ALCOHOLS IV	P	0.01-0.05	2	10	GC-FID	CCT
n-, sec-, & t-Butyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Butyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Butyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
tert-Butyl alcohol	1400	ALCOHOLS I	P	0.01-0.2	1	10	GC-FID	CCT
n- & sec-Butyl alcohol	1401	ALCOHOLS II	F	0.01-0.2	2	10	GC-FID	CCT
n-Butylamine	2012	*n*-BUTYLAMINE	F	0.01-1.0	2	100	GC-FID	SG + H_2SO_4
Butyl cellosolve	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Butyl cellosolve	1403	ALCOHOLS IV	P	0.01-0.05	1	10	GC-FID	CCT
1,3-Butylene glygol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Butyl glycidyl ether	1615	BUTYL GLYCIDYL ETHER	P	0.01-0.2	15	30	GC-FID	CCT
n-Butyl mercaptan	2525	*n*-BUTYL MERCAPTAN	F	0.01-0.05	1	4	GC-FPD	Chrom 104
n-Butyl mercaptan	2542	MERCAPTANS	P	0.1-0.2	10	150	GC-FPD	GFF/HgAc
p-tert-Butyltoluene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	29	GC-FID	CCT
Butyraldehyde	2539	ALDEHYDES, SCREENING	P	0.05	5	5	GC-FID/MS	XAD-2/HMP
Cadmium	7300	ELEMENTS by ICP	P	1 - 4	13	2000	ICP-AES	MCEF
Cadmium & compounds	7048	CADMIUM and cpds, as Cd	F	1 - 3	25	1500	FAAS	MCEF
Calcium	7300	ELEMENTS by ICP	P	1 - 4	5	200	ICP-AES	MCEF
Calcium & compounds	7020	CALCIUM and cpds as Ca	F	1 - 3	20	400	FAAS	MCEF
Camphor	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Capsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	P	1 - 3	5	1000	HPLC-FL	GFF
Carbaryl (Sevin)	5006	CARBARYL	F	1 - 3	20	400	VIS	GFF
Carbitol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Carbon black	5000	CARBON BLACK	F	1 - 2	30	570	Grav	PVC
Carbon, elemental	5040	ELEMENTAL CARBON (DIESEL EXHAUST)	P	1 - 4	106	4300	EGA/TOA	QFF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Carbon dioxide	6603	CARBON DIOXIDE	F	0.02-0.1	NA	80% Vol	GC-TCD	air bag
Carbon disulfide	1600	CARBON DISULFIDE	F	0.01-0.2	2	25	GC-FPD	CCT & dry tube
Carbon monoxide	6604	CARBON MONOXIDE	F	NA	NA	NA	Sensor	Port instr
Carbon tetrachloride	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	3	150	GC-FID	CCT
delta-3-Carene	1552	TERPENES	P	0.01-0.02	2	30	GC-FID	CCT
Chlordane	5510	CHLORDANE	F	0.5-1.0	10	200	GC-ECD	MCEF & Chrom 102
Chlorinated camphene	5039	CHLORINATED CAMPHENE	P	0.2-1	2	30	GC-ECD	MCEF
Chlorinated diphenyl oxide	5025	CHLORINATED DIPHENYL OXIDE	P	0.5-1.5	8	200	GC-ECN	MCEF
Chlorinated terphenyl	5014	CHLORINATED TERPHENYL	P	1 - 3	100	1500	GC-ECD	GFF
Chlorine	6011	CHLORINE and BROMINE	F	0.3-1.0	2	90	IC	Ag F
Chloroacetaldehyde	2015	CHLOROACETALDEHYDE	F	0.05-0.2	3	15	GC-ECD	SG
Chloroacetic acid	2008	CHLOROACETIC ACID	F	0.05-0.2	1	100	IC	SG
Chlorobenzene	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1.5	40	GC-FID	CCT
Chlorobromomethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.5	8	GC-FID	CCT
Chlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE	F	0.01-0.05	1	4	GC-FID	2CCT (lg+sm)
Chlorodiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	P	0.05-0.2	1	50	GC-ECD	GFF & Florisil
2-Chloroethanol	2513	ETHYLENE CHLOROHYDRIN	P	0.01-0.2	2	35	GC-FID	PCT
Chloroform	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1	50	GC-FID	CCT
4-Chloronitrobenzene	2005	NITROBENZENES	F	0.01-1.0	1	150	GC-FID	SG
p-Chlorophenol	2014	*p-CHLOROPHENOL*	F	0.05-0.2	1.5	40	HPLC-UV	SG
Chloroprene	1002	β-CHLOROPRENE	F	0.01-0.1	1.5	8	GC-FID	CCT
Chlorpyrifos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1.0	12	240	GC-FPD	OVS-2
Chromic acid	7600	CHROMIUM, HEXAVALENT	F	1 - 4	8	400	VIS	PVC
Chromic acid	7604	CHROMIUM, HEXAVALENT	F	1 - 4	100	1000	IC	PVC
Chromium	7024	CHROMIUM and cpds, as Cr	F	1 - 3	10	1000	FAAS	MCEF
Chromium	7300	ELEMENTS by ICP	P	1 - 4	5	1000	ICP-AES	MCEF
Chromium, hexavalent	7600	CHROMIUM, HEXAVALENT	F	1 - 4	8	400	VIS	PVC
Chromium, hexavalent	7604	CHROMIUM, HEXAVALENT	F	1 - 4	100	1000	IC	PVC
Chromium, hexavalent	9101	CHROMIUM, HEXAVALENT in settld dust	NA	NA	NA	NA	Spot	Test strip
Chrysene	5506; 5515	POLYNUCLEAR AROMATIC HC	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Coal tar naphtha	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Coal tar pitch volatiles	OSHA 58	COAL TAR PITCH VOLATILES		1.5-2.0	480	960	Grav & HPLC-UV	GFF
Cobalt	7300	ELEMENTS by ICP	P	1 - 4	25	2000	ICP-AES	MCEF
Cobalt & compounds	7027	COBALT and cpds, as Co	F	1 - 3	30	1500	FAAS	MCEF
Copper	7300	ELEMENTS by ICP	P	1 - 4	5	1000	ICP-AES	MCEF
Copper (dust & fume)	7029	COPPER (dust & fumes)	F	1 - 3	50	1500	FAAS	MCEF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Cresol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Cresol, all isomers	2546	CRESOLS and PHENOL	P	0.01-0.1	1	24	GC-FID	XAD-7
Crotonaldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Crotonaldehyde	3516	CROTONALDEHYDE	F	0.1-0.2	1	49	DPP	BuB
Cryofluorane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE, & CHLORODIFLUOROMETHANE	F	0.01-0.05	1	4	GC-FID	2 CCT
Cumene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	30	GC-FID	CCT
Cyanides	7904	CYANIDES, aerosol and gas	F	0.5-1.0	10	180	ISE	MCEF & BuB
Cyanides	6010	HYDROGEN CYANIDE	F	0.05-0.2	0.6	90	VIS	soda lime
Cyanuric acid	5030	CYANURIC ACID	P	1 - 3	10	1000	HPLC-UV	PVC
Cyclohexane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	2.5	5	GC-FID	CCT
Cyclohexanol	1402	ALCOHOLS III	P	0.01-0.2	1	10	CG-FID	CCT
Cyclohexanone	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Cyclohexanone	1300	KETONES I	F	0.01-0.2	1	10	CG-FID	CCT
Cyclohexene	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	5	7	CG-FID	CCT
1,3-Cyclopentadiene	2523	1,3-CYCLOPENTADIENE	F	0.01-0.05	1	5	GC-FID	Chrom 104/ maleic anh.
2,4-D	5001	2,4-D and 2,4,5-T	F	1 - 3	15	200	HPLC-UV	GFF
n-Decane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Demeton	5514	DEMETON	F	0.2-1.0	30	500	GC-FPD	MCEF &XAD-2
Diacetone alcohol	1402	ALCOHOLS III	P	0.01-0.2	1	10	GC-FID	CCT
o-Dianisidine	5013	DYES	P	1 - 3	150	500	HPLC-UV	PTFE
Diatomaceous earth	7501	SILICA, AMORPHOUS	P	1 - 3	50	400	XRD	PVC/CYC
Diazinon	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Diazomethane	2515	DIAZOMETHANE	P	0.2	6	30	GC-FID	XAD-2 (coated)
Dibenz(a,h) anthracene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Diborane	6006	DIBORANE	F	0.5-1.0	60	260	PES	PTFE & CCT w/oxidizer
Dibromodifluoromethane	1012	DIFLUORODIBROMOMETHANE	P	0.01-0.2	2.5	10	GC-FID	2 CCT
2-Dibutylaminoethanol	2007	AMINOETHANOL COMPOUNDS	P	0.01-0.2	4	24	GC-FID	SG
Dibutyl phosphate	5017	DIBUTYL PHOSPHATE	P	1-3	50	250	GC-FPD	PTFE
Dibutyl phthalate	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	F P	1-3	6	200	GC-FID	MCEF
Dibutyltin bis(isooctyl mercaptoacetate)	5504	ORGANOTIN COMPOUNDS	F	1-1.5	50	500	HPLC/GFAAS	GFF + XAD-2
o-, *p*-Dichlorobenzene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
o-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1	80	GC-FID	CCT
p-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1	10	GC-FID	CCT
3,3'-Dichlorobenzidine	5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE	F	0.2	20	100	HPLC-UV	GFF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Dichlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	F	0.01-0.05	1	4	GC-FID	2 CCT (lg + sm)
1,1-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.5	15	GC-FID	CCT
1,2-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.5	50	GC-FID	CCT
Dichloroethyl ether	1004	DICHLOROETHYL ETHER	F	0.01-1.0	2	15	GC-FID	CCT
1,2-Dichloroethylene	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.2	5	GC-FID	CCT
Dichlorofluoromethane	2516	DICHLOROFLUOROMETHANE	F	0.01-0.05	0.25	3	GC-FID	2 CCT (lg)
Dichloromethane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
1,1-Dichloro-1-nitroethane	1601	1,1-DICHLORO-1-NITROETHANE	F	0.01-1.0	1.5	15	GC-FID	PCT
1,2-Dichloropropane	1013	PROPYLENE DICHLORIDE	F	0.01-0.2	0.1	3.5	GC-ECN	PCT
1,2-Dichlorotetra-fluoroethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	F	0.01-0.05	1	4	GC-FID	2 CCT (lg + sm)
Dicrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Diethanolamine	3509	AMINOETHANOL COMPOUNDS II	P	0.5-1.0	5	300	IC	IMP
Diethylamine	2010	AMINES, ALIPHATIC	P	0.01-1.0	3	30	GC-FID	SG
2-Diethylaminoethanol	2007	AMINOETHANOL COMPOUNDS I	P	0.01-0.2	4	24	GC-FID	SG
Diesel exhaust	5040	ELEMENTAL CARBON (DIESEL EXHAUST)	P	1 - 4	106	4300	EGA/TOA	QFF
Diethylene glycol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Diethylene glycol ether	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Diethylenetriamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	U	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Di-(2-ethylhexyl) phthalate	5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE	F P	1 - 3	10	200	GC-FID	MCEF
Difluorodibromomethane	1012	DIFLUORODIBROMOMETHANE	P	0.01-0.2	2.5	10	GC-FID	2 CCT
Difluorodichloromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	F	0.01-0.05	1	4	GC-FID	2 CCT
Dihydrocapsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	P	1 - 3	7	1000	HPLC-FL	GFF
Diisobutyl ketone	1300	KETONES I	F	0.01-0.2	1	10	GC-FID	CCT
Dimethylacetamide	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	F	0.01-1.0	15	80	GC-FID	SG
Dimethylamine	2010	AMINES, ALIPHATIC	P	0.01-1.0	3	30	GC-FID	SG
N,N-Dimethylaniline	2002	AMINES, AROMATIC	P	0.02-1.0	3	30	GC-FID	SG
Dimethylarsinic acid	5022	ARSENIC, ORGANO-	F	1 - 3	50	1000	IC-HYAAS	PTFE
Dimethylformamide	2004	DIMETHYLACETAMIDE & DIMETHYLFORMAMIDE	F	0.01-1.0	15	80	GC-FID	SG
1,1-Dimethylhydrazine	3515	1,1-DIMETHYLHYDRAZINE	P	0.2-1.0	2	100	VIS	BuB (.1 M HCl)
N,N-Dimethyl-*p*-toluidine	2002	AMINES, AROMATIC	P	0.02-1.0	20	100	GC-FID	SG
Dimethyl sulfate	2524	DIMETHYL SULFATE	P	0.01-0.2	0.25	12	GC-ECN	Por P
Dioxane	1602	DIOXANE	F	0.01-0.2	0.5	15	GC-FID	CCT
Diphenyl	2530	DIPHENYL	F	0.01-0.5	15	30	GC-FID	Tenax GC

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Disulfoton	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Dyes- benzidine-, o-tolidine-, o-dianisidine-	5013	DYES, BENZIDINE-, o- TOLIDINE-, o- DIANISIDINE	P	1 - 3	150	500	HPLC-UV	PTFE
Elements	7300	ELEMENTS by ICP	P	1 - 4	Var	Va	ICP-AES	MCEF
Endrin	5519	ENDRIN	F	0.5-1.0	12	400	GC-ECD	MCEF & Chrom 102
Epichlorohydrin	1010	EPICHLOROHYDRIN	F	0.01-0.2	2	30	GC-FID	CCT
EPN	5012	EPN	F	1 - 2	15	700	GC-FPD	GFF
1,2-Epoxypropane	1612	PROPYLENE OXIDE	P	0.01-0.2	0.5	5	GC-FID	CCT
Ethanol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Ethanol	1400	ALCOHOLS I	P	0.01-0.05	0.1	1	GC-FID	CCT
Ethanolamine	2007	AMINOETHANOL COMPOUNDS I	P	0.01-0.2	4	24	GC-FID	SG
Ethion; Ethoprop	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
2-Ethoxyethanol	1403	ALCOHOLS IV	P	0.01-0.05	1	6	GC-FID	CCT
2-Ethoxyethyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Ethyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Ethyl acetate	1457	ETHYL ACETATE	F	0.01-0.2	0.1	10	GC-FID	CCT
Ethyl acrylate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Ethyl amyl ketone	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Ethylbenzene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	24	GC-FID	CCT
Ethyl bromide	1011	ETHYL BROMIDE	P	0.01-0.2	0.5	4	GC-FID	CCT
Ethyl butyl ketone	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Ethyl chloride	2519	ETHYL CHLORIDE	F	0.02-0.05	0.3	3	GC-FID	2 CCT (lg))
Ethylene chlorohydrin	2513	ETHYLENE CHLOROHYDRIN	P	0.01-0.2	2	35	GC-FID	PCT
Ethylenediamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	U	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Ethylene dibromide	1008	ETHYLENE DIBROMIDE	P	0.02-0.2	0.1	25	GC-ECD	CCT
Ethylene dichloride	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1	50	GC-FID	CCT
Ethylene glycol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Ethylene glycol dinitrate	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	F	0.2-1.0	3	100	GC-ECD	Tenax GC
Ethylene oxide	1614	ETHYLENE OXIDE	F	0.05-0.15	1	24	GC-ECD	PCT w/HBr
Ethylene oxide	3702	ETHYLENE OXIDE by portable GC	F	> 0.02	NA	80% vol	GC-PID	air bag
Ethylene thiourea	5011	ETHYLENE THIOUREA	P	1 - 3	200	800	VIS	PVC or MCEF
Ethylenimine	3514	ETHYLENIMINE	F	0.2	1	48	HPLC-UV	BuB
Ethyl ether	1610	ETHYL ETHER	P	0.01-0.2	0.25	3	GC-FID	CCT
Ethyl formate	1452	ETHYL FORMATE	P	0.01-0.2	0.3	10	GC-FID	CCT
Ethyl mercaptan	2542	MERCAPTANS	P	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Famamiphos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Fibrous glass	7400	ASBESTOS & other FIBERS by PCM	F	0.5-16	400	var	PCM	MCEF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Fluoranthene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Fluorene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Fluorides	7902	FLUORIDES, aerosol & gas	P	1 - 2	12	800	ISE	MCEF & pad w/ Na_2CO_3
Fluorides	7906	FLUORIDES by IC	P	1 - 2	1-sol 120-insol	800	IC	MCEF & pad w/ Na_2CO_3
Fluorotrichloromethane	1006	FLUOROTRICHLOROMETHANE	F	0.01-0.05	0.3	7	GC-FID	CCT (lg)
Fonofos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1.0	12	240	GC-FPD	OVS-2
Formaldehyde	2541	FORMALDEHYDE	P	0.01-0.1	1	36	GC-FID	XAD-2/HMP
Formaldehyde	3500	FORMALDEHYDE	F	0.2-1.0	1	100	VIS	PTFE & 2 IMP
Formaldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Formaldehyde	5700	FORMALDEHYDE on dust	F	2	240	1050	HPLC-UV	IOM/PVC
Formic acid	2011	FORMIC ACID	P	0.05-0.2	1	24	IC	PTFE & SG (washed)
Furfural	2529	FURFURAL	F	0.01-0.05	1	12	GC-FID	XAD-2/HMP
Furfural	2539	ALDEHYDES, SCREENING	P	0.05	5	5	GC-FID/MS	XAD-2/HMP
Furfuryl alcohol	2505	FURFURYL ALCOHOL	F	0.01-0.05	3	25	GC-FID	Por Q
Glutaraldehyde	2532	GLUTARALDEHYDE	P	0.01-0.05	4	39	HPLC-UV	SG/DNPH
Glycerin mist	0500	PARTICULATES N.O.R.	F	1 - 2	7	133	Grav	PVC
Glycidol	1608	GLYCIDOL	F	0.01-1.0	5	100	GC-FID	CCT
Glycols	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Heptanal	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
n-Heptane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
n-Heptane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	4	4	GC-FID	CCT
Hexachlorobutadiene	2543	HEXACHLOROBUTADIENE	F	0.05-0.2	1	100	GC-ECD	XAD-2
Hexachloro-1,3-cyclopentadiene	2518	HEXACHLORO-1,3-CYCLOPENTADIENE	F	0.01-0.2	0.25	80	GC-ECD	2 Por T
Hexachloroethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	3	70	GC-FID	CCT
Hexamethylene-diisocyanate	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Hexamethylene-diisocyanate	5521	ISOCYANATES, MONOMERIC	U	1.0	5	500	HPLC-ECHD	IMP
Hexanal	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Hexanal	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
n-Hexane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
n-Hexane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	4	4	GC-FID	CCT
2-Hexanone	1300	KETONES I	F	0.01-1.0	1	10	GC-FID	CCT
Hydrazine	3503	HYDRAZINE	F	0.2-1.0	7	100	VIS	BuB
Hydrogen bromide	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Hydrogen chloride	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG
Hydrogen cyanide	6010	HYDROGEN CYANIDE	F	0.05-0.2	2	90	VIS	soda lime
Hydrogen cyanide	7904	CYANIDES, AEROSOL & GAS	F	0.5-1.0	7	100	ISE	MCEF
Hydrogen flouride	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG
Hydrogen flouride	7902	FLUORIDES, AEROSOL & GAS	P	1 - 2	12	800	ISE	MCEF & pad w/Na_2CO_3
Hydrogen flouride	7906	FLUORIDES by IC	P	1 - 2	1	800	IC	MCEF & pad w/Na_2CO_3
Hydrogen sulfide	6013	HYDROGEN SULFIDE	F	0.1-1.5	1.2	40	IC	PTFE & CCT (lg)
Hydroquinone	5004	HYDROQUINONE	F	1 - 4	30	180	HPLC-UV	MCEF
Indeno [1,2,3-cd] pyrene	5506; 5515	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Iodine	6005	IODINE	F	0.5-1.0	15	225	IC	CCT w/alkali
Iron	7300	ELEMENTS by ICP	P	1 - 4	5	100	ICP-AES	MCEF
Isoamyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Isoamyl alcohol	1402	ALCOHOLS III	P	0.01-0.2	1	10	GC-FID	CCT
Isobutyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Isobutyl alcohol	1401	ALCOHOLS II	F	0.01-0.2	2	10	GC-FID	CCT
Isobutyraldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Isocyanates	5521	ISOCYANATES, MONOMERIC	U	1.0	5	500	HPLC-ECHD	IMP
Isocyanates	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Isophorone	2506	ISOPHORONE	F	0.01-1.0	2	25	GC-FID	PCT
Isopropyl acetate	1454	ISOPROPYL ACETATE	P	0.02-0.2	0.1	9	GC-FID	CCT
Isopropyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Isopropyl alcohol	1400	ALCOHOLS I	P	0.01-0.2	0.2	3	GC-FID	CCT
Isopropyl ether	1618	ISOPROPYL ETHER	F	0.01-0.05	0.1	3	GC-FID	CCT
Isopropyl glycidyl ether	1620	ISOPROPYL GLYCIDYL ETHER	P	0.01-0.2	1	30	GC-FID	CCT
Isovaleraldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
Kepone	5508	KEPONE	P	0.5-1.0	50	600	GC-ECD	MCEF & IMP
Kerosene	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Lead	7082	LEAD by FAAS	F	1 - 4	200	1500	FAAS	MCEF
Lead	7105	LEAD by GFAAS	P	1 - 4	1	1500	GFAAS	MCEF
Lead	7300	ELEMENTS by ICP	P	1 - 4	1250	2000	ICP-AES	MCEF
Lead	7700	LEAD in Air by Chemical Spot Test	P	2	10	240	Spot	MCEF
Lead	9100	LEAD in Surface Wipe Samples	NA	NA	NA	NA	AAS; ICP	Wipes
Lead sulfide	7505	LEAD SULFIDE	P	1.7 or 2.2	600	1000	XRD	CYC & PVC
Limonene	1552	TERPENES	P	0.01-0.2	2	30	GC-FID	CCT
Limonene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Lindane	5502	ALDRIN and LINDANE	F	0.2-1.0	18	240	GC-ECN	GFF & BuB
Lithium	7300	ELEMENTS by ICP	P	1 - 4	100	2000	ICP-AES	MCEF

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Lithium hydroxide	7401	ALKALINE DUSTS	F	1 - 4	70	1000	Titration	PTFE
Magnesium	7300	ELEMENTS by ICP	P	1 - 4	5	67	ICP-AES	MCEF
Malathion	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	60	GC-FPD	OVS-2
Maleic Anhydride	3512	MALEIC ANHYDRIDE	F	0.2-1.5	40	500	HPLC-UV	BuB
Manganese	7300	ELEMENTS by ICP	P	1 - 4	5	200	ICP-AES	MCEF
MBK	1300	KETONES I	F	0.01-0.2	1	10	GC-FID	CCT
MDI (4,4'-methylene-bisphenyl isocyanate)	5521	ISOCYANATES, MONOMERIC	U	1.0	5	500	HPLC-ECHD	IMP
MDI (4,4'-methylene-bisphenyl isocyanate)	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Mercury	6009	MERCURY	P	0.15-0.25	2	100	AAS-cold vap	Hopcalite
Mercaptans	2542	MERCAPTANS	P	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Mesityl oxide	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Metals in air	7300	ELEMENTS by ICP	P	1 - 4	var	2000	ICP-AES	MCEF
Methamidophos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Methanol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Methanol	2000	METHANOL	F	0.02-0.2	1	5	GC-FID	SG
2-Methoxyethyl acetate	1451	METHYL CELLOSOLVE ACETATE	F	0.01-0.2	0.2	20	GC-FID	CCT
2-Methoxyethanol	1403	ALCOHOLS IV	P	0.01-0.05	6	50	GC-FID	CCT
Methyl acetate	1458	METHYL ACETATE	F	0.01-0.2	0.2	10	GC-FID	CCT
Methyl acrylate	1459	METHYL ACRYLATE	P	0.01-0.2	1	5	GC-FID	CCT
Methylal	1611	METHYLAL	F	0.01-0.2	1	3	GC-FID	CCT
Methyl-(n-amyl)-ketone	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Methylarsonic acid	5022	ARSENIC, ORGANO-	F	1 - 3	50	1000	IC-HYAAS	PTFE
Methyl bromide	2520	METHYL BROMIDE	F	0.01-0.1	1	6	GC-AED	PCT(2) + dry tube
Methyl cellosolve	1403	ALCOHOLS IV	P	0.01-0.05	6	50	GC-FID	CCT
Methyl cellosolve acetate	1451	METHYL CELLOSOLVE ACETATE	F	0.01-0.2	0.2	20	GC-FID	CCT
Methyl chloride	1001	METHYL CHLORIDE	F	0.01-0.1	0.4	3	GC-FID	2 CCT (lg+sm)
Methyl chloroform	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.1	8	GC-FID	CCT
Methyl Chloroform	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Methyl cyanide	1606	ACETONITRILE	P	0.01-0.2	3	25	GC-FID	CCT
Methyl cyclohexane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	4	4	GC-FID	CCT
Methylcyclohexanol	1404	METHYLCYCLOHEXANOL	F	0.01-0.2	1	15	GC-FID	CCT
Methylcyclohexanone	2521	METHYLCYCLOHEXANONE	F	0.01-0.05	1	6	GC-FID	Por Q
Methylene chloride	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Methylene chloride	1005	METHYLENE CHLORIDE	F	0.01-0.2	0.5	2.5	GC-FID	2 CCT
4,4'-Methylenedianiline	5029	4,4'-METHYLENEDIANILINE	P	1 - 2	10	1000	HPLC-UV	GFF/H_2SO_4
4,4-Methylene diphenyl diisocyanate	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Methyl ethyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Methyl ethyl ketone	2500	METHYL ETHYL KETONE	F	0.01-0.2	0.25	12	GC-FID	Carbon beads
Methyl ethyl ketone peroxide	3508	METHYL ETHYL KETONE PEROXIDE	P	0.5-0.2	52	520	VIS	IMP
5-Methyl-3-heptanone	1301	KETONES II	F	0.01-0.2	1	25	GC-FID	CCT
Methyl iodide	1014	METHYL IODIDE	P	0.01-1.0	15	50	GC-FID	CCT
Methyl isoamyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
Methyl isobutyl carbinol	1402	ALCOHOLS III	P	0.01-0.2	1	10	GC-FID	CCT
Methyl isobutyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Methyl isobutyl ketone	1300	KETONES I	F	0.01-0.2	1	10	GC-FID	CCT
Methyl mercaptan	2542	MERCAPTANS	P	0.1-0.2	10	150	GC-FPD	GFF/HgAc
Methyl methacrylate	2537	METHYL METHACRYLATE	F	0.01-0.05	1	6	GC-FID	XAD-2
Methyl parathion	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Methyl phenol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
α-Methyl styrene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	30	GC-FID	CCT
Methyl tert-butyl ether	1615	METHYL tert-BUTYL ETHER	P	0.1-0.2	2	96	GC-FID	2 CCT (lg)
Mevinphos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1.0	12	240	GC-FPD	OVS-2
Mineral spirits	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Molybdenum	7300	ELEMENTS by ICP	P	1 - 4	5	67	ICP-AES	MCEF
Monocrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Monomethylaniline	3511	MONOMETHYLANILINE	P	0.2-1.0	11	100	GC-FID	BuB/H_2SO_4
Monomethylhydrazine	3510	MONOMETHYLHYDRAZINE	F	0.5-1.5	3	20	VIS	BuB/HCl
Naphtha (coal tar)	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Naphthalene	1501	HYDROCARBONS, AROMATIC	P	0.01-1.0	100	200	GC-FID	CCT
Naphthalene	5506	POLYNUCLEAR AROMATIC H/C	P	2.0	200	1000	HPLC-UV; GC-FID	PTFE & XAD-2
Naphthylamines	5518	NAPHTHYLAMINES	P	0.2-0.8	30	100	GC-FID	GFF & SG
Nickel	7300	ELEMENTS by ICP	P	1 - 4	25	1000	ICP-AES	MCEF
Nickel carbonyl	6007	NICKEL CARBONYL	P	0.05-0.2	7	80	GFAAS	CCT (low Ni)
Nicotine	2544	NICOTINE	P	1.0	60	400	GC-NPD	XAD-2
Nitric acid	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG (washed)
Nitric oxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	F	0.025	1.5	6	VIS	MS w/TEA & oxidizer
p-Nitroaniline	5033	*p*-NITROANILINE	F	1 - 3	16	350	HPLC-UV	MCEF
Nitrobenzene	2005	NITROBENZENES	F	0.01-1	10	150	GC-FID	SG
p-Nitrochlorobenzene	2005	NITROBENZENES	F	0.01-1	1	150	GC-FID	SG
Nitroethane	2526	NITROETHANE	F	0.01-0.05	1.5	3	GC-FID	2XAD-2
Nitrogen dioxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	F	0.025-0.2	1.5	6	VIS	MS w/TEA
Nitroglycerin	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	F	0.2-1.0	3	100	GC-ECD	Tenax-GC
Nitromethane	2527	NITROMETHANE	F	0.01-0.05	1.2	3	GC-FPD	Chrom 106

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
2-Nitropropane	2528	2-NITROPROPANE	F	0.01-0.05	0.1	2	GC-FID	Chrom 106
Nitrosamines	2522	NITROSAMINES	P	0.2-2.0	15	1000	GC-TEA	Thermosorb/N
Nitrotoluene	2005	NITROBENZENES	F	0.01-0.2	1	30	GC-FID	SG
Nitrous oxide	6600	NITROUS OXIDE	F	NA	NA	80% Vol	IR	air bag
Nuisance dusts	0500	PARTICULATES N.O.R.	F	1 - 2	7	133	GRAV	PVC
n-Octane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
n-Octane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	4	4	GC-FID	CCT
Octamethylcyclotetra-siloxane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
1-Octanethiol	2510	1-OCTANETHIOL	F	0.01-0.2	1	15	GC-FPD	Tenax GC
Oil mist (mineral)	5026	OIL MIST, MINERAL	F	1 - 3	20	500	IR	PVC or MCE
Organophosphorus Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Oxygen	6601	OXYGEN	F	NA	1	NA	Sensor	portable
Paraquat	5003	PARAQUAT	F	1 - 4	40	1000	HPLC-UV	PTFE
Parathion	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1.0	12	240	GC-FPD	OVS-2
Particulates N.O.R.	0600	PARTICULATES, N.O.R, RESP.	F	1.7 or 2.2	20	400	Grav.	CYC & PVC
Pentachlorobenzene	5517	POLYCHLOROBENZENES	F	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
Pentachloroethane	2517	PENTACHLOROETHANE	F	0.01-0.2	1	10	GC-ECD	Por R
Pentachlorophenol	5512	PENTACHLOROPHENOL	F	0.5-1.0	48	480	HPLC-UV	MCEF & BuB
Pentamidine	5032	PENTAMIDINE ISETHIONATE	P	1 - 2	50	1500	HPLC/FL	PVC/opaque
n-Pentane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
n-Pentane	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.05	2	2	GC-FID	CCT
2-Pentanone	1300	KETONES I	F	0.01-2.0	1	10	GC-FID	CCT
Perchloroethylene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Petroleum ether/naphtha	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Phenol	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Phenol	2546	CRESOLS and PHENOL	P	0.01-0.1	1	24	GC-FID	XAD-7
Phenyl ether	1617	PHENYL ETHER	P	0.01-0.2	1	50	GC-FID	CCT
Phenyl ether-diphenyl mixture	2013	PHENYL ETHER-DIPHENYL MIXTURE	P	0.01-0.2	1	40	GC-FID	SG
Phenyl glycidyl ether	1619	PHENYL GLYCIDYL ETHER	P	0.01-1	80	150	GC-FID	CCT
Phenylhydrazine	3518	PHENYLHYDRAZINE	F	0.2-1.0	25	120	VIS	BuB/HCl
Phorate	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Phosdrin (mevinphos)	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	480	GC-FPD	OVS-2
Phosphine	6002	PHOSPHINE	F	0.01-0.2	1	16	VIS	SG/$Hg(CN)_2$
Phosphoric acid	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG (washed)
Phosphorus	7300	ELEMENTS by ICP	P	1 - 4	50	2000	ICP-AES	MCEF
Phosphorus	7905	PHOSPHORUS	F	0.01-0.2	5	100	GC-FPD	Tenax GC
Phosphorus trichloride	6402	PHOSPHORUS TRICHLORIDE	P	0.05-0.2	11	100	VIS	BuB/H_2O

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Pinene	1552	TERPENES	P	0.01-0.2	2	30	GC-FID	CCT
Pinene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Platinum	7300	ELEMENTS by ICP	P	1 - 4	13	2000	ICP-AES	MCEF
PAH	5506	POLYNUCLEAR AROMATIC H/C	P	2.0	200	1000	HPLC-FL/UV	PTFE & XAD-2
Polyacrylate	5035	SUPER ABSORBENT POLYMER	P	1 - 2	50	1500	ICP or AAS	PVC
Polychlorobiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	P	0.05-0.2	1	50	GC-ECD	GFF & Florisil
Potassium hydroxide	7401	ALKALINE DUSTS	F	1 - 4	70	1000	titration	PTFE
Propionaldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP
n-Propyl acetate	1450	ESTERS I	P	0.01-0.2	1	10	GC-FID	CCT
n-Propyl alcohol	1401	ALCOHOLS II	F	0.01-0.2	1	10	GC-FID	CCT
Propylene dichloride	1013	PROPYLENE DICHLORIDE	F	0.01-0.2	0.1	3.8	GC-ECN	PCT
Propylene glycol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Propylene oxide	1612	PROPYLENE OXIDE	P	0.01-0.2	0.5	5	GC-FID	CCT
Pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	P	2.0	200	1000	HPLC-FL/UV; GC-FID	PTFE & XAD-2
Pyrethrum	5008	PYRETHUM	F	1 - 4	20	400	HPLC-UV	GFF
Pyridine	1613	PYRIDINE	F	0.01-1.0	18	150	GC-FID	CCT
Ribavirin	5027	RIBAVIRIN	U	1 - 4	5	1000	HPLC-UV	GFF
Ronnal	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	60	GC-FPD	OVS-2
Rotenone	5007	ROTENONE	F	1 - 4	8	400	HPLC-UV	PTFE
Rubber solvent	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Selenium	7300	ELEMENTS by ICP	P	1 - 4	5	2000	ICP-AES	MCEF
Silica, amorphous	7501	SILICA, AMORPHOUS	P	1.7 or 2.2	50	400	XRD	PVC (total) or PVC & CYC
Silica in coal mine dust	7603	SILICA in coal mine dust	U	1.7 or 2.2	300	1000	IR	CYC & PVC
Silica, crystalline	7601	SILICA, CRYSTALLINE	P	1.7 or 2.2	400	800	VIS	CYC & MCE or PVC
Silica, crystalline	7602	SILICA, CRYSTALLINE (IR)	P	1.7 or 2.2	400	800	IR	CYC & MCE or PVC
Silica, crystalline, respirable	7500	SILICA, CRYSTALLINE, RESP.	P	1.7 or 2.2	400	1000	XRD	CYC & PVC
Silver	7300	ELEMENTS by ICP	P	1 - 4	250	2000	ICP-AES	MCEF
Sodium hexafluoro-aluminate	7902	FLUORIDES, aerosol & gas	P	1 - 2	12	800	ISE	MCEF & pad w/Na_2CO_3
Sodium hexafluoro-aluminate	7906	FLUORIDES by IC	P	1-2	120	800	IC	MCEF & pad w/Na_2CO_3
Sodium hydroxide	7401	ALKALINE DUSTS	F	1 - 4	70	1000	Titration	PTFE
Stibine	6008	STIBINE	F	0.01-0.2	4	50	VIS	SG w/$HgCl_2$
Stoddard solvent	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
Strychnine	5016	STRYCHNINE	F	1 - 3	70	1000	HPLC-UV	GFF
Styrene	1501	HYDROCARBONS, AROMATIC	P	0.01-1.0	1	14	GC-FID	CCT

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Sulfur dioxide	6004	SULFUR DIOXIDE	P	0.5-1.5	4	200	IC	MCEF & pad w/Na_2CO_3
Sulfur hexafluoride	6602	SULFUR HEXAFLUORIDE	F	0.01-0.05	NA	80% Vol	GC-ECD	air bag
Sulfuric acid	7903	ACIDS, INORGANIC	F	0.2-0.5	3	100	IC	SG (washed)
Sulfuryl fluoride	6012	SULFURYL FLUORIDE	F	0.05-0.1	1.3	10	IC	CCT (lg)
Sulprofos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FPD	OVS-2
Super absorbent polymer	5035	SUPER ABSORBENT POLYMER	P	1 - 3	60	1500	ICP or AAS	PVC
2,4,5-T	5001	2,4-D and 2,4,5-T	F	1 - 3	15	200	HPLC-UV	GFF
Tellurium	7300	ELEMENTS by ICP	P	1 - 4	25	2000	ICP-AES	MCEF
Terbufos	5600	ORGANOPHOSPHORUS PESTICIDES	F	0.2-1	12	240	GC-FID	OVS-2
Terpenes	1552	TERPENES	P	0.01-2	2	30	GC-FID	CCT
o-Terphenyl	5021	o-TERPHENYL	P	1 - 3	2	30	GC-FID	PTFE
1,1,2,2-Tetrabromoethane	2003	1,1,2,2-TETRABROMOETHANE	P	0.2-1.0	50	100	GC-FID	SG
Tetrabutyltin	5504	ORGANOTIN COMPOUNDS	F	1-1.5	50	500	HPLC/HGAAS	GFF & XAD-2
1,2,4,5-Tetrachlorobenzene	5517	POLYCHLOROBENZENES	F	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
1,1,2,2-Tetrachloro-2,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUORO-ETHANE	P	0.01-0.035	0.5	2	GC-FID	CCT
1,1,1,2-Tetrachloro-1,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUORO-ETHANE	P	0.01-0.035	0.5	2	GC-FID	CCT
1,1,2,2-Tetrachloroethane	1019	1,1,2,2-TETRACHLOROETHANE	P	0.01-0.2	3	30	GC-FID	PCT
Tetrachloroethylene	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.2	40	GC-FID	CCT
Tetraethylene glycol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Tetraethyl lead	2533	TETRAETHYL LEAD (as Pb)	F	0.01-1.0	30	200	GC-PID	XAD-2
Tetraethyl pyrophosphate	2504	TETRAETHYL PYROPHOSPHATE	F	0.01-0.2	20	48	GC-FPD	2 Chrom 102
Tetrahydrofuran	1609	TETRAHYDROFURAN	P	0.01-0.2	1	8	GC-FID	CCT
Tetramethyl lead	2534	TETRAMETHYL LEAD (as Pb)	F	0.01-0.2	15	100	GC-PID	XAD-2
Tetramethyl thiourea	3505	TETRAMETHYL THIOUREA	P	0.2-1.0	50	250	VIS	IMP/H_2O
Tetranitromethane	3513	TETRANITROMETHANE	F	0.5-1.0	20	250	GC-FID	IMP/EtAc
Thallium	7300	ELEMENTS by ICP	P	1 - 4	25	2000	ICP-AES	MCEF
Thiram	5005	THIRAM	F	1 - 4	10	400	HPLC-UV	PTFE
Tin, organic compds as Sn	5504	ORGANOTIN CPDS. (as Sn)	F	1-1.5	50	500	HPLC/GFAAS	GFF & XAD-2
Titanium	7300	ELEMENTS by ICP	P	1 - 4	5	100	ICP-AES	MCEF
o-Tolidine	5013	DYES	P	1 - 3	150	500	HPLC-UV	PTFE
Toluene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Toluene	4000	TOLUENE	F	NA	(15 min)	(8 h)	GC-FID	passive
Toluene	1500	HYDROCARBONS, BP 36-126°C	F	0.01-0.2	2	8	GC-FID	CCT
Toluene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	8	GC-FID	CCT

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
2,4 & 2,6-Toluenediamine	5516	2,4- & 2,6-TOLUENEDIAMINE	P	1.0	30	500	HPLC-UV	IMP
Toluene-2,4-diisocyanate	2535	TOLUENE-2,4-DIISOCYANATE	F	0.2-1.0	2	170	HPLC-UV	GW coated
Toluene-2,4-diisocyanate	5521	ISOCYANATES, MONOMERIC	U	1.0	5	500	HPLC-ECHD	IMP
Toluene-2,4-diisocyanate	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Toluene-2,6-diisocyanate	5522	ISOCYANATES	P	1 - 2	15	360	HPLC-FL	IMP
Toluene-2,6-diisocyanate	5521	ISOCYANATES, MONOMERIC	U	1.0	5	500	HPLC-ECHD	IMP
o-Toluidine	2002	AMINES, AROMATIC	F	0.02-1.0	10	150	GC-FID	SG
Tribromomethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	4	70	GC-FID	CCT
Tributyl phosphate	5034	TRIBUTYL PHOSPHATE	P	1 - 3	2	100	GC-FPD	MCEF
Tributyltin chloride	5504	ORGANOTIN COMPOUNDS	F	1-1.5	50	500	HPLC/GFAAS	GFF & XAD-2
1,2,4-Trichlorobenzene	5517	POLYCHLOROBENZENES	F	0.01-0.2	3	12	GC-ECD	PTFE & XAD-2
1,1,2-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	2	60	GC-FID	CCT
1,1,1-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.1	8	GC-FID	CCT
1,1,1-Trichloroethane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Trichloroethylene	1022	TRICHLOROETHYLENE	P	0.01-0.2	1	30	GC-FID	CCT
Trichloroethylene	3701	TRICHLOROETHYLENE by portable GC	F	> 0.02	NA	80% Vol	GC	air bag
Trichlorofluoromethane	1006	FLUOROTRICHLOROMETHANE	F	0.01-0.05	0.3	7	GC-FID	CCT
Trichloromethane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	1	50	GC-FID	CCT
1,2,3-Trichloropropane	1003	HYDROCARBONS, HALOGENATED	P	0.01-0.2	0.6	60	GC-FID	CCT
Trichcylohexyltin hydroxide	5504	ORGANOTIN COMPOUNDS	F	1-1.5	50	500	HPLC-GFAAS	GFF & XAD-2
1,1,2-Trichloro 1,2,2-trifluoroethane	1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	P	0.01-0.05	0.1	3	GC-FID	CCT
1,1,2-Trichloro 1,2,2-trifluoroethane	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Triethanolamine	3509	AMINOETHANOL COMPOUNDS II	P	0.5-1.0	5	300	IC	IMP
Triethylene glycol	5523	GLYCOLS	P	0.5-2	5	60	GC-FID	OVS-7
Triethylenetetramine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	U	0.01-0.1	1	20	HPLC-UV	XAD-2 w/10% NITC
Trifluorobromomethane	1017	TRIFLUOROBROMOMETHANE	P	0.01-0.05	0.1	1	GC-FID	2 CCT (lg+sm)
Trimellitic anhydride	5036	TRIMELLITIC ANHYDRIDE	P	1.5-2	400	1000	GC-FID	PVC
2,4,7-Trinitrofluoren-9-one	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	P	1 - 3	100	500	HPLC-UV	PTFE
Triorthocresyl phosphate	5037	TRIORTHOCRESYL PHOSPHATE	P	1 - 3	2	100	GC-FPD	MCEF
Triphenyl phosphate	5038	TRIPHENYL PHOSPHATE	P	1 - 3	10	400	GC-FPD	MCEF
Tungsten, soluble/insoluble	7074	TUNGSTEN (soluble/insoluble)	F	1 - 4	200	1000	FAAS	MCEF
Turpentine	1551	TURPENTINE	F	0.01-0.2	1	10	GC-FID	CCT
Turpentine	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Valeraldehyde	2536	VALERALDEHYDE	F	0.01-0.04	0.5	10	GC-FID	XAD-2/HMP
Valeraldehyde	2539	ALDEHYDES, SCREENING	P	0.01-0.05	5	5	GC-FID/MS	XAD-2/HMP

Chemical	Meth. No.	Method Name	Eval	Flow Rate (L/min)	Min. Vol. (L)	Max. Vol. (L)	Analytical Technique	Sampler
Vanadium	7300	ELEMENTS by ICP	P	1 - 4	5	2000	ICP-AES	MCEF
Vanadium oxides	7504	VANADIUM OXIDES	P	1.7 or 2.2	200	1000	XRD	CYC & PVC
Vinyl acetate	1453	VINYL ACETATE	U	0.1-0.2	0.75	24	GC-FID	MS (carbon)
Vinyl benzene	1501	HYDROCARBONS, AROMATIC	P	.01-1	1	14	GC-FID	CCT
Vinyl bromide	1009	VINYL BROMIDE	F	0.01-0.2	2	10	GC-FID	CCT (lg)
Vinyl chloride	1007	VINYL CHLORIDE	F	0.05	0.7	5	GC-FID	2 CCT
Vinylidene chloride	1015	VINYLIDENE CHLORIDE	F	0.01-0.2	2.5	7	GC-FID	CCT
Vinyl toluene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	1	24	GC-FID	CCT
VM&P naphtha	1550	NAPHTHAS	F	0.01-0.2	1.3	20	GC-FID	CCT
VOCs	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Warfarin	5002	WARFARIN	P	1 - 4	200	1000	HPLC-UV	PTFE
Xylene	2549	VOLATILE ORGANIC CPDS (Screening)	P	0.01-0.05	1	6	TD/GC-MS	TD
Xylene	1501	HYDROCARBONS, AROMATIC	P	0.01-0.2	2	23	GC-FID	CCT
2,4-Xylidine	2002	AMINES, AROMATIC	F	0.02-0.2	3	20	GC-FID	SG
Yttrium	7300	ELEMENTS by ICP	P	1 - 4	5	1000	ICP-AES	MCEF
Zinc and compounds	7030	ZINC and compounds, as Zn	P	1 - 3	2	400	FAAS	MCEF
Zinc	7300	ELEMENTS by ICP	P	1 - 4	5	200	ICP-AES	MCEF
Zinc oxide	7502	ZINC OXIDE	F	1 - 3	10	400	XRD	PVC
Zirconium	7300	ELEMENTS by ICP	P	1 - 4	5	200	ICP-AES	MCEF

METHOD FINDER KEY TO ABBREVIATIONS

Sampling Media/Devices

Ag F	Silver membrane filter
BuB	Bubbler
CCT	Coconut shell charcoal tube
Chrom	Chromosorb
CYC	Cyclone
DNPH	Dinitrophenylhydrazine HCl
Dry	Drying tube
GFF	Glass fiber filter
GW	Glass wool
HMP	2-(Hydroxymethyl)piperidine
IMP	Impinger
IOM	Inspirable dust sampler
MCEF	Mixed cellulose ester filter
MS	Molecular sieve
NITC	1-naphthylisothiocyanate
OVS-2	OSHA versatile sampler (quartz filter/XAD-2)
OVS-7	OSHA versatile sampler (glass fiber filter/XAD-7)
Pad	Cellulose backup pad
PCT	Petroleum charcoal tube
Por	Poropak
PTFE	Polytetrafluoroethylene (Teflon) filter
PVC	Polyvinyl chloride filter
QFF	Quartz fiber filter
SG	Silica gel
TD	Thermal desorption tube
TEA	Triethanolamine

Analytical Techniques

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

Evaluation

F	Full evaluation
P	Partial evaluation
U	Unrated

NA	Not applicable
Var	Variable

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E. DEVELOPMENT AND EVALUATION OF METHODS

by Eugene R. Kennedy, Ph.D., Thomas J. Fischbach, Ruiguang Song, Ph.D. Peter M. Eller, Ph.D., Stanley A. Shulman, Ph.D., NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS

Contents:

1. METHOD DEVELOPMENT

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

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

procedures for proper handling and use of the analyte can be prepared. These also aid in establishment of analyte purity. Potential sources of this information include chemical reference books, health hazard evaluation reports, bulk sample analyses, material safety data sheets, chemical process information, etc.

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

a. Preliminary Experimentation

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

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

b. Recovery of the Analyte from the Medium

During the course of method development experiments, the ability to recover the analyte from the sampling medium should be determined. A suggested experiment to accomplish this entails the fortification of sets of 6 samplers with amounts of analyte equivalent to sampling concentrations of 0.1, 0.5, 1.0, and 2.0 (or higher) times the exposure limit for a minimum of 4 h at the typical sampling rate used for that type of sampler. If the analyte

has a ceiling or short-term exposure limit, the amount of analyte fortified should be adjusted for the shorter sampling time required for this type of exposure limit. If the sampler has a backup section, then a like number of separate backup sections should be fortified with amounts of analyte equivalent to 25% of the amount fortified on the front sections of the samplers, since this amount has been used to characterize the breakthrough limit of useful samples [2]. Samples (and backup sections) should be prepared for analysis and analyzed according to previously determined procedures. Results of these analyses should be expressed in terms of estimated percent recovery according to the following formula:

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

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

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

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

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

c. Stability of the Analyte on the Medium

An extension to the experiment described above may be performed to investigate potential stability problems early in the experimentation. An additional set of fortified samples at each of the 4 concentrations should be prepared and analyzed after 7-days' storage at room temperature. Recovery should be similar to the above results within experimental error. Discrepancies larger than those expected by experimental error indicate sample stability problems that will need correcting by additional developmental effort (e.g., refrigerated storage). Comparison of results can be performed with statistical tests, such as an analysis of variance (ANOVA) [5] test of the "Day" difference or a paired t-test [6] of the means of the Day 1 and Day 7 storage results.

2. METHOD EVALUATION

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

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

a. Feasibility of Analyte Generation

In order to provide a realistic test of the method under study, air concentrations covering the range from 0.1 to 2 times the exposure limit of the analyte should be generated. The

generated atmospheres should be homogeneous in concentration and representative of the environment encountered when sampling for the analyte in the workplace.

When attempting to generate a concentration of an analyte, the impact of environmental conditions, such as temperature, pressure, humidity, and interferences, on sampler performance and/or generation should be considered. The effect of elevated temperature on the collection medium of a sampler may decrease the capacity of the sampler or may decompose the analyte during generation and sampling. Reduced pressure may also reduce the capacity of a sampler. High relative humidity in many instances has been observed to reduce sampler capacity [3]. In other instances it has increased sampler capacity [11]. A typical interference(s) should be generated along with the analyte to approximate a typical workplace sampling environment.

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

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

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

b. Capacity of the Sampler and Sampling Rate

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

Flow rates typical for the media selected should be used. These may range from 0.01 - 4 L/min, depending on sampler type. At extremely low flow rates (ca. 5 mL/min), the effect of diffusion of the analyte into the sampler must be considered. Flow rates should be kept at a high enough rate to prevent diffusion from having a positive bias in the sampler. Sampling should be performed at three different flow rates covering the range appropriate for the particular sampler type, unless the sampler is designed to operate at only one flow rate. Sampling times should range from 22.5 min for STELs to 900 min (15 h) for time-weighted averages. Shorter sampling times (e.g., 7.5 to 22.5 min) may be used for ceiling © measurements. Flow rates should be based on accurately calibrated sampling pumps or critical orifices. The amount of analyte collected at the lowest flow rate and shortest sampling time should be greater than the limit of quantitation of the method. The generated concentration used for capacity determination should be at least 2 times the highest published exposure limit and verified by an independent method.

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

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

If the collection process is based primarily on adsorption, breakthrough time should be proportional to the inverse of the flow rate [14]. This relationship can be checked by plotting the 5% breakthrough time versus the inverse of the flow rate. If the resulting plot is a straight line, then this relationship should hold for all flow rates in the flow rate range studied. Some nonlinearity in the plot may be noted due to experimental variability and assumptions made to simplify the relationship of breakthrough time and flow rate. Results from these experimental trials should provide a prediction of the capacity of the sampler

at various flow rates and sampling times. If the flow rates and sampling times used in the experiment do not provide for sufficient capacity, a lower flow rate range may have to be studied and the experiment repeated.

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

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

c. Sampling and Analysis Evaluation

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

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

d. Sample Stability

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

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

e. Precision, Bias, and Accuracy

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

Bias is assumed to be homogeneous over the evaluation range. This assumption should be tested by estimating the bias at each concentration and testing these for homogeneity

using the procedures described in the literature [1]. Method bias should be less than 10%. A test for this is also described [18].

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

If the results for 4 concentrations fail the 25% accuracy criterion, then the set of samples collected at 0.1 x exposure limit should be excluded from the data set. The pooled $\hat{S}_{rT}$ and the bias should be recalculated on this reduced data set before performing the accuracy analysis described in the previous paragraph.

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

3. FIELD EVALUATION

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

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

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

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

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

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

4. DOCUMENTATION

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

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

If an acceptable method is developed, a sampling and analytical method should be prepared in appropriate format. The format of the resulting method should provide clear instructions for the use of the method. Sampling, sample workup, and analysis procedures should be clearly described. The necessary equipment and supplies for the method should be listed clearly in the method. A summary of the evaluation of the method should be included, as well as a discussion of method applicability and lists of interferences and related references. As a check on the clarity and performance, new methods should be reviewed and submitted to a user check (i.e., the method is used to analyze spiked or generated samples of known concentration by someone other than the researcher who developed it) and to a collaborative test, if feasible.

5. APPENDIX - ACCURACY AND ITS EVALUATION

In the development of a sampling and analytical method, one of the goals is to minimize the measurement error to the lowest feasible and practical levels. It is assumed that all

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

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

Accuracy, bias, and imprecision have the following relationship:

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

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

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

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

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

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

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

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

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

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Figure 1: Nomogram Relating Accuracy to Precision and Bias

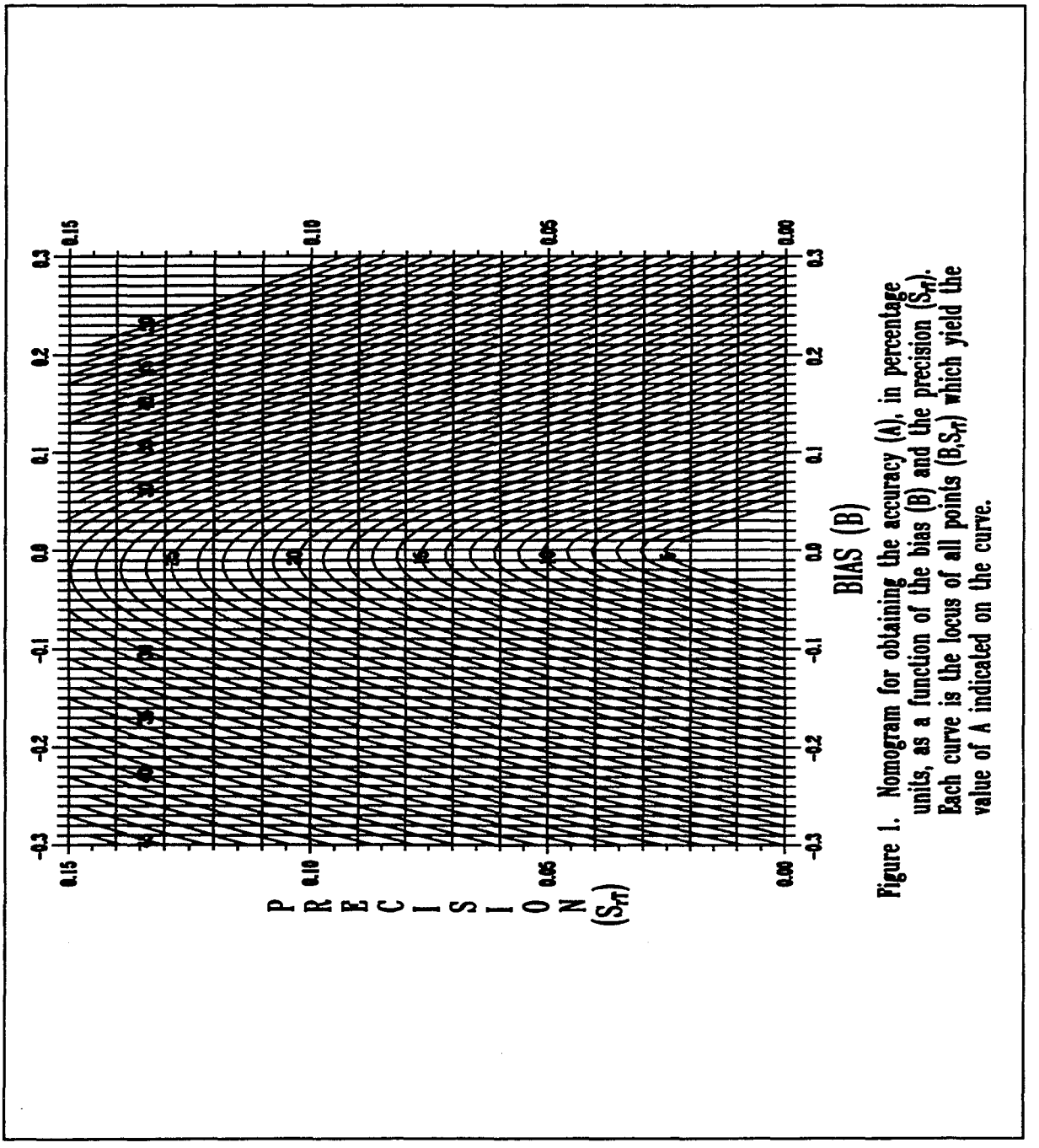

Figure 1. Nomogram for obtaining the accuracy (A), in percentage units, as a function of the bias (B) and the precision (S_{rT}). Each curve is the locus of all points (B,S_{rT}) which yield the value of A indicated on the curve.

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

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

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

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

F. APPLICATION OF BIOLOGICAL MONITORING METHODS

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

1. INTRODUCTION

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

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

2. GENERAL CONSIDERATIONS

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

water soluble than the parent chemical. Where metabolism yields more than one product, the relative amounts of each and the parent-metabolite ratios are affected by an individual's general health status, diet, genetic makeup, degree of hydration, time after exposure, and other factors. The kidney is the major organ of excretion and is the primary route for water-soluble substances. These substances enter the urine by either glomerular filtration, tubular secretion, or sometimes both mechanisms.

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

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

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

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

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

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

c. When the site of critical action for a toxicant is known, the concentration of the biomarker at that site can be used as a measure of the biologically effective dose. Carboxyhemoglobin is such a biomarker for carbon monoxide poisoning. In this case, the biomarker level is correlated with the health effect.

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

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

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

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

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

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

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

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

solvent, which would cause differences in concentration between capillary blood (mainly arterial blood) and venous blood.

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

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

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

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

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

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

3. PRACTICAL CONSIDERATIONS

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

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

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

3. The method should have a sufficiently low limit of detection to differentiate exposed from nonexposed workers. A method developed when biological monitoring reference

levels were higher may be inadequate for measuring exposures at and below the current guidelines.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3. High level of analytical quality control

4. Participation in proficiency testing programs, if available

5. Documented instrument evaluation and maintenance programs

6. Investigation of communication failures and complaints

7. Documentation of performance and corrective actions

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

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

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

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

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

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

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

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

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

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

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

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

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

4. INTERPRETATION OF RESULTS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

normal occupational exposure and may affect significantly the metabolism of industrial chemicals.

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

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

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G. AEROSOL PHOTOMETERS FOR RESPIRABLE DUST MEASUREMENTS

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

Contents:

1. INTRODUCTION

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

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

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

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

*aerodynamic diameter

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

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

2. PRINCIPLES OF OPERATION

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

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

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

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

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

3. SAMPLING CONSIDERATIONS

a. Safety

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

b. Applications

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

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

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

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

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

4. DATA ACQUISITION AND TREATMENT

a. Calibration

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

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

b. Operation

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

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

5. INSTRUMENTS

a. MIE, Inc.

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

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

b. MST Measurement Systems, Inc.

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

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

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

c. ppm Enterprises

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

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

d. Sensidyne, Inc.

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

e. A. P. Buck, Inc.

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

6. REFERENCES

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

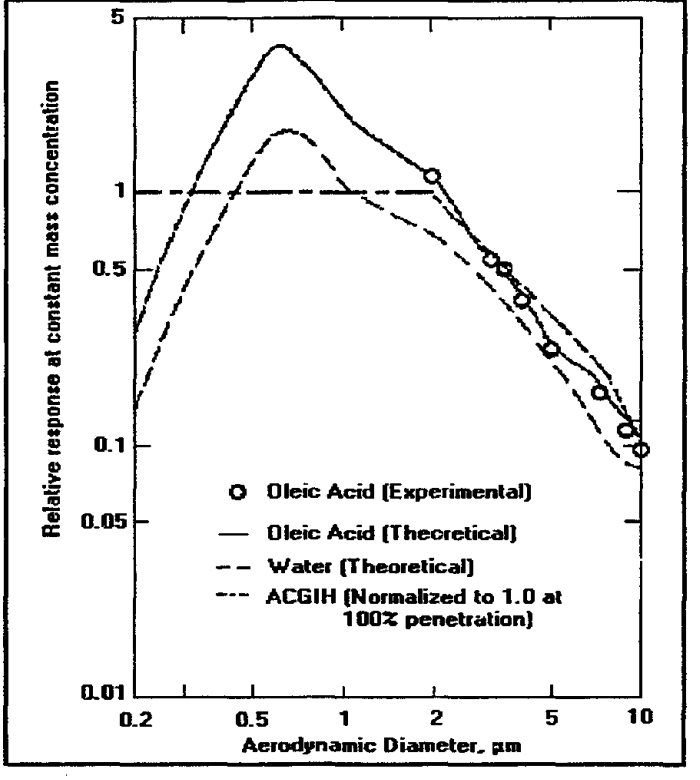

Figure 1

Diagram showing the components of an aerosol photometer.

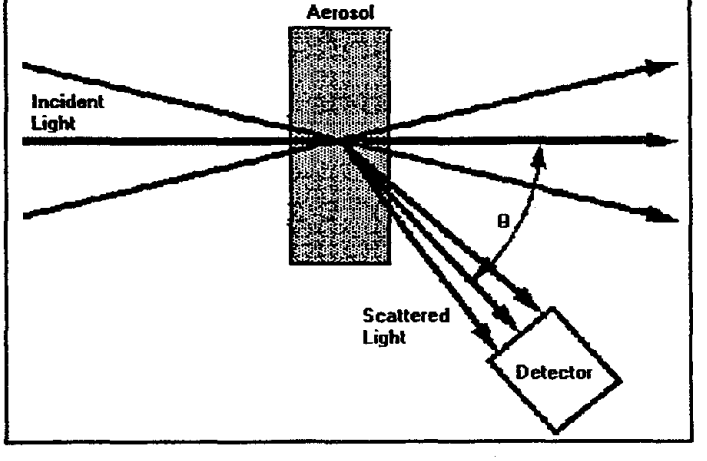

Figure 2

H. PORTABLE ELECTROCHEMICAL SENSOR METHODS

by W. J. Woodfin, NIOSH/DPSE

Contents: Page

1. INTRODUCTION

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

2. PRINCIPLES OF OPERATION

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

3. SAMPLING CONSIDERATIONS

a. Safety

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

b. Applications

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

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

c. Environmental Conditions

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

4. DATA ACQUISITION AND TREATMENT

a. Calibration

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

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

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

b. Sampling and Measurement Procedure

(1) Toxic Gases

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

(2) Oxygen

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

c. Limits of Performance

(1) Temperature Limits

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

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

(2) Interferences

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

5. MANUFACTURERS

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

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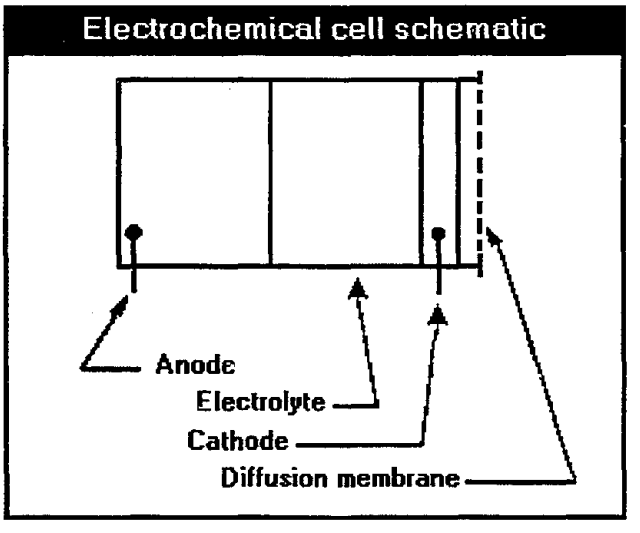

Figure 1

I. PORTABLE GAS CHROMATOGRAPHY

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

Contents:

1. INTRODUCTION

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

2. PRINCIPLES OF OPERATION

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

a. Injection

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

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

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

b. Separation

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

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

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

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

c. Detectors

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

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

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

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

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

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

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

d. Limitations

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

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

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

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

3. SAMPLING CONSIDERATIONS

a. Safety

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

b. Type of sample

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

c. Column Selection

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

(1) Retention time is proportional to column length.

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

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

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

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

4. DATA ACQUISITION AND TREATMENT

a. Types

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

b. Calibration

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

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

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

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

c. Procedure

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

d. Indications

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

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J. SAMPLING AND CHARACTERIZATION OF BIOAEROSOLS‡

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

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

1. INTRODUCTION

a. General

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

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

b. Indoor and Outdoor Bioaerosols

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

c. Viable and Nonviable Bioaerosols

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

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

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

2. PRINCIPLES OF BIOAEROSOL COLLECTION

a. General Principles

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

b. Impaction

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

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

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

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

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

c. Filtration

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

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

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

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

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

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

d. Impingement

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

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

e. Characteristics of Several Bioaerosol Samplers

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

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

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

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

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

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

Where:

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

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

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

✓ = Satisfactory for specified application.

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

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

C = Good for very low to very high concentrations;

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

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

F = For desiccation-resistant bacteria only;

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

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

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

3. SAMPLING CONSIDERATIONS

a. Safety

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

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

b. Environmental Conditions

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

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

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

c. Flow Calibration

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

d. Culture Media

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

(1) Fungi

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

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

(2) Bacteria

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

(3) Thermophilic *Actinomycetes*

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

(4) Additional Media

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

e. Blanks

(1) Laboratory Media Blanks

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

(2) Field Blanks

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

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

a. Sample Preparation

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

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

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

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

b. Enumeration

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

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

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

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

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

(3) Limitations

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

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

c. Identification of Culturable Bioaerosols

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

(1) Classical or General Microbiology

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

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

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

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

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

Fungi are very difficult to classify [Smith 1990].

(2) Clinical and Environmental Microbiology

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

(I) Biochemical Analyses

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

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

(ii) Cellular Fatty Acid Analysis

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

d. Interpretation of Data

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

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

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

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

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

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

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

a. Microscopy

(1) Bright-Field or Light

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

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

(2) Phase Contrast

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

(3) Fluorescence

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

(4) Electron

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

b. Endotoxin Assay

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

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

c. Immunoassays

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

(1) Radioimmunoassays (RIA)

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

(2) Fluorescent Immunoassays (FIA)

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

(3) Enzyme Immunoassays (EIA)

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

d. Gene Probes

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

(1) Nick-translated DNA Probes

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

(2) Synthetic Oligomer DNA Probes

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

(3) Polymerase Chain Reaction (PCR)

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

(4) Restriction Fragment Length Polymorphic (RFLP) Analysis

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

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

6. MANUFACTURERS

Impaction Samplers

Andersen 6-Stage, 2-Stage, and 1-Stage
Graseby Andersen
500 Technology Court
Smyrna, GA 30082-5211
(404) 319-9999
(800) 241-6898

SAS, and Compact SAS
Spiral Biotech, Inc.
7830 Old Georgetown Road
Bethesda, MD 20814
(301) 657-1620

Mattson-Garvin Slit-to-Agar
Barramundi Corporation
P.O. Drawer 4259
Homosassa Springs, FL 32647
(904) 628-0200

Cassella Slit Sampler
BGI Incorporated
58 Guinan Street
Waltham, MA 02154
(617) 891-9380

Reuter Centrifugal Sampler
BIOTEST Diagnostics Corp.
66 Ford Road, Suite 131
Denville, NJ 07834
(201) 625-1300
(800) 522-0090

Allergenco MK-2
Allergenco/Blewstone Press
P.O. Box 8571
Wainwright Station
San Antonio, TX 78208
(210) 822-4116

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26338 Esperanza Drive
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England
0923-773134

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One Alewife Center
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Gelman Sciences Inc.
600 South Wagner Road
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(313) 665-0651

Millipore Corporation
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(617) 275-9200
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Impingement Samplers

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(609) 692-3333

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Rickmansworth, Hertfordshire WD3 1PJ
England
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1155 16th Street, NW
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Buyers' Guide Edition and
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Shelton, CT 06484-0870
(203) 926-9310

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AMMONIA by IC 6016

NH_3 MW: 17.03 CAS: 7664-41-7 RTECS: BO0875000

METHOD: 6016, Issue 1 **EVALUATION: FULL** **Issue 1: 15 May 1996**

OSHA : 50 ppm
NIOSH: 25 ppm; STEL 35 ppm; Group III Pesticide
ACGIH: 25 ppm; STEL 35 ppm
(1 ppm = 0.697 mg/m³ @ NTP)

PROPERTIES: gas; MP -77.7 °C; BP -33.4 °C; VP 888 kPa (8.76 atm) @ 21.1 °C; vapor density 0.6 (air = 1); explosive range 16 to 25% v/v in air

SYNONYMS: none

SAMPLING

SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel) a 0.8-μm MCE prefilter may be used to remove particulate interferences.

FLOW RATE: 0.1 to 0.5 L/min

VOL-MIN: 0.1 L @ 50 ppm
-MAX: 96 L @ 50 ppm [1]

SHIPMENT: routine

SAMPLE STABILITY: at least 35 days @ 5 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 17 to 68 mg/m³ [1] (30-L samples)

BIAS: - 2.4% [1]

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

ACCURACY: ± 14.5%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: ammonium ion (NH_4^+)

EXTRACTION: 10 mL deionized water

INJECTION VOLUME: 50 μL

ELUENT: 48 mM HCl/4 mM DAP-HCl/4 mM L-histidine-HCl; 1 mL/min
alternate: 12 mM HCl/0.25 mM DAP-HCl/ 0.25 mM L-histidine-HCl; 1 mL/min

COLUMNS: HPIC-CS3 cation separator; HPIC-CG3 cation guard; CMMS-1 cation micromembrane suppressor

CONDUCTIVITY SETTING: 30 μS full scale

CALIBRATION: standard solutions of NH_4^+ in deionized water

RANGE: 4 to 100 μg per sample [3]

ESTIMATED LOD: 2 μg per sample [3]

PRECISION ($\hat{S}_r$): 0.038 [2]

APPLICABILITY: The working range is 24 to 98 ppm (17 to 68 mg/m³) for a 30-L sample. This method is applicable to STEL measurements when sampled at ≥0.2 L/min.

INTERFERENCES: Ethanolamines (monoethanolamine, isopropanolamine, and propanolamine) have retention times similar to NH_4^+.
The use of the alternate (weak) eluent will aid in separating these peaks.

OTHER METHODS: This method combines the sampling procedure of methods S347 [4] and 6015 with an ion chromatographic analytical procedure similar to Method 6701 [5] and OSHA Method ID-188 [3].

REAGENTS:

1. Water, deionized, filtered.
2. Sulfuric acid (H_2SO_4), 0.01 N:*
   Add 0.28 mL conc. H_2SO_4 to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
3. Hydrochloric acid (HCl), 1 N:*
   Add 82.5 mL conc. HCl to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
4. 2,3-diaminopropionic acid monohydrochloride (DAP-HCl)
5. L-histidine monohydrochloride monohydrate (L-histidine-HCl)
6. Eluent (48 mM HCl/4 mM DAP-HCl/4 mM L-histidine-HCl): Place 0.560 g DAP-HCl and 0.840 g L-histidine-HCl in a 1-L volumetric flask. Add 48 mL of 1 N HCl, dilute to volume with deionized water. Prepare monthly.
7. Alternate eluent (12 mM HCl/0.25 mM DAP-HCl/0.25 mM L-histidine-HCl): Dilute 252 mL strong eluent and 36 mL 1 N HCl to 4 L with deionized water. Prepare fresh for each use.
8. Tetramethylammonium hydroxide (TMAOH), 25%, (Aldrich Chemical Co. Milwaukee, WI).
9. Regenerant solution: Dilute 57.4 mL of 25% TMAOH to 4 L with deionized water.
10. Ammonia stock solution, 1000 µg/mL as NH_3 (1059 µg/mL as NH_4^+): Dissolve 3.1409 g ammonium chloride in deionized water. Dilute to 1 L.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Prefilter: 37-mm mixed cellulose ester membrane filter, 0.8-µm pore size, stainless steel or porous plastic screen in two piece cassette filter holder.
   b. Sulfuric acid-treated silica gel, glass tube, unsealed and fire-polished, 6.0 cm long, 6-mm OD, 4-mm ID, containing two sections of 20/40 mesh sulfuric acid-treated silica gel (200 mg front/100 mg back) separated and held in place with plugs of silylated glass wool, and capped with plastic caps. Tubes are commercially available.
2. Personal sampling pump, 0.1 to 0.5 L/min, with flexible tubing.
3. Ion Chromatograph with conductivity detector, cation column and guard, and cation micromembrane suppressor (see p 6016-1).
4. Syringes, 10-mL, polyethylene, Luer tip.
5. Centrifuge tubes, 15-mL, graduated, plastic with screw caps.
6. Volumetric flasks, 10-, 50-, 100-mL, and 1-L.
7. Syringe filters, 13-mm, 0.8-µm, membrane filter.
8. Micropipets, disposable tips.
9. Analytical balance (sensitivity to 0.01 mg).

SPECIAL PRECAUTIONS: Concentrated acids are corrosive to skin. Handle acid in a fume hood. Wear protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 0.1 to 96 L.
3. Cap the sampling tubes with plastic (not rubber) caps immediately after sampling.
4. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove caps from sampling tubes. Transfer the front and back sections of sulfuric acid-treated silica gel to separate 15-mL graduated centrifuge tubes.
   NOTE: Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.

6. Add 10 mL of deionized water to each centrifuge tube. Cap and shake vigorously. Allow to stand 45 minutes with occasional shaking. (Desorption is complete in 45 minutes.)
   NOTE: Analyses should be completed within one day after the ammonia is desorbed.
7. Transfer samples to 10-mL syringes fitted with inline syringe filters for manual injection or transfer to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 1 to 110 µg NH_3 per sample (about 0.11 to 12 µg/mL NH_4^+).
   a. Add known aliquots of ammonia stock solution to 0.01 N H_2SO_4 in 10-mL volumetric flasks.
      NOTE: Prepare standards just before use.
   b. Analyze working standards together with samples and blanks (steps 9 through 11).
   c. Prepare calibration graph (peak height vs. µg NH_3).

MEASUREMENT:

9. Set ion chromatograph to conditions given on page 6016-1, according to manufacturer's instructions.
10. Inject 50-µL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
11. Measure peak height.
    NOTE: If peak height exceeds linear calibration range, dilute with 0.01 N H_2SO_4, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

12. Determine the mass, µg, of ammonia 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.
13. Calculate concentration, C, of NH_3 in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method combines the sampling procedure of NIOSH Methods S347 [4] and 6015 with the ion chromatographic analytical procedure of NIOSH Method 6701 [5] and OSHA Method ID-188 [3]. This method will serve as an alternate analytical procedure to the automated spectrophotometric procedure of method 6015. Although the methods from which this method is derived are fully evaluated methods, the combination of the sulfuric acid-treated silica gel sampler and IC analysis has not received a full evaluation as such. During the development of the passive monitor method for ammonia (6701), sulfuric acid-treated silica gel tubes were used as one of the reference methods [5]. The silica gel samples with IC analysis showed good agreement with the other reference methods, bubbler collection with colorimetric analysis using Nessler's Reagent, and bubbler collection with IC analysis.

A storage stability study compared the sulfuric acid-treated silica gel tube and sulfuric acid-treated carbon beads used in OSHA Method ID-188. When stored at room temperature for five days and then refrigerated for 21 days, silica gel samples had a mean recovery of 102 ± 3.8% (n = 8), while carbon beads had a mean recovery of 95 ± 1.6% (n = 8). The samples stored on carbon beads for 35 days showed significantly lower (although still acceptable) recovery compared to samples stored for 14 days: 103 ± 3.8% for silica gel (n = 12), and 108 ± 7.0% for carbon beads (n = 12) [2].

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METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE/QASA

n-BUTYL MERCAPTAN 2525

$CH_3CH_2CH_2CH_2SH$ MW: 90.19 CAS: 109-79-5 RTECS: EK6300000

METHOD: 2525, Issue 2 **EVALUATION: FULL** **Issue 1: 5 May 1989**
Issue 2: 15 May 1996

OSHA: 0.5 ppm
NIOSH: C 0.5 ppm
ACGIH: 0.5 ppm
(1 ppm = 3.69 mg/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: butanethiol; 1-butanethiol; 1-mercaptobutane

SAMPLING

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

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L
-MAX: 4 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

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

BIAS: - 2% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 14.2%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE

ANALYTE: n-butyl mercaptan

DESORPTION: 1 mL acetone; stand 15 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 150 °C
-DETECTOR: 200 °C
-COLUMN: 140 °C

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

CARRIER GAS: N_2, 50 mL/min

CALIBRATION: standard solutions of n-butylmercaptan in acetone

RANGE: 20 to 200 µg per sample [2]

ESTIMATED LOD: 3 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.015 @ 30 to 110 µg per sample [1]

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

INTERFERENCES: None identified.

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

REAGENTS:

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

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

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

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

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range 0.3 to 20 µg/mL.
   a. Add known amounts of calibration stock solution to acetone in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area squared vs. µg n-butyl mercaptan).
9. Determine desorption efficiency (DE) at least once for the batch of Chromosorb 104 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

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

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

MEASUREMENT:

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

CALCULATIONS:

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

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

EVALUATION OF METHOD:

This method was validated over the range 17 to 74 mg/m^3 at 22 °C and 759 mm Hg using a 1.5-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.062 with an average recovery of 0.98. The concentration of n-butyl mercaptan was independently determined from the syringe delivery rate and dilution flow rates. Desorption efficiency was 0.90 in the range 28 to 110 µg per sample. The breakthrough volume (effluent concentration = 5% of influent concentration) was 4.0 L; this was determined by sampling humid air (94% relative humidity), containing 74 mg/m^3 n-butyl mercaptan at 0.023 L/min.

REFERENCES:

[1] NIOSH [1977]. Backup data report for S350, prepared under NIOSH Contract 210-76-0123.
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METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE. Method S350 was originally validated under NIOSH Contract 210-76-0123.

CAPSAICIN and DIHYDROCAPSAICIN

(1) $C_{18}H_{27}NO_3$	MW: 305.40	CAS: 404-86-4	RTECS: RA8530000
(2) $C_{18}H_{29}NO_3$	307.48	19408-84-5	RA5998000

METHOD: 5041, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA: no PELs
NIOSH: no RELs
ACGIH: no TLVs

PROPERTIES: (1) white solid; MP 65 °C; BP 210-220 °C @ 0.01 mm Hg; VP not significant @ 25 °C
(2) white solid; VP not significant @ 25 °C

NAMES & SYNONYMS: (1) capsaicin: *trans*-8-methyl-*N*-vanillyl-6-nonenamide
(2) dihydrocapsaicin: 8-methyl-*N*-vanillylnonanamide

SAMPLING

SAMPLER: FILTER (13-mm glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: (1) 5L @ 0.01 mg/m^3
(2) 7 L @ 0.01 mg/m^3

-MAX: 1000 L

SHIPMENT: ship at 0 °C

SAMPLE STABILITY: at least 26 days @ 5 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, FLUORESCENCE DETECTOR

ANALYTES: capsaicin and dihydrocapsaicin

EXTRACTION: 2 mL acetonitrile; ultrasonic bath, 10 min

INJECTION VOLUME: 25 µL

MOBILE PHASE: 48% acetonitrile/52% water v/v; 1 mL/min

COLUMN: 3.9-mm ID x 15 cm stainless steel packed with 10-µm µ-Bondapak C_{18}

DETECTOR: fluorescence: excitation 281 nm; emission 312 nm

CALIBRATION: standard solutions of capsaicin and dihydrocapsaicin in acetonitrile

RANGE: (1) 0.050 to 100 µg/sample
(2) 0.067 to 100 µg/sample

ESTIMATED LOD: (1) 0.015 µg/sample
(2) 0.02 µg/sample

PRECISION ($\hat{S}_r$): (1) 0.042 @ 0.13 to 17 µg/sample
(2) 0.065 @ 0.11 to 3 µg/sample

APPLICABILITY: This method has been used to analyze samples collected at a pickle and pepper processing plant [1]. Analyte concentrations in sample solutions are not expected to exceed 0.2 µg/mL when samples are collected in this type of environment.

INTERFERENCES: Capsaicin and dihydrocapsaicin exhibit baseline separation at concentrations of 0.2 µg/mL and less. At higher concentrations, baseline separation can be achieved by increasing the water in the mobile phase to about 55%. Nordihydrocapsaicin causes little interference during measurement of capsaicin because its abundance is relatively small in *Capsicum* fruit [3].

OTHER METHODS: HPLC methods for one or both analytes in solution have been published [3-8]. None have been published for air analysis.

REAGENTS:

1. Capsaicin, ≥98% pure.*
2. Dihydrocapsaicin, ≥90% pure.*
3. Water, distilled.
4. Acetonitrile, chromatographic quality.*
5. Capsaicin calibration and recovery stock solution, 0.8 mg/mL: Dissolve 20 mg of capsaicin in acetonitrile to make 25 mL solution. Store at 5 °C. Prepare fresh bimonthly.
6. Dihydrocapsaicin calibration and recovery stock solution, 0.8 mg/mL: Dissolve 20 mg dihydrocapsaicin in acetonitrile to make 25 mL solution. Store at 5 °C. Prepare fresh bimonthly.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter in 2-piece filter holder (Swinnex, Millipore Corp., or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. HPLC, fluorescence detector, ex 281nm, em 312 nm; recorder, integrator, and column (page 5041-1).
4. Vials, 4-mL, with PTFE-lined caps.
5. Graduated cylinder, 1-L, readable to 10 mL.
6. Volumetric flasks, 25- and 10-mL.
7. Syringes: 10-mL; 500-µL, readable to 10 µL; 100-µL, readable to 1 µL; 10 µL, readable to 0.1 µL.
8. Ultrasonic water bath.
9. Film, plastic, flexible, water resistant.
10. Syringe filters, 3-mm PTFE membrane, 0.45-µm pore size, in polypropylene housing.
11. Tweezers.
12. Dust mask.

SPECIAL PRECAUTIONS: Capsaicin and dihydrocapsaicin are toxic, are classified as mutagens, and can destroy certain sensory nerve cells [9,10]. Inhalation of aerosols of these compounds will result in prolonged coughing or sneezing. Exposure by inhalation can take place during weighing operations; thus, a dust mask is recommended. Skin contact will cause a burning sensation. Ingestion can cause intolerable burning and gastrointestinal disorders.

Acetonitrile is toxic and is a fire hazard (flash point = 12.8 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach the sampler to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 7 to 1000 L.
   NOTE: Limit the maximum loading of particulate matter on the filter to approximately 0.5 mg.
4. Seal ends of sampler with plastic film. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Transfer the 13-mm glass fiber filter to a 4-mL vial.
6. Add 2 mL of acetonitrile to the vial and cap securely.
7. Place the sample vial into an ultrasonic bath and agitate for 10 min.
8. Filter the sample solution through a PTFE membrane filter.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range of interest: 0.008 to 10 µg/mL for capsaicin; 0.01 to 10 µg/mL for dihydrocapsaicin.
   a. Prepare working standards from calibration stock solution in acetonitrile.
      NOTE: Working standards may be stored in tightly sealed vials at 5 °C for at least 9 weeks.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graphs for capsaicin and dihydrocapsaicin (peak area or height vs. µg of analyte).

10. Determine recoveries (R) at least once for each lot of glass fiber filters in the calibration range (step 9). Prepare three filters at each of five concentration levels plus three media blanks.
    NOTE: Use separate filters for each analyte unless chromatographic conditions have been modified to permit baseline separation at concentrations >0.2 µg/mL (see APPLICABILITY and INTERFERENCES, Page 5041-1).
    a. Place 13-mm glass fiber filters into 4-mL vials.
    b. With a microliter syringe, fortify each filter with recovery solution.
    c. Allow the uncapped vials to stand overnight at room temperature.
    d. Prepare and analyze with working standards (steps 5 through 8, and steps 12 and 13).
    e. Prepare graph of R vs. µg of analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes for each analyte to ensure that the respective calibration graphs are in control.

MEASUREMENT:

12. Set high performance liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5041-1. Inject 25-µL sample aliquot manually or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with acetonitrile, reanalyze, and apply appropriate dilution factor in calculations.
13. Measure peak area or height for each analyte.

CALCULATIONS:

14. Determine the mass, µg (corrected for R), of each analyte found on the filter (W) and the average media blank (B).
15. Calculate the concentration, C, of each analyte in the air volume sampled (L):

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

EVALUATION OF METHOD:

Average recoveries of capsaicin after fortification of 13-mm glass fiber filters with 0.13-, 0.28-, 0.58-, 1.1-, 2.9-, and 17-µg quantities of the compound were 1.02, 0.95, 0.98, 0.99, 1.04, and 1.00, respectively; precision ($\hat{S}$) was 0.042 (35 samples, pooled). After 28 days storage at 5 °C, the average recovery of 0.99-µg quantities of capsaicin from glass fiber filters was 0.96; S_r was 0.023 (6 samples). In addition, the average recovery of 0.99-µg quantities of capsaicin from glass fiber filters after 28 days storage at room temperature was 0.92; S_r was 0.052 (6 samples). These data for stored samples suggest that recovery and precision of measurement are improved when samples are stored at the lower temperature. Empty glass vials were fortified with 0.90-µg quantities of capsaicin and stored uncapped for three days at room temperature. The average recovery from the vials was 0.98; thus, the vapor pressure of capsaicin at room temperature is insignificant.

A standard solution of capsaicin in acetonitrile at a concentration of 0.5 µg/mL was found to be stable during 9 weeks storage at 5 °C. The container was sealed tightly to prevent evaporation of solvent during refrigeration.

Average recoveries of dihydrocapsaicin after fortification of 13-mm glass fiber filters with 0.11-, 0.28-, 1.1-, and 3.0-µg quantities of the compound were 0.94, 1.03, 0.99, and 0.93, respectively; precision ($\hat{S}_r$) was 0.065 (23 samples, pooled). After 26 days storage at 5 °C, the average recovery from glass fiber filters fortified with 0.88 µg of dihydrocapsaicin was 0.88; S_r was 0.047 (6 samples).

This method was not evaluated with controlled atmospheres in a laboratory. However, the method was employed for measurement of capsaicin and dihydrocapsaicin in air at a pickle pepper processing plant [1,11]. A curious phenomenon was the fact that in each of many of the samples the ratio of capsaicin to dihydrocapsaicin was less than 1:1. Generally, capsaicin is the capsaicinoid that occurs in *Capsicum* fruit in the greatest abundance [3].

REFERENCES:

[1] Tucker SP [in preparation]. Determination of capsaicin and dihydrocapsaicin in air in a pickle and pepper processing plant. Cincinnati, OH: National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering (DPSE).
[2] Tucker SP [1995]. Backup data report for method 5041, Capsaicin and Dihydrocapsaicin. National Institute for Occupational Safety and Health, DPSE, Unpublished report.
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[11] Tucker SP [1994]. Analytical report for Sequence #8015, DPSE/MRSB. Cincinnati, OH: National Institute for Occupational Safety and Health. Unpublished report.

METHOD WRITTEN BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE

CARBON MONOXIDE 6604

CO MW: 28.00 CAS: 630-08-0 RTECS: FG3500000

METHOD: 6604, Issue 1 **EVALUATION: FULL** **Issue 1: 15 May 1996**

OSHA: 50 ppm
NIOSH: 35 ppm; C 200 ppm
ACGIH: 25 ppm
(1 ppm = 1.14 mg/m^3)

PROPERTIES: gas; BP -192 °C; MP -207 °C; vapor density (air = 1) 0.967; flammable (explosive) limits in air 12.5 to 74.2%

SYNONYMS: monoxide; carbon oxide; carbonic oxide; flue gas

SAMPLING

SAMPLER: PORTABLE DIRECT-READING CO MONITOR

VOL-MIN: instrument dependent
-MAX: none

SHIPMENT: routine shipment of instrumentation

SAMPLE STABILITY: at least 7 days @ 25 °C [1] (aluminized air bags)

BLANKS: fresh air or compressed CO-free air from cylinder

ACCURACY

RANGE STUDIED: 0 to 200 ppm

BIAS: - 1.7% [2]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.022 [2]

ACCURACY: ± 6.0%

MEASUREMENT

TECHNIQUE: ELECTROCHEMICAL SENSOR

ANALYTE: carbon monoxide (CO)

CALIBRATION:
- ZERO: CO-free air
-SPAN: standard cylinders of span gas in the desired range

RANGE: 0 to 200 ppm

ESTIMATED LOD: 1 ppm

PRECISION ($\bar{S}_r$): 0.035 @ 20 ppm
0.012 @ 50 ppm
0.008 @ 100 ppm [2]

APPLICABILITY: Portable, direct-reading carbon monoxide monitors are applicable to any work environment for personal or area monitoring.

INTERFERENCES: Several gaseous pollutants (e.g., NO_2, SO_2) may cause an interference at levels over 5 ppm. If these or other pollutants are known or suspected to be present, use a monitor with a chemical interference scrubber over the sensor. Unknown pollutants may require further experimentation to determine their effect on the sensor. As tested, SO_2 (5 ppm), CO_2 (5000 ppm), methylene chloride (500 ppm), diesel fuel (6 µL/L, about 0.3 ppm benzene), and gasoline vapor (1 µL/L, about 1 ppm benzene) had no impact on most monitor readings [2]. Some monitors are equipped with a chemical interference scrubber while others offer this as an option.

OTHER METHODS: Bag samples may be collected in aluminized bags (2-L or larger) and analyzed later by placing the calibration cap over the sensor and pumping the sample across the sensor at a nominal rate of 0.250 L/min with a personal sampling pump.

REAGENTS:

1. CO*calibration gas, 20 to 50 ppm, compressed gas cylinder, appropriate pressure regulator, and other items as recommended by manufacturer for field check of monitor response.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Carbon monoxide monitor: Envirocheck I single sensor CO Monitor (Quest Technologies); CO262 or STX70 (Industrial Scientific); MiniCO (MSA); or other electrochemical CO monitor with equivalent performance specifications.
2. Personal sampling pump, 0.250 L/min, with inlet and outlet, used for bag filling and sample analysis when off-site analysis is needed.
3. Air bags, aluminized, 2-L, or other appropriate sizes (optional).
4. Replacement batteries or battery recharger, as appropriate for monitor.

SPECIAL PRECAUTIONS: Carbon monoxide is a highly flammable, dangerous fire and explosive risk, and is toxic by inhalation. Shipments of compressed calibration gases must comply with 49 CFR 1992 regulations.

SAMPLING AND MEASUREMENT:

1. Zero monitor with CO-free air at the same temperature and relative humidity as the work environment, if possible.
   NOTE: Monitors are more sensitive to temperature variations than to humidity variations. Most monitors have temperature compensating circuitry.
2. For personal monitoring, locate the monitor as near the worker's breathing zone as possible.
3. For area monitoring, locate monitor in an area with good air circulation about 60 to 70 inches above the floor.
   NOTE: Make sure the sensor is not obstructed in either application.

CALIBRATION AND QUALITY CONTROL:

4. Calibrate with a standard calibration mixture of CO in air from a pressurized cylinder at the CO level recommended by the monitor manufacturer (Normally, 20 to 50 ppm CO). The monitor should be calibrated at the temperature and relative humidity as near as possible to that of the work environment in which it will be used.
5. Check the calibration daily and recalibrate whenever the monitor reading varies from the span gas by 5% or more, or as the manufacturer recommends.

CALCULATIONS:

6. Read concentration directly from the monitor display.

   Some monitors (data logger models) will maintain a continuous record of the data as it is accumulated and will calculate the Average, TWA, Peak, etc. concentrations. These data may be read from the display at any time. Some monitors will also store this information for downloading to a computer or printer at the end of the monitoring period. Other monitors only display the current reading, requiring the operator to manually record the data. All monitor models are equipped with alarms that will warn

the user (audibly, visually or both) whenever the concentration of CO exceeds the preset level of the alarm. Many are equipped with two-level alarms [3].

EVALUATION OF METHOD:

The performance of six direct-reading carbon monoxide monitors was evaluated over a period of 12 months at CO concentrations up to 200 ppm and a range of ambient temperatures and relative humidities. Most of the tests were conducted at or near the PEL. For mean recovery studies, six different monitors were used and readings were taken approximately 1 h apart. Recovery at 20 ppm was 105% (n = 42); at 50 ppm, 99.6% (n = 36); and at 100 ppm, 99.9% (n = 30). Thus, the overall mean bias was calculated at - 1.7%. The precision ($\tilde{S}_r$) at 20 ppm was 0.035 (35 readings from 5 monitors over a 7-h period). At 50 ppm, $\tilde{S}_r$ was 0.012 (30 readings from 5 monitors over a 6-h period), and at 100 ppm, $\tilde{S}_r$ was 0.008 (36 readings from 6 monitors over a 6-h period). Tests also were conducted to determine response time, zero and span drift, alarm decibel level, battery life, life of the sensors, as well as the effects of selected interferences (gases, vapors, and RF) and the effects of handling and transporting to remote sites.

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[2] Woodfin WJ, Woebkenberg ML [in preparation]. An evaluation of portable direct-reading carbon monoxide monitors.
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METHOD WRITTEN BY:

W. James Woodfin, NIOSH, DPSE, MRB

CHROMIUM, Hexavalent, in Settled Dust Samples 9101

Cr(VI) MW: 52.00 CAS: 18540-29-9 RTECS: GB6262000

METHOD: 9101, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

PURPOSE: Estimation of soluble hexavalent chromium content of settled dust.

LIMIT OF DETECTION: **1 µg Cr(VI)** per sample

FIELD EQUIPMENT:
1. Chromate (Diphenylcarbazide reagent) test kit (Chemetrics Chromate Kit, or equivalent)
2. Sulfuric acid, 20% w/v (included in test kit)
3. Extraction solution, 2% NaOH/3% Na_2CO_3 in deionized water
4. Deionized water
5. Centrifuge tubes, 15-mL, graduated, clear plastic with screw-caps, disposable
6. Spatula, ~0.1 cm^3 capacity
7. pH paper

PROCEDURE:
1. Place 1 spatula full of dust (approximately 0.1 cm^3; the size of a small pea) to be tested in a 15-mL clear plastic centrifuge tube. Add extraction solution up to the 2-mL mark. Cap the tube and shake vigorously.

2. Allow the tube to stand for 10 minutes, or longer, with occasional shaking.
   NOTE: Gently heating the tube in hot water will increase the sensitivity of the test.

3. Uncap the centrifuge tube and add deionized water to the 7-mL mark. Mix and allow the residue to settle.

4. Decant or pipet approximately 3 mL of the supernatant liquid into a second tube.
   NOTE: The sample may be filtered, if excessively turbid.

5. Add 9 drops of 20% sulfuric acid (3 drops /mL of decanted liquid), cap the tube, and invert to mix the contents.

6. Check the pH of the liquid with pH paper. If necessary, add 20% sulfuric acid dropwise to bring to pH <1.

7. Follow the instructions for color development.

NOTE: For more accurate determination of total hexavalent chromium in the dust, send a sample to the laboratory for analysis by Method 7600 or 7604.

METHOD WRITTEN BY: Mark B. Millson, MRSB/DPSE, and Peter M. Eller, Ph.D., QASA/DPSE

ELEMENTAL CARBON (DIESEL EXHAUST) 5040

C MW: 12.01 CAS: none RTECS: none

METHOD: 5040, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA :
NIOSH: see APPENDIX A
ACGIH:

PROPERTIES: nonvolatile solid; MP >350 °C

SYNONYMS (related terms): soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (quartz fiber, 37-mm; size-selective impactor may be required, see INTERFERENCES)	**TECHNIQUE:**	EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	elemental carbon (EC)
VOL-MIN:	106 L @ 40 $\mu g/m^3$	**FILTER PUNCH SIZE:**	1.54 cm^2
-MAX:	4300 L (for filter load ~ 20 $\mu g/cm^2$)	**CALIBRATION:**	methane injection [1]
SHIPMENT:	routine	**RANGE:**	0.76 to 54 μg per filter portion
SAMPLE STABILITY:	stable	**ESTIMATED LOD:**	0.2 μg per filter portion
BLANKS:	2 to 10 field blanks per set	**PRECISION ($\hat{S}_r$):**	0.10 @ 1 μg C, 0.01 @ 10 to 72 μg C
ACCURACY			
RANGE STUDIED:	4.0 mg/m^3 (60-L sample) [1]		
BIAS:	none [1]		
OVERALL PRECISION ($\hat{S}_{rT}$):	see EVALUATION OF METHOD		
ACCURACY:	see EVALUATION OF METHOD		

APPLICABILITY: The working range is 4.4 to 312 $\mu g/m^3$ with an LOD of ~1.3 $\mu g/m^3$ for a 960-L air sample collected on a 37-mm filter with a 1.54 cm^2 punch from the sample filter. If a lower LOD is desired, a larger sample volume and 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.3 $\mu g/m^3$) [1]. The split between organic-based carbon (OC) and EC may be affected at higher EC loadings (e.g., >30 $\mu g/cm^2$ of filter), depending on type and amount of OC present. If pyrolysis correction is not required, an upper limit of ~800 $\mu g/m^3$ (90 $\mu g/cm^2$) can be determined, but post-analysis designation of OC-EC split may be necessary [1].

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolytic correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Carbonate and cigarette smoke do not interfere. Various EC sources (diesel engines, carbon black, coal dust, and humic acid) may be present [1]. For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC are described in the literature [4].

REAGENTS:

1. Aqueous organic carbon solutions (e.g., sucrose), 0.10 to 2.4 mg C per mL solution.
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

EQUIPMENT:

1. Sampler: Quartz fiber filter, precleaned (clean in low temperature asher 2 to 3 h, or muffle furnace at ~ 800 °C), 37-mm, in a 3-piece, 37-mm cassette with support pad (stainless steel or cellulose).
2. Personal sampling pump, 1 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer, or other analyzer capable of EC speciation (see APPENDIX B).
4. Punch (e.g., cork borer) for removal of filter sample portion.
   NOTE: Portion ≥ 0.5 cm^2 with diameter or width of $\leq$ 1 cm is recommended.
5. Syringe, 10-µL

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Sampler should be used in open-face configuration.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette.
3. Sample at an accurately known flow rate between 1 and 4 L/min.
4. After sampling, replace top piece of cassette and pack securely for shipment to laboratory.
   NOTE: If the EC in the sample is more difficult to oxidize (e.g., graphite) than typical black carbon (e.g., soot), notify the laboratory of this fact.

SAMPLE PREPARATION:

5. Use punch to cut out a representative portion of the sample filter for analysis. Take care not to disturb deposited material and avoid hand contact with sample.

CALIBRATION AND QUALITY CONTROL:

6. Perform CH_4 calibration injection at end of each sample analysis.
7. If a particular sample filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition. Analyze at least one duplicate and others as required to replicate 10% of the samples for sets of up to 50 samples and 5% of the samples over 50.
   NOTE: Precision in duplicate analyses of a filter is usually better than 2%.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. Using a microliter syringe, apply known volume of OC standard solution directly onto portion taken (step 5) from a precleaned blank filter.
   b.. Allow H_2O to evaporate and analyze with samples and blanks (steps 10 and 11).
9. Determine instrument blank (results of analysis with no sample present) for each sample set.

MEASUREMENT:

10. Set analyzer according to manufacturer's recommendations (see APPENDIX B). Place sample portion into sample oven.
    NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require increased analysis time to ensure that all EC in the sample is quantified.
11. Determine EC (and OC) mass, μg, as provided by analyzer and divide by sample punch area, cm^2, to report result in terms of μg C per cm^2 of filter.

CALCULATIONS:

12. Multiply the reported EC value by filter deposit area, cm^2, (typically 8.55 cm^2 for a 37-mm filter) to calculate total mass, μg, of EC on each sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b). (OC masses may be calculated similarly.)
13. Calculate EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} = \frac{W_{EC} - W_b}{V}, \ mg/m^3$$

EVALUATION OF METHOD:

Currently, a suitable EC standard reference material is not available for verification of the accuracy of the method in the determination of EC. For this reason, only the accuracy of the method in the analysis of various OC standards and carbonaceous dusts for total carbon could be examined [1]. A commercial instrument was used for method evaluation [5]. No discernable differences in the responses of five different compounds were noted. Linear regression of the data for all five compounds gave a slope and correlation coefficient near unity [**m** = 0.99 (± 0.01), r^2 = 0.999, n = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition, results (total carbon) of analysis of different carbonaceous materials were in good agreement with those reported by two other independent laboratories. These findings indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate carbon determination.

To calculate the estimated LOD of the method (i.e., ≈ 0.24 μg C or 0.15 μg C/cm^2), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82 μg C (or from 0.15 to 1.83 μg C per cm^2 of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., μg C reported vs. actual) were then used to calculate the LOD as 3 σ_y/**m** (where σ_y is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = $3\sigma_{blank}$, which gives a value of ≈ 0.22 μg C. The mean (n = 40) instrumental blank was ≈ 0.02 (± 0.07) μg C.

Because the split between EC and OC is method-dependent [1,4], and no suitable EC standard exists for assessment of a particular method's accuracy, various methods can be compared on a relative basis only. At present, the thermal-optical method is considered unbiased (i.e., it is the reference method), and the overall precision reflects the method accuracy. The S_r of the mean EC concentration (4 mg/m^3) found using fourteen samplers (two each of seven types) for collection of diesel exhaust was 5.6%. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n = 14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [6] is fulfilled. The amount of EC collected (240 μg per sample) would be equivalent to sampling an EC level of 250 $\mu g/m^3$ for 8 h at 2 L/min.

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Application of the method for monitoring exposures to diesel particulate matter in the mining industry may require use of a size-selective sampling strategy in some situations [11]. In coal mines, a specialized impactor [2,3] with a sub-μm cutpoint is required to minimize the contribution of coal-source EC [2].

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METHOD WRITTEN BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE.

APPENDIX A.

Diesel exhaust has been classified by IARC as a probable human carcinogen [8]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced[9,10]. The American Conference of Governmental Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m^3 for diesel particulate (see Notice of Intended Changes for 1995-1996) [12]. The TLV applies to submicrometer particulate matter, which includes the solid carbon particle core and particulate-adsorbed components. A submicrometer size fraction was selected so that interference of other larger dusts is minimized. If other submicrometer particulate (e.g., cigarette smoke, fumes, oil mists) is present, it will interfere in the gravimetric determination of diesel particulate.

APPENDIX B. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION:

In the thermal-optical analysis of carbonaceous aerosols, speciation of various carbon types (organic, carbonate, and elemental) is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below. The instrument is a modified version of a design previously described in the literature [11]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). He-Ne laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850 °C are employed during the analysis, quartz-fiber filters are required for sample collection. A punch from the sample filter is taken for analysis, and organic carbon (OC) and elemental carbon are reported in terms of $\mu g/cm^2$ of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. At the end of the analysis (after the EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate carbon (if present) are evolved in an inert helium atmosphere as the temperature is raised (stepped) to about 850 °C. Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2 (at 950 °C), CO_2 is reduced to CH_4 in a Ni/firebrick methanator (at 450 °C), and CH_4 is quantified by an FID. In the second stage of the analysis, the oven temperature is reduced, an oxygen-helium mix (2% O_2 in He) is introduced into the sample oven, and the oven temperature is again raised to about 850 °C. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs. The point at which the filter transmittance reaches its initial value is defined as the "split" between EC and OC. Carbon evolved prior to the split is considered OC (or carbonate), and carbon volatilized after the split (excluding that from the CH_4 standard) is considered elemental. The presence of carbonate can be verified through analysis of a second portion (punch) of the filter after its exposure to HCl vapor. In the second analysis, the absence of the suspect peak is indicative of carbonate carbon in the original sample.

Currently, only one commercial laboratory (Sunset Laboratory) performs thermal-optical analyses. To support the new method, a collaborative effort between NIOSH researchers and the instrument's developer is underway. During 1996, a thermal-optical instrument will be constructed and evaluated. This effort will assist in the transfer of this technology to other interested parties.

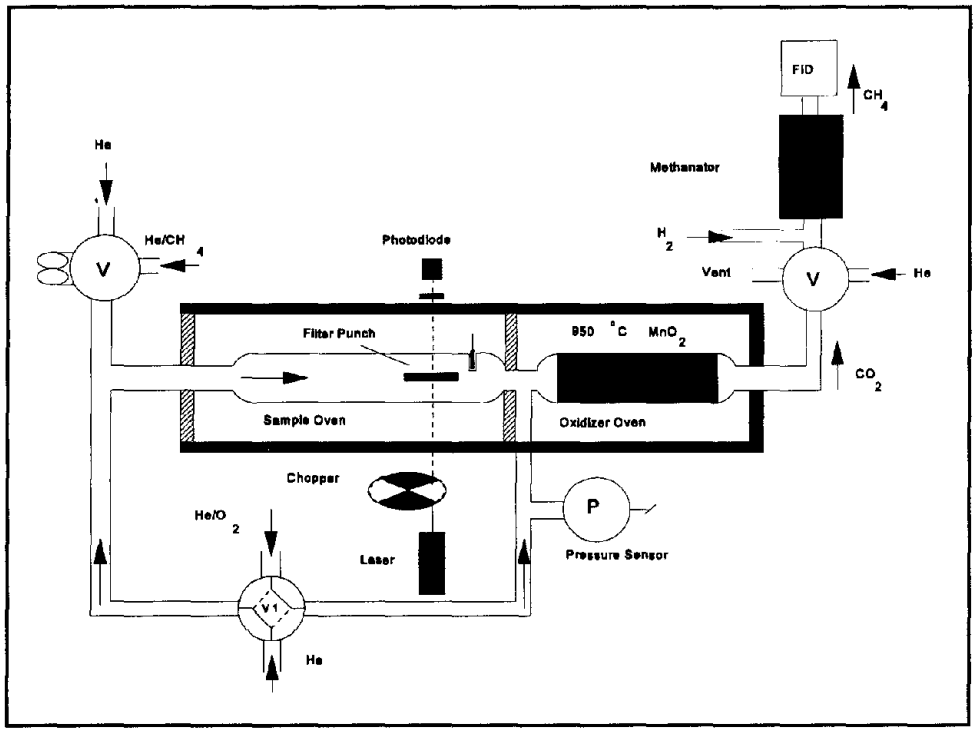

Figure 1. Schematic of Thermal-Optical Analyzer.

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

METHOD: 5523, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA: No PEL
NIOSH: No REL
ACGIH: C 50 ppm (ethylene glycol)
(1 ppm = 2.54 mg/m³ @ NTP)

PROPERTIES: See Table 1

NAMES & SYNONYMS: (1) ethylene glycol: 1,2-ethanediol; (2) propylene glycol: 1,2-propanediol
(3) 1,3-butylene glycol: 1,3-butanediol (4) diethylene glycol: 2-hydroxyethyl ether, 2,2'-oxydiethanol

SAMPLING

SAMPLER: XAD-7 OVS tube (glass fiber filter, 13-mm; XAD-7, 200mg/100mg)

FLOW RATE: 0.5 to 2 L/min

VOL-MIN: 5 L
-MAX: 60 L

SHIPMENT: pack in dry ice for shipment

SAMPLE STABILITY: 28 days @ 5 °C [1]
ethylene glycol 14 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: compounds above

DESORPTION: 2 mL methanol; ultrasonicate 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 40 °C, 8 °C/min to 230 °C

CARRIER GAS: He_2 @ 30 mL/min

COLUMN: Rtx-35 fused silica capillary, 30 m, 0.53-mm ID, 3-µm film

CALIBRATION: solutions of glycols in methanol

RANGE: 15 to 800 µg/sample

ESTIMATED LOD: see Table 2

PRECISION ($\hat{S}_r$): 0.04 to 0.09 [1]

APPLICABILITY: Under the GC parameters given in the method, the glycols listed above are baseline separated and can be identified based on retention time and quantified. Hexylene glycol can be determined by this method; however, no sampling or analytical evaluation has been conducted.

INTERFERENCES: No specific interferences were identified. The method yields baseline separation for all analytes.

OTHER METHODS: This method replaces NMAM 5500 [2], which was found deficient in the collection of ethylene glycol in aerosol form. Also ethylene glycol was not separated from propylene glycol by the chromatography.

REAGENTS:

1. Ethylene glycol, reagent grade.*
2. Propylene glycol, reagent grade.*
3. 1,3-Butylene glycol, reagent grade.*
4. Diethylene glycol, reagent grade.*
5. Triethylene glycol, reagent grade.*
6. Tetraethylene glycol, reagent grade.*
7. Methanol, chromatographic grade.*
8. Calibration stock solution, 10 mg/mL: Weigh aliquots of each glycol and dissolve in methanol.
9. Helium, purified.
10. Hydrogen, prepurified.
11. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: XAD-7 OVS tube, 13-mm OD, containing two sections of XAD-7 (200 mg front/100 mg back section) separated by polyurethane foam plug. A glass fiber filter plug precedes the front section and a polyurethane foam plug follows the back section. Tubes are commercially available (SKC, Inc., #226-57).
2. Personal sampling pump, 0.5 to 2 mL/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (page 5523-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Vials, 4 mL, with screw caps.
7. Syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.

SPECIAL PRECAUTIONS: Inhalation of glycol mists causes respiratory irritation, shortness of breath, and coughing. Methanol is flammable and a dangerous fire risk. Work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove front and rear caps from the tube immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 5 to 60 L.
4. Cap the samplers and pack securely in dry ice for shipment.

SAMPLE PREPARATION:

5. Place front sorbent section and glass fiber filter in a 4-mL screw cap vial. Place backup sorbent section in a separate vial. Discard foam plugs.
6. Add 2 mL of methanol to each vial and cap.
7. Place vials in an ultrasonic bath for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to methanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. µg glycol).
9. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 8).
   a. Prepare three samplers at each of six levels plus three media blanks.

b. Inject a known amount of calibration stock solution directly onto the filter of OVS tubes. Draw air through the sampler at 1 L/min for 60 min.
c. Cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg analyte recovered.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5523-1. Inject 1-µL sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

The method was evaluated for six glycols (ethylene, propylene, 1,3-butylene, diethylene, triethylene, and tetraethylene). Desorption efficiency (DE) was determined by spiking known amounts of each glycol in methanol solution onto the glass fiber filter plug of the XAD-7 OVS tubes, drawing air through the spiked tubes at 1 L/min for 60 min, and analyzing. Recovery data along with LODs and LOQs for each analyte are listed in Table 2. When stored at 5 °C, ethylene glycol samples on XAD-7 OVS tubes were stable for 14 days, and the other glycols were stable up to 28 days. Glycol aerosols were generated at three concentration levels (6 samples per concentration) from a ROSCO™ Model 1500 Fog Machine. Precision [as calculated from the pooled relative standard deviation ($\hat{S}_r$)] and mean bias for the glycols are as follows:

Analyte	Range Studied (µg/sample)	Precision ($\hat{S}_r$)	Bias
Ethylene glycol	33 to 218	0.043	-15%
Propylene glycol	26 to 187	0.062	-3.2%
1,3-butylene glycol	34 to 178	0.054	-0.5%
Diethylene glycol	68 to 219	0.047	-0.2%
Triethylene glycol	33 to 201	0.075	-4.0%
Tetraethylene glycol (2 levels)	32 to 197	0.035	+20%

The low recovery for ethylene glycol possibly may be attributed to increased volitility when sampled at 1 L/min [1]. Although hexylene glycol is separated by the chromatographic conditions given in the method, no evaluation of sampling or analytical parameters was done for this compound.

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METHOD WRITTEN BY:

Stephanie M. Pendergrass, MRSB, DPSE

TABLE 1. GLYCOLS GENERAL INFORMATION

Analyte	Formula	MW	CAS #	RTECS #	Properties
Ethylene glycol	$C_2H_6O_2$	62.07	107-21-1	KW2975000	liquid; BP 197.2 °C; FP -13 °C; d 1.113 g/mL @ 20 °C; n_D 1.4310; vp 0.007 kPa (0.05 mm Hg) @ 20 °C; explosive limits 3.2 to 15.3% v/v in air
Propylene glycol	$C_3H_8O_2$	76.10	57-55-6	TY2000000	liquid; BP 188 °C; FP -60 °C ; d 1.038 g/mL @ 20 °C; n_D 1.4320; vp 0.009 kPa (0.07 mm Hg) @ 20 °C; explosive limits 2.6 to 12.5% v/v in air
1,3-Butylene glycol	$C_4H_{10}O_2$	90.12	107-88-0	EK0440000	liquid; BP 207.5 °C; d 1.0059 g/mL @ 20 °C; n_D 1.4400; vp 0.06 mm Hg @ 20 °C
Diethylene glycol	$C_4H_{10}O_3$	106.12	111-46-6	ID5950000	liquid; BP 245 °C; FP -6.5 °C; d 1.118 g/mL @ 20 °C; n_D 1.4460 @ 25 °C; vp <0.01 mm Hg @ 20 °C; explosive limits 3 to 7% v/v in air
Triethylene glycol	$C_6H_{14}O_4$	150.17	112-27-6	YE4550000	liquid; BP 285 °C; FP -5 °C; d 1.125 g/mL @ 20 °C; n_D 1.4550; vp <0.001 mm Hg @ 20 °C; explosive limits 0.9 to 9.2% v/v in air
Tetraethylene glycol	$C_8H_{18}O_5$	194.23	112-60-7	XC2100000	liquid; BP 327.3 °C; FP -4 °C; d 1.125 g/mL @ 20 °C; n_D 1.4577; vp >0.001 mm Hg @ 20 °C

TABLE 2. GLYCOL RECOVERY DATA

Analyte	LOD (µg/sample)	LOQ (µg/sample)	Desorption Efficiency Spikes[a]		$\hat{S}_r$[b]
			100 µg (% Recovery)	200 µg (% Recovery)	
Ethylene glycol	7	22	93.4	101	0.059
Propylene glycol	6	13	83.4	92.5	0.064
1,3-Butylene glycol	6	12	98.8	102	0.072
Diethylene glycol	16	48	94.6	114	0.041
Triethylene glycol	14	42	85.3	98.7	0.043
Tetraethylene glycol	14	42	111	141	0.092

[a] n = 6 for each spiking level
[b] Pooled Relative Standard Deviation

2,4-TDI:	$CH_3C_6H_3(NCO)_2$	MW: 174.16	CAS: 584-84-9	RTECS:	CZ6300000
2,6-TDI:	$CH_3C_6H_3(NCO)_2$	174.16	91-08-7		CZ6310000
MDI:	$CH_2(C_6H_4NCO)_2$	250.26	101-68-8		NQ9350000
HDI:	$OCN(CH_2)_6NCO$	168.20	822-06-0		MO1740000

METHOD: 5522, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

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

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

SAMPLER: IMPINGER (tryptamine/DMSO; 20 mL)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 15 L @ 35 μg TDI / m^3
-MAX: 360 L

SHIPMENT: ship in screw cap vial

SAMPLE STABILITY: at least 28 days in dark @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

BULK: isocyanate-based oligomers, 1 to 2 mL

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, FLUORESCENCE DETECTOR

ANALYTE: tryptamine derivatives of isocyanates

INJECTION VOLUME: 25 μL

MOBILE PHASE: acetonitrile (40 to 50%)/0.6% sodium acetate buffer (60 to 50%); 1 mL/min

COLUMN: 3.9-cm ID x 150 mm stainless steel packed with 10-μm μ-Bondapak C_{18}

DETECTOR: fluorescence: ex 275 nm; em 320 nm (electrochemical, +0.80V - optional)

CALIBRATION: tryptamine derivatives in sampling medium

RANGE:
2,4-TDI: 0.3 to 14.0 μg/sample
2,6-TDI: 0.6 to 14.0 μg/sample
MDI: 1.0 to 10.0 μg/sample
HDI: 0.6 to 20.0 μg/sample [1]

ESTIMATED LOD:
2,4-TDI: 0.1 μg/sample
2,6-TDI: 0.2 μg/sample
MDI: 0.3 μg/sample
HDI: 0.2 μg/sample [1]

PRECISION ($\bar{S}_r$):
2,4-TDI: 0.059 MDI: 0.029
2,6-TDI: 0.062 HDI: 0.045 [1]

APPLICABILITY: The working range for TDI is 10 to 250 $\mu g/m^3$ for a 50-L air sample. This method determines the air concentration of monomers and estimates the concentration of oligomers of specific diisocyanates. It is applicable to vapors and aerosols, such as those produced in a spray-painting operation. The method is not applicable to mixtures of different isocyanates, nor to condensation aerosols from inefficient collection by impingers.
NOTE: This method should be used for area sampling only because of the potential exposure hazard from DMSO solutions.

INTERFERENCES: Any substance which elutes with the tryptamine derivatives and fluoresces will interfere with the analysis, e.g., some aromatic diamines. Mobile phase conditions can be adjusted to separate most co-eluting peaks.

OTHER METHODS: This method is a modification of a method developed by the Occupational Health Laboratory, Ontario Ministry of Labour [2]. NIOSH Method 5521 is an alternate method for the determination of monomers of 2,4-TDI, 2,6-TDI, MDI, and HDI.

REAGENTS:

1. Water, deionized, distilled.
2. Acetonitrile, HPLC grade.
3. Dimethyl sulfoxide (DMSO), HPLC grade.*
4. Sodium acetate trihydrate.
5. Glacial acetic acid, reagent grade.
6. Toluene, HPLC grade.
7. *n*-Propanol, reagent grade.
8. Heptane, reagent grade.
9. Buffer solution: Dissolve 20.4 g sodium acetate trihydrate in 2 L distilled-deionized water. Add glacial acetic acid to pH 5.5.
10. Mobile phase, acetonitrile and buffer solution.
11. Sampling medium, 450 µg/mL,
    (a) For sampling in ambient temperatures >60 °F: tryptamine, 99+% pure, in DMSO;
    (b) For ambient temperatures <60 °F: 80/20 (v/v) DMSO/ acetonitrile containing tryptamine, 99+% pure.
    NOTE: Recrystallize tryptamine in acetonitrile before use. (Stable up to 6 mo. in the dark at ambient temperature.)
12. Tryptamine derivatives of isocyanates* (See APPENDIX).
13. Helium. prepurified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Midget impinger containing 20 mL sampling medium.
2. Personal sampling pump, 1 to 2 L/min, with flexible tubing.
3. HPLC, fluorescence detector, ex 275 nm, em 320 nm; integrator and column (page 5522-1). (Electrochemical detector optional for confirmation of fluorescent peaks.)
4. Vials, 20- and 40-mL, scintillation, with PTFE-lined caps.
5. Pipets, 20-mL.
6. Cylinders, graduated, 25-mL.
7. Syringes, 25-µL, or fixed sample loop.
8. Volumetric flasks, 10-mL.
9. Fritted glass funnel.
10. Filtering flasks.

SPECIAL PRECAUTIONS: Isocyanates are known respiratory irritants. Prepare standards and derivatives in a fume hood. DMSO is readily absorbed into the skin. Wear neoprene latex gloves when handling the solvent, sampling media, and field samples [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 20 mL sampling medium to an impinger, and connect to sampling pump with flexible tubing.
   NOTE: Prepare field blank samples by transferring 20 mL sampling medium to 20-mL vials.
3. Sample at an accurately known flow rate between 1 and 2 L/min for a total sample size of 15 to 360 L.
4. Transfer the sample solution to a 40-mL vial for shipment. Secure screw cap with sealing band.
5. Obtain a bulk sample (1 to 2 mL) and the material safety data sheet for any isocyanate-based oligomer used at the worksite.

SAMPLE PREPARATION:

6. Measure the final volume of the sample solution.
7. Transfer an aliquot of each sample to a HPLC autosampler vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards in the range of interest.
   a. Prepare working standards containing 0.01 to 10.0 µg/mL of the appropriate monomeric tryptamine derivative in the sampling medium.

b. Analyze together with samples, controls, and blanks (steps 10 through 12).
c. Prepare calibration graph (response vs. μg per mL monomeric diisocyanate-tryptamine derivative).

9. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

10. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5522-1. Inject 25-μL sample aliquot with a syringe, a fixed volume sample loop, or an autosampler.
11. Measure fluorescent response for all peaks in the chromatogram.
    NOTE: If peak response is above the linear range of the working standards, dilute with sampling medium, reanalyze, and apply the appropriate dilution factors in the calculations.
12. To investigate any intrinsic fluorescence in the bulk sample, add an aliquot of the bulk sample to 100% DMSO containing no tryptamine reagent and run a chromatogram.
    NOTE: If the bulk sample is not soluble in DMSO, prepare a stock solution in an alternative solvent such as dichloromethane. Add aliquots of the stock solution to DMSO.

CALCULATIONS:

13. Determine solution concentration (μg/mL) of each monomer derivative in the sample, C_s, and average media blank, W_b, from calibration graph (step 8.c.). Then sum the responses of all other peaks in the chromatogram, read solution concentration, C_s (μg/mL), from calibration graph, and report as oligomer diisocyanate-tryptamine derivative.
    NOTE: Report the results for each monomer separately and the isocyanate-based oligomers as a group.
14. Using the solution volumes (mL) of the samples, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of each monomer and oligomer in the volume of air sampled, V (L), applying the ratio of molecular weight of diisocyanate, MW_{DI} (see Table 1), to the molecular weight of diisocyanate-tryptamine derivative, MW_{DIT} (see APPENDIX):

$$C = \frac{(C_s V_s - C_b V_b)(MW_{DI} / MW_{DIT})}{V}, \ mg / m^3$$

EVALUATION OF METHOD:

During method development, the performance of the fluorescence detector was verified through the use of a second detector in series (an electrochemical detector).

Recovery studies were conducted by analyzing groups of five to six samples of each diisocyanate. Vapor spikes of 2,4-TDI, 2,6-TDI, and HDI were prepared. Because of the low vapor pressure of MDI, liquid spikes were prepared instead of vapor spikes. For 2,4-TDI, 3 concentrations ranging from 4.9 to 60 μg per sample yielded an average recovery of 90.5%. For 2,6-TDI, 3 concentrations ranging from 6.0 to 60 μg per sample yielded an average recovery of 102.8%. For HDI, 3 concentrations ranging from 5.0 to 47 μg per sample yielded an average recovery of 89.5%. For MDI, 3 concentrations ranging from 3.2 to 72 μg per sample yielded an average recovery of 96.4%. The recovery studies also were conducted in the presence of 17% water, since the DMSO solvent is known to be hygroscopic. The recoveries for 2,4-TDI, HDI, and MDI with 17% water present were measured at one concentration level with an average recovery of 94.5%.

Storage stability studies were conducted at one concentration level by spiking groups of five to six impinger samplers with each diisocyanate-tryptamine derivative and storing at room temperature in the dark. Since

the DMSO solvent is hygroscopic, additional storage studies were conducted in the presence of 17% water for each of the four diisocyanate-tryptamine derivatives. The average recovery for the four diisocyanate-tryptamine derivatives measured at one level was 95.8% for a 28-day storage period. Some of the samples were stored over a period of several months. HDI derivative had a recovery of 96.4% after 4 months. MDI derivative was stable for 5 months with a 98.9% recovery.

No interference in the method was found from acetone, methyl ethyl ketone, benzaldehyde, acetophenone, or cyclohexanone. Aromatic diamines with the same retention times as the analytes are potential interferences. Therefore, the use of an electrochemical detector is recommended for confirmation of isocyanate peaks.

Because of the high solidification point of DMSO, the addition of a reagent to lower the freezing point was necessary for sampling in environments <60 °F. An 80:20 DMSO:acetonitrile solution containing the derivatizing reagent is recommended. Recovery studies were conducted in 80:20 DMSO:acetonitrile. For each diisocyanate, liquid spikes were prepared in groups of six samples at 3 concentration levels. The average recoveries were 84% for 2,4-TDI, 104% for 2,6-TDI, 85% for HDI, and 88% for MDI. Storage stability studies of six samples at one level for each diisocyanate-tryptamine derivative yielded an average recovery for the four diisocyanate-tryptamine derivatives of 96% for 7 days and 95% for 28 days.

For more detail, see the Backup Data Report for this method [1].

REFERENCES:

[1] Key-Schwartz RJ, Tucker SP [1994]. Backup data report for isocyanates, Method 5522, NIOSH/DPSE. Unpublished report.

[2] Wu WS, Stoyanoff RE, Szklar RS, Gaind VS, Rakanovic M [1990]. Application of tryptamine as a derivatising agent for airborne isocyanate determination. Analyst *115*: 801-807.

[3] Schwope AD, Randel MA, Broome MG [1981]. Dimethyl sulfoxide permeation through glove materials. Am Ind Hyg Assoc J *42*(10): 722-725.

METHOD WRITTEN BY:

Rosa J. Key-Schwartz, Ph.D. and Samuel P. Tucker, Ph.D., MRSB/DPSE

TABLE 1: SYNONYMS, EXPOSURE LIMITS, AND PROPERTIES

Compounds (Synonyms)	Exposure Limits, $\mu g/m^3$*			Properties
	(OSHA)	(NIOSH)	(ACGIH)	
2,4-TDI (toluene-2,4-diisocyanate)	140 (ceiling)	lowest feasible (Ca)	36 140 STEL (Ca)	liquid; d 1.224 g/mL @ 20 °C; BP 251 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C; MP 19.5 -21.5 °C
2,6-TDI (toluene-2,-6-diiocyanate)	no PEL	lowest feasible (Ca)	no TLV	liquid; d 1.22 g/mL @ 20 °C; VP 1.3 Pa (0.01 mm Hg) @ 20 °C
MDI (4,4'-methylenediphenyl isocyanate; diphenylmethane-4,4'-diisocyanate; methylenebis phenyl isocyanate)	200 (ceiling)	50; 200/10 min (ceiling)	51	solid (fused); d 1.23 g/mL @ 25 °C; MP 37.2 °C; VP 0.19 Pa (0.00014 mm Hg) @ 25 °C
HDI (hexamethylene diisocyanate)	no PEL	35; 140/10 min (ceiling)	34	liquid; d 1.04 g/mL @ 20 °C; BP 255 °C; 7 Pa (0.05 mm Hg) @ 25 °C

* 1 ppm = 7100 $\mu g/m^3$ TDI; 10208 $\mu g/m^3$ MDI; 7350 $\mu g/m^3$ HDI;
Ca = Carcinogen

APPENDIX: PREPARATION OF TRYPTAMINE DERIVATIVE

Dissolve 0.00250 mole (0.41 g) of tryptamine (>99% purity) in 300 mL of toluene. Heat the solution to 60°C while stirring until much of the tryptamine is dissolved. Dissolve 0.001 mole (150-300 mg) of isocyanate in 20 mL of toluene. Add the isocyanate solution to the tryptamine solution. The tryptamine derivative will precipitate as a white gel. Collect the precipitate in a fritted-glass funnel by suction filtration. For the tryptamine derivatives of HDI and MDI, dissolve the precipitate in 100 mL (for HDI) or 450 mL (for MDI) of hot n-propanol. Filter the solution and allow it to cool. Collect the crystals. For the tryptamine derivatives of 2,4- and 2,6-TDI, dissolve the precipitate in 50 mL of hot n-propanol. Filter the solution and allow to cool. Add heptane (175 mL for 2,4-TDI and 100 mL for 2,6-TDI) and collect the precipitate in a fritted-glass funnel by suction filtration. For all derivatives, dry in a vacuum oven at 60°C to remove solvent.

The tryptamine derivatives and their melting points are as follows:

TRYPTAMINE DERIVATIVES

Diisocyanate	Tryptamine Derivative	MP (°C)	MW (g/mol)
2,4-TDI	2,4-TDI-tryptamine	216-219	494.60
2,6-TDI	2,6-TDI-tryptamine	298-301	494.60
MDI	MDI-tryptamine	~270	570.70
HDI	HDI-tryptamine	201-201.5	488.64

LEAD in Air by Chemical Spot Test 7700

Pb MW: 207.19 CAS: 7439-92-1 RTECS: OF7525000

METHOD: 7700, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA: 0.05 mg/m^3
NIOSH: <0.1 mg/m^3
ACGIH: 0.15 mg/m^3

PROPERTIES: soft metal; d 11.3 g/cm^3; MP 327.5 °C; valences +2, +4 in salts

SYNONYMS: None

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 2 L/min [1]

VOL-MIN: 10 L @ 0.05 mg/m^3 [1]
-MAX: 240 L

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 per set (for laboratory analysis)

ACCURACY

RANGE STUDIED: <0.01 to >100.0 μg Pb per filter

BIAS: not applicable

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

ACCURACY: not applicable

MEASUREMENT

TECHNIQUE: CHEMICAL SPOT TEST KIT (Rhodizonate-based)

ANALYTE: rhodizonate complex of lead

POSITIVE INDICATOR: yellow/orange to pink/red color change (under acidic conditions) [2]

PERFORMANCE PARAMETERS:

Positive result: ≥ 0.57 μg Pb @ 95% confidence level [1]

Negative result: ≤ 10.2 μg Pb @ 95% confidence level [1]

APPLICABILITY: This is a qualitative method only, designed for use in the field. A characteristic color change indicates the presence of lead above a certain mass, as determined by performance parameters for a given test kit. If quantitative results are needed, the filter samples, test kit components, and backup pads may be shipped to the laboratory for analysis by NIOSH methods 7300, 7082, 7105, or equivalent.

INTERFERENCES: Tl^+, Ag^+, Cd^{2+}, Ba^{2+}, and Sn^{2+} also form colored compounds with sodium rhodizonate, but with less sensitivity than that of Pb^{2+}, and only the lead-rhodizonate complex gives the characteristic red color [2].

OTHER METHODS: Laboratory methods for the determination of lead include NIOSH methods 7300 (Elements by ICP), 7082 (Lead by Flame AAS), and 7105 (Lead by Graphite Furnace AAS). ASTM E 1553 is an alternate sample collection procedure [3].

REAGENTS:

1. Rhodizonate-based spot test kit (Merck EM Quant Lead Test™ or equivalent).
   NOTE 1: Rhodizonate may degrade quickly over time. Follow manufacturer's recommendations for maintaining viability of reagents.
   NOTE 2: Performance parameters on page 7700-1 apply only to Merck EM Quant Test kit (See APPENDIX).

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-µm pore size, 37-mm, in 2- or 3-piece cassette with cellulose backup pad.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Sealable plastic bags.
4. Gloves, powderless, plastic

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min (2 L/min recommended) for a total sample size of 10 to 240 L.

SPOT TESTING (Qualitative measurement):

3. Don a clean pair of gloves.
4. Using an appropriate tool, remove the top portion of the filter cassette (after sample has been collected for desired time period).
5. Apply the spot test to the center of the filter, following manufacturer's instructions.
6. Record results as positive for lead if a characteristic color change is observed, or negative if no characteristic color change is observed.
   NOTE: For rhodizonate-based lead spot tests (under acidic conditions), the characteristic color change is from yellow or orange to pink or red [2].

LABORATORY ANALYSIS (Optional):

7. Re-cap filter cassettes.
8. Place filter samples and test kit components in resealable plastic bag for shipment to laboratory.
9. Analyze by NIOSH method 7300, 7082, 7105, or equivalent method for lead.
   NOTE: The backup pad must be analyzed for lead that may have wicked through the filter during qualitative measurement (step 5 above).

EVALUATION OF METHOD:

A commercial rhodizonate-based spot test kit (Merck EM Quant Lead Test™) was evaluated for its potential use in the detection of lead in airborne particulate [1]. Personal sampling pumps were used to collect 371 air samples on cellulose ester membrane filters at various worksites where lead was a suspected air contaminant. Each filter sample was tested with an individual chemical spot test, and the samples (test kits included) were then analyzed using NIOSH method 7105. Experimental data were statistically modeled in order to estimate the performance parameters of the spot test kit (see APPENDIX). A positive reading was found at 95% confidence for lead mass values above 10.2 µg Pb per filter, while 95% confidence of a negative reading was found for lead masses below 0.57 µg Pb per filter.

REFERENCES:

[1] Ashley K, Fischbach TJ, Song R [in press]. Evaluation of a chemical spot test kit for the detection of airborne particulate lead in the workplace. Am Ind Hyg Assoc J.
[2] Feigel F, Anger V [1972]. Spot tests in inorganic analysis. Amsterdam: Elsevier, pp. 282-287, 564-566, 569.
[3] ASTM [1994]. ASTM E 1553, Standard practice for collection of airborne particulate lead during abatement and construction activities. In: ASTM standards on lead-based paint abatement in buildings. Philadelphia, PA: American Society for Testing and Materials.

METHOD WRITTEN BY:

Kevin E. Ashley, Ph.D., DPSE/MRB

APPENDIX: CALCULATION OF PERFORMANCE PARAMETERS

Example calculations are illustrated here for the performance parameters of the Merck EM Quant Lead Test™; performance parameters for other spot test kits should be estimated by statistical modeling before being used for field screening applications. Note that these calculations assume that the short-term exposures are representative of a full 8-h workday.

Consider first the case of a positive test result after 5 min of sampling at 2.0 L/min (minimum lead mass of 0.57 µg for a total sampling volume of 10 L):

$$0.057\ \mu g\ Pb/L\ (X\ 1000\ L/m^3) = 57\ \mu g\ Pb/m^3,$$

which is in excess of the OSHA permissible exposure limit (PEL) of 50 $\mu g/m^3$ for an 8-h workday.

Consider secondly the case of a negative test result after 2 h of sampling at 2.0 L/min (maximum lead mass of 10.2 µg for a total sampling volume of 240 L):

$$0.0425\ \mu g\ Pb/L\ (X\ 1000\ L/m^3) = 42.5\ \mu g\ Pb/m^3,$$

which is below the OSHA PEL for an 8-h workday.

Similar computations may be carried out for other sampling volumes and spot test kits, provided that the performance parameters for the test kits are known.

LEAD in Surface Wipe Samples 9100

Pb MW: 207.19 CAS: 7439-92-1 RTECS: OF7525000

METHOD: 9100, Issue 2 **EVALUATION: NOT APPLICABLE** **Issue 1: 15 August 1994**
Issue 2: 15 May 1996

PURPOSE: Determination of surface contamination by lead and its compounds.

LIMIT OF DETECTION: 2 μg Pb per sample (0.02 $\mu g/cm^2$ for 100-cm^2 area) by flame AAS [1] or ICP [2];
0.1 μg Pb per sample (0.001 $\mu g/cm^2$ for 100-cm^2 area) by graphite furnace AAS [3,4].

FIELD EQUIPMENT:
1. Resealable hard-walled sample containers, e.g., 50-mL plastic centrifuge tubes [5].
2. Wipes: Disposable towellettes moistened with a wetting agent.
   NOTE 1: Wipes selected for use should contain insignificant (<5 µg Pb) background lead levels [4,5]. Wipes should be individually wrapped and pre-moistened; for example, Wash'n Dri™ hand wipes (or equivalent).
   NOTE 2: Whatman filters should NOT be used for wipe sampling, because they are not sufficiently durable.
3. Powderless plastic gloves, disposable.
4. Template, plastic or steel; 10 cm x 10 cm or other standard size.
5. Tape Measure.
6. Masking Tape.

SAMPLING:
1. Don a clean pair of gloves.
2. Place the template over the area to be sampled, and secure the outside edges with masking tape. If the area to be sampled is in a confined area and a template cannot be used, measure the sampling area with the tape measure, and delineate the area to be sampled with masking tape.
3. Remove a wipe from its package, and unfold it.
4. Re-fold the wipe into fourths, and wipe the surface to be sampled with firm pressure. Use an overlapping "S" pattern to cover the entire surface area with horizontal strokes.
5. Fold the exposed side of the wipe in, and wipe the same area using vertical "S"-strokes.
6. Fold the wipe once more to reveal an unexposed surface, and wipe the surface a third time as described in step 4.
7. Fold the wipe, exposed side in, and place it into a clean hard-walled sample container (e.g., 50-mL centrifuge tube). Seal securely, and clearly label the sample container.
   NOTE: Compositing of wipe samples is not recommended, because (a) they cause sample preparation and analytical difficulties, and (b) site-specific analytical information is lost.
8. Clean the template in preparation for the next wipe sample.
9. Discard gloves.
10. Field blanks: 5% of samples, at least two per sample set. Remove unexposed wipes from their packaging and place into sample containers.

SAMPLE PREPARATION: Use the procedure of NIOSH Method 7105 or equivalent [3,6], including final sample dilution to 10 mL.

NOTE: Additional portions of nitric acid may be needed for complete digestion of the wipe sample. Include appropriate media and reagent blanks.

MEASUREMENT: Depending on detection limit required, use the procedures of NIOSH methods 7082 (Lead by flame AAS) [1], 7300 (Elements by ICP) [2], or 7105 (Lead by graphite furnace AAS) [3], or equivalent methods [6,7].

REFERENCES:

[1] NIOSH [1994]. Lead by FAAS: Method 7082. In: Eller PM, Cassinelli ME, Eds., NIOSH Manual of analytical methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 94-113.

[2] *Ibid.* Elements by ICP: Method 7300.

[3] *Ibid.* Lead by GFAAS: Method 7105.

[4] Millson M, Eller PM, Ashley K [1994]. Evaluation of wipe sampling materials for lead in surface dust. Am Ind Hyg Assoc J *55*: 339-342.

[5] ASTM [1994]. Emergency standard practice for field collection of settled dust samples using wipe sampling methods for lead determination by atomic spectrometry techniques: ASTM ES 30. In: ASTM standards on lead-based paint abatement in buildings. Philadelphia, PA: American Society for Testing and Materials.

[6] *Ibid.* Emergency standard practice for hot plate digestion of dust wipe samples for determination of lead by atomic spectrometry: ASTM ES 36.

[7] *Ibid.* Standard test method for analysis of digested samples for lead by inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption (FAAS), or graphite furnace atomic absorption (GFAAS) techniques: ASTM E 1613.

METHOD WRITTEN BY:

Peter M. Eller, Ph.D., QASA/DPSE, and Kevin Ashley, Ph.D., MRB/DPSE

METHYL BROMIDE 2520

CH_3Br MW: 94.94 CAS: 74-83-9 RTECS: PA4900000

METHOD: 2520, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1990**
Issue 2: 15 May 1996

OSHA: C 20 ppm (skin)
NIOSH: lowest feasible; carcinogen; Group I Pesticide
ACGIH: 5 ppm (skin)
(1 ppm = 3.95 mg/m³ @ NTP)

PROPERTIES: gas; d 1.73 g/mL @ 0 °C; BP 4 °C; vp 189.34 kPa (1420 mm Hg) @ 20 °C

SYNONYMS: monobromomethane; bromomethane

SAMPLING

SAMPLER: SOLID SORBENT TUBES (two petroleum charcoal tubes, 400 mg and 200 mg; drying tube, 9-g Na_2SO_4, necessary at humidity >50%)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 5 L with drying tube, 1 L w/o dying tube [1]

SHIPMENT: ship on dry ice at -10 °C [1]

SAMPLE STABILITY: six days at -10 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.84 to 32.0 ppm (5-L samples)

BIAS: - 5.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089

ACCURACY: ± 19.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ATOMIC EMISSION DETECTION (GC-AED) monitoring Br, C and H channels

ANALYTE: methyl bromide

DESORPTION: 400 mg tube: 3 mL methylene chloride; 200 mg tube: 2 mL methylene chloride

INJECTION VOLUME: 1 µL

TEMPERATURE -INJECTION: 250 °C
-TRANSFER LINE/CAVITY BLOCK: 250 °C
-COLUMN: 30 °C, 3.5 min; 12 °C/min to 130 °C; hold 1 min.

CARRIER GAS: Helium

COLUMN: DB-1 capillary, 30 m x 0.32-mm ID, 1.0-µm film thickness; 1 m x 0.53-mm deactivated fused silica pre-column

CALIBRATION: brominated compounds in methylene chloride

RANGE: 33.0 to 2687 µg bromine per sample

ESTIMATED LOD: 16.6 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.066 [1]

APPLICABILITY: The working range is 0.84 to 32.0 ppm (3.3 to 126 mg/m³) for a 5-L sample. Ceiling measurement samples may require dilution when analyzed.

INTERFERENCES: Water vapor interferes with collection at relative humidities (RH) >50%. To eliminate the interference, precede the sampling train with a drying tube, and limit the sample volume to 5 L. If drying tubes are not available, limit the sample volume to 1 L under humid conditions.

OTHER METHODS: This is Method 2520 [2] revised to account for humidity effects, as well as instability of standards and samples. Other researchers [3] have prepared methyl bromide standards gravimetrically and used GC-ECD for analysis. The gravimetric calibration procedure did not give consistent results when compared with the procedure used in this revision of Method 2520. GC-ECD with a Porapak Q capillary column may be an alternative technique to GC-AED, if other bromine standards are used to confirm the concentration of methyl bromide standards.

REAGENTS:

1. Eluant: methylene chloride, chromatographic grade*
2. Methyl bromide, 99.5%*
3. Calibration stock solution: To 4 mL of methylene chloride, add 12 μL dibromomethane.
   NOTE: Other brominated compounds may be used if liquid at room temperature.
4. Desorption stock solution: Bubble methyl bromide gas slowly into chilled eluant. Determine the methyl bromide concentration by comparison with calibration standards.
5. Helium, prepurified, 99.995%
6. Oxygen, ultra purified, as reagent gas for plasma, 30 psi.
7. Air, filtered.
8. Dry ice, flaked, for chilling solvent.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: two glass tubes, each tube, 10-cm long, 8-mm OD, 6-mm ID, containing 20/40 activated (60 °C) petroleum charcoal, first tube 400 mg, second tube 200 mg, held in place with silylated glass wool plugs; drying tube, glass, 9 g sodium sulfate. Tubes are connected in series with short pieces of plastic tubing. Pressure drop across sampler <3.4 kPa (2.5 cm Hg) at 1.0 L/min airflow. Tubes are commercially available (SKC, Inc.#226-38-02, or equivalent).
   NOTE: If RH ≥50%, precede sampling train with drying tube.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, atomic emission detector (helium plasma), integrator or computer, and column (page 2520-1).
4. Vials, 4-, and 10-mL, glass, with PTFE-lined caps.
5. Syringe, gas-tight, 10-mL.
6. Microliter syringes, 10-μL, 50-μL, 100-μL, 250-μL, 500-μL for preparing standard solutions.
7. Pipettes, 2-mL, graduated in 0.1-mL increments.

SPECIAL PRECAUTIONS: Methylene chloride is a suspect carcinogen. Methyl bromide is a suspect carcinogen and is toxic by ingestion, inhalation, and skin absorption [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: Place drying tube in front of the sorbent train.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 1.0 to 5.0 L.
   NOTE: Limit sample volume to 1.0 L if RH ≥ 50% and no drying tube is used.
4. Separate the front and back tubes immediately after sampling. Cap the tubes. Pack securely in dry ice for shipment. Store at -10 °C until analysis.

SAMPLE PREPARATION:

5. Place the sorbent sections from each sampling tube in separate vials. Discard the glass wool plugs.
6. Add 3.0 mL chilled eluant (methylene chloride) to each 400-mg section, and 2.0 mL chilled eluant to each 200-mg section. Immediately cap each vial.
7. Allow to stand at least 30 minutes at room temperature with occasional agitation. Rechill before transferring to autosampler vials or diluting.
   NOTE: Because of the volatility of the analyte, it is suggested that any dilutions be prepared at the time

of transfer to autosampler vials. Dilutions can be stored in the freezer until determined that they are needed.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.14 to 272 μg methyl bromide per sample from calibration stock solution.
   NOTE: 0.085 μmoles bromine per μL is equivalent to a methyl bromide concentration of 8.07 μg/μL.
   a. Add known aliquots (2.0-, 20-, 45-, and 120-μL) of calibration stock solution to methylene chloride in 10-mL vials with PTFE-lined caps. Take 1 mL of lowest standard and dilute to 10 mL with methylene chloride. Transfer standards to autosampler vials and immediately cap each vial.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. concentration).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Inject a known amount (1 to 10 μL) of methyl bromide desorption stock solution (concentration determined against other brominated compounds) , or a serial dilution thereof, directly onto media blank samplers with a microliter syringe.
   b. Cap the tubes. Allow to stand overnight at 0 °C.
   c. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs μg bromine 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-atomic emission detector to manufacturer's recommendations and to conditions given on page 2520-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Methyl bromide elutes before the methylene chloride solvent peak. Vent the solvent peak to avoid extinguishing the helium plasma. Vent time ranges from 3.2 to 5.9 mins; this may need to be adjusted for each system.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluant, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of methyl bromide found in the 400-mg sample tube (W_f) and 200-mg sample tube (W_b), and in the average media blanks for the 400-mg (B_f) and 200-mg (B_b) sorbent tubes.
14. Calculate concentration, C, of methyl bromide in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method 2520 for methyl bromide, issued in August 1990 [2], was based on method S372 [5]. This issue (Issue 2, dated 1/15/96) of Method 2520 was further revised to account for the effect of humidity and to address the instability of standards and samples [1]. The addition of a drying tube to the sampling train helped reduce the

effects of >50% RH. The analytical technique was changed to GC with atomic emission detection (GC-AED). The atomic emission detector monitors individual elements, in this case bromine, independent of the source compound. Calibration can be done with brominated compounds that are liquid at room temperature, thereby eliminating the need for methyl bromide standards. Methylene chloride replaced carbon disulfide as desorption solvent.

This revised Method 2520 (issued 1/15/96) for methyl bromide was evaluated at 7.8, 20.0, and 125.0 mg/m^3 (2, 5, and 32 ppm) [1]. Test atmospheres were generated by delivering methyl bromide gas from two diffusion tubes kept at -12 °C into an airstream flowing at 12 L/min. Humidity was added downstream when needed, and airflow passed through two mixing chambers before reaching a sampling manifold. The concentration was monitored with a total hydrocarbon analyzer and confirmed by calibrating against other brominated standards by GC-AED. Three compounds used as calibration standards (dibromomethane, 1-bromopropane, and 1-bromobutane) were chosen as closest in chemical structure to methyl bromide, although a compound-independent response was assumed [6]. A three-compound calibration was used during the development of the GC-AED analytical procedure. Since there was good agreement between the three compounds, the method was written with only one brominated standard, dibromomethane.

When challenged with methyl bromide at a calculated concentration of 27 ppm, the capacity of the sampler (a 400-mg petroleum charcoal tube plus a 200-mg petroleum charcoal tube) at 40% RH and 20°C was 1386.5 µg regardless of flow rate (10.5, 40, or 100 mL/min). However, at 100% RH and 39°C, the average capacity fell to 298.6 µg. With a 9-g sodium sulfate drying tube in line, the capacity was increased to 651.8 µg (concentration averaged 33 ppm). Even with a drying tube in line, severe breakthrough occurred at the 10-L sample volume (50% was found on the back tube). Without the use of a drying tube, a 1-L sample volume is recommended, based on a 170.6 µg capacity (1.6 L) found at the 40 mL/min rate multiplied by the 0.67 caution factor.

Recovery fell below 70% for sample loadings less than 58 µg, when carbon disulfide was used for desorption (Figure 1). This would not allow accurate sampling at 2 ppm, the exposure level most frequently encountered. Therefore, alternate desorption solvents were tested. Desorption with methylene chloride improved recovery at the 15-µg level to 76.7%. However, sample stability still fell below 70% after storage for six days at -10°C regardless of sample level. This stability limitation remains a concern and rapid sample analysis is required.

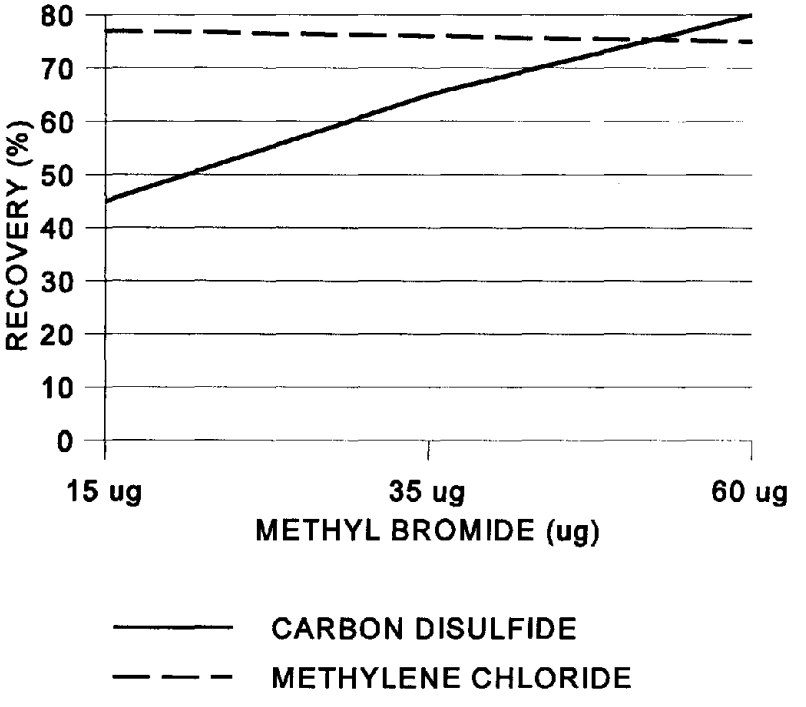

FIGURE 1. COMPARISON OF DESORPTION SOLVENTS

REFERENCES:

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METHOD REVISED BY:

Yvonne T. Gagnon, MRB/DPSE/NIOSH

METHYL ETHYL KETONE 2500

$CH_3COCH_2CH_3$ MW: 72.11 CAS: 78-93-3 RTECS: EL6475000

METHOD: 2500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: Rev., 15 May 1996

OSHA : 200 ppm
NIOSH: 200 ppm: STEL 300 ppm
ACGIH: 200 ppm: STEL 300 ppm
(1 ppm = 2.95 mg/m^3 @ NTP)

PROPERTIES: liquid; d 0.805 g/mL @ 20 °C; BP 79.6 °C; MP -86 °C; VP 13 kPa (100 mm Hg; 13% v/v) @ 25 °C; explosive range 2 to 10% v/v in air

SYNONYMS: 2-butanone; MEK

SAMPLING

SAMPLER: SOLID SORBENT TUBE (beaded carbon, ~150 mg/~75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 200 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: at least 90 days @ - 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 295 to 1180 mg/m^3

BIAS: 6.21%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069 [2]

ACCURACY: ± 17.83%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl ethyl ketone (MEK)

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 55 to 75 °C

CARRIER GAS: N_2 or He, 25 mL/min

COLUMN: glass or stainless steel, 4 m x 2-mm ID; 20% SP-2100/0.1% Carbowax 1500 on Supelcoport 100/120

CALIBRATION: MEK solutions in CS_2

RANGE: 0.15 to 5 mg per sample

ESTIMATED LOD: 4 µg per sample [2,3]

PRECISION ($\hat{S}_r$): 0.04 [1]

APPLICABILITY: The working range is 17 to 560 ppm (50 to 1650 mg/m^3) for a 3-L air sample. The method is applicable to 15-min samples. This method was developed to give improved sample stability compared to conventional charcoal tubes [3,4]. Side-by-side comparisons of this method and Method S3 were made in a sporting goods manufacturing plant in which MIBK, THF, and toluene were also present. This method has also been used successfully for methyl isobutyl ketone [1] and acetone [5].

INTERFERENCES: Under the given conditions, acetone and isopropanol have retention times similar to MEK. Mass spectrometry and other GC columns, e.g., SP-1000, or 30 m x 0.32-mm WCOT capillary coated with 1 µm DB-1, are aids to resolving interferences.

OTHER METHODS: This method is similar, except for the sampler, to Methods P&CAM 127 [6] and S3 [7,8], which it replaces.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) benzene* or other suitable internal standard.
2. Methyl ethyl ketone
3. Nitrogen or helium, purified.
4. Hydrogen prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID. Two sections of 20/40 mesh beaded carbon separated by 2-mm foam plug (front = ~150 mg, back = ~75 mg). Tubes are commercially available: Anasorb 747 (SKC 226-81), Anasorb CMS (SKC 226-121), Carboxen-564 (Supelco ORBO-90), or equivalent.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2500-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C). Work with it only in a hood. Benzene is a human carcinogen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 12 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

NOTE: Store samples in a freezer.

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 4 to 500 μg MEK per sample.
   a. Add known amounts of MEK to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. μg MEK).
9. Determine desorption efficiency (DE) at least once for each batch of sorbent used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

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

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2500-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

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

CALCULATIONS:

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

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

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

EVALUATION OF METHOD:

The method was evaluated with spiked samplers and with atmospheres generated by syringe pump/air dilution, verified by infrared absorption. For Ambersorb XE-347 samplers, breakthrough (80% RH, 200 ppm, 0.3 L/min) = 16.4 L; DE (4 to 18 mg per sample) = 1.03; storage stability (0.7 to 4 mg per sample) = 90% after six weeks at 25 °C; precision and accuracy as given on page 2500-1 (15 samples) [2]. A user check gave an estimated LOD of 4 μg MEK per sample [3].

Storage stability of MEK and methyl isobutyl ketone (MIBK) on Anasorb CMS samplers was determined for the Proficiency Analytical Testing (PAT) program [1]. Stability of MEK (0.125, 0.622, and 2.282 mg per sample) was 94 to 99% after 90 days at -5 °C. Only the highest level (2.282 mg) was stable (96% recovery) at ambient temperature for 30 days, and was stable for 180 days (98% recovery) at freezer temperatures (-5 °C). Results were similar for MIBK, although all concentration levels (0.103, 0.516, and 2.064 mg per sample) were stable for 30 days at ambient temperatures.

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METHOD REVISED BY:

Judd C. Posner, Ph.D., and Mary Ellen Cassinelli, NIOSH/DPSE.

OIL MIST, MINERAL 5026

C_nH_{2n+2} where n ≥ 16 MW: not pertinent CAS: 8012-95-1 RTECS: PY8030000

METHOD: 5026, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: Rev.: 15 May 1996

OSHA : 5 mg/m³
NIOSH: 5 mg/m³; STEL 10 mg/m³
ACGIH: 5 mg/m³ (as sampled by a method which does not collect vapor)

PROPERTIES: liquid; d 0.8 to 0.9 g/mL @ 20 °C; BP 360 °C; vapor pressure negligible

SYNONYMS: airborne mist of white mineral oil or the following water-insoluble petroleum-based cutting oils: cable oil; cutting oil; drawing oil; engine oil; heat-treating oils; hydraulic oils; machine oil; transformer oil.

SAMPLING		MEASUREMENT	
SAMPLER:	MEMBRANE FILTER (37-mm diameter, 0.8-μm MCE, 5-μm PVC, 2-μm PTFE, or glass fiber)	**TECHNIQUE:**	INFRARED SPECTROPHOTOMETRY
FLOW RATE:	1 to 3 L/min	**ANALYTE:**	mineral oil
VOL-MIN:	20 L @ 5 mg/m³	**EXTRACTION:**	10 mL CCl_4
-MAX:	500 L	**IR SCAN:**	3200 to 2700 cm^{-1} vs. blank CCl_4
SHIPMENT:	routine	**CALIBRATION:**	standard solutions of mineral oil in CCl_4
SAMPLE STABILITY:	stable	**RANGE:**	0.1 to 2.5 mg per sample
BLANKS:	2 to 10 field blanks per set	**ESTIMATED LOD:**	0.05 mg per sample [3]
		PRECISION ($\hat{S}_r$):	0.05 [3]

ACCURACY

RANGE STUDIED:	2.5 to 11.7 mg/m³ [1] (100-L samples)
BIAS:	- 0.84% [1,2]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.065 [1]
ACCURACY:	± 11.8%

APPLICABILITY: The working range is 1 to 20 mg/m³ for a 100-L air sample. This method is applicable to all trichlorotrifluoroethane-soluble mineral oil mists, but not to (nor does OSHA's standard cover) semi-synthetic or synthetic cutting fluids.

INTERFERENCES: Any aerosol (e.g., tobacco smoke) which absorbs infrared radiation near 2950 cm-1 interferes.

OTHER METHODS: This revises P&CAM 283 [3]. P&CAM 159 [4] and S272 [5] use similar samplers with measurement by fluorescence spectrophotometry. These methods have not been revised because of limited applicability (i.e., not all mineral oils contain fluorescent components and other fluorescent compounds interfere). Infrared analysis overcomes both of these limitations.

REAGENTS:

1. Carbon tetrachloride* (CCl_4), reagent grade.
2. Stock mineral oil standard, 20 mg/mL. Weigh 1.0 g of the bulk mineral oil sample into a 50-mL volumetric flask. Dilute to volume with CCl_4. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: membrane filter, 37-mm, 0.8-μm MCE, 5-μm PVC, 2-μm PTFE, or glass fiber filter, with cellulose backup pad in two-piece filter cassette.
   NOTE 1: High concentrations of oil mist may plug membrane filters. Glass fiber filters have a higher capacity for oil mist than membrane filters.
   NOTE 2: Handle filters carefully with tweezers to avoid contamination by skin oil.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Infrared spectrophotometer, double beam, dispersive, with scanning capability in the 3200-2700 cm^{-1} region, and two 10-mm spectrophotometer cells, infrared quartz with PTFE stoppers mounted in demountable cell holders.
   NOTE: Standard glass cells may be used if infrared quartz cells are not available.
4. Vials, scintillation, 20-mL, with foil-lined or PTFE-lined caps.*
5. Volumetric flasks, 10-, 25-, and 50-mL.*
6. Volumetric pipet or reagent dispenser, 10-mL.*
7. Pipets, 2- to 250-μL.
8. Tweezers.

* Rinse glassware with CCl_4. Air dry.

SPECIAL PRECAUTIONS: Carbon tetrachloride is a suspected human carcinogen. Handle in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 3 L/min for a total sample size of 20 to 500 L.
   NOTE: High concentrations of oil mist may plug membrane filters creating unacceptably high pressure drops. If this occurs, terminate sampling.
3. Collect 5 to 10 mL of unused, undiluted mineral oil in a vial. Submit with samples for standard preparation.

SAMPLE PREPARATION:

4. Using tweezers, transfer each sample or blank filter to a vial. Add 10.0 mL CCl_4. Cap and shake vigorously.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards.
   a. Add known amounts of stock mineral oil standard to CCl_4 in 10-mL volumetric flasks and dilute to the mark to obtain mineral oil concentrations in the range 5 to 250 μg/mL.
   b. Analyze with samples and blanks (step 8).
   c. Prepare calibration graph (peak absorbance vs. μg mineral oil).
6. Determine recovery (R) at least once for each lot of filters used for sampling in the range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of stock mineral oil standard onto the filter. Allow solvent to evaporate.
   b. Store samples overnight in filter cassettes.
   c. Prepare and analyze with working standards.
   d. Prepare a graph of R vs. μg mineral oil recovered.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

8. Scan each standard solution and each blank or sample filter extract from 3200 to 2700 cm^{-1} in absorbance mode vs. CCl_4 in reference beam. Record absorbance at wavelength of largest absorbance near 2940 cm^{-1} (± 11.8%).

CALCULATIONS:

9. Determine the mass, μg (corrected for R), of mineral oil found in the sample (W) and in the average media blank (B) from the calibration graph.
10. Calculate concentration, C, of mineral oil in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

The sampling portion of this method was evaluated over the range 2.5 to 11.7 mg/m^3 at 22 °C and 755 mm Hg using 100-L air samples of Gulf machine cutting oil with measurement by fluorescence spectrophotometry. Mixed cellulose ester filters, 0.8-μm pore size, were used for sampling [1,5]. The overall precision was 0.065 with an average recovery of 98%. The infrared measurement method was subsequently evaluated by NIOSH [2,3]. Precision and accuracy of the infrared and fluorescence spectrophotometric techniques are similar.

Issue 1 of this method (dated 8/15/87) used Freon 113 as the solvent. However, since Freons are known atmospheric ozone depleters, carbon tetrachloride, the original solvent used in P&CAM 283, is again specified, although it is a suspected human carcinogen.

PTFE filters (e.g., Gelman Zefluor) also may be used to sample oil mists. They have lower blanks than PVC, since PTFE has fewer extractables with CCl_4 than other membrane filters.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as PB 274-248 from NTIS, Springfield, VA 22161.

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[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 283, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

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[5] Ibid., Vol. 3, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

Charles Lorberau and Robert Glaser, NIOSH/DPSE.

$C_{10}H_{16}$ MW: 136.24 CAS: Table 1 RTECS: Table 1

METHOD: 1552, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA: no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm = 5.57 mg/m³ @ NTP)

PROPERTIES: Table 1

NAMES AND SYNONYMS: (1) limonene, d-,l-: cinene
(2) α-pinene: 2-pinene
(3) β-pinene: nopinene, pseudopinene
(4) 3-carene: isodiprene

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 100 mg/m³ [1,2]
-MAX: 30 L @ 100 mg/m³ [1,2]

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 5 °C [3]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: limonene, α-pinene, β-pinene, 3-carene

DESORPTION: 1 mL CS_2, stand 30 min [4]

INJECTION VOLUME: 1 μL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 to 135 °C @ 10 °C/min

CARRIER GAS: He, 30 mL/min

COLUMN: Stabilwax, 30 m, 0.53-mm ID, 3-μm film

CALIBRATION: standard solutions of terpenes in CS_2

RANGE: 2 to 840 μg/sample [1-3]

ESTIMATED LOD: Table 2

PRECISION ($\hat{S}_r$): Table 2

APPLICABILITY: The working range is 0.02 to 36 ppm (0.13 to 200 mg/m³) for a 15-L sample. This method may be applicable to other monocyclic and dicyclic terpenes that exhibit acceptable stability on charcoal tubes and in carbon disulfide (desorption solvent).

INTERFERENCES: Other terpenes or compounds with similar retention times may interfere. There is also the possibility of interfering peaks from the decompositional rearrangement of some terpenes from prolonged storage on charcoal or in carbon disulfide [3,4].

OTHER METHODS: This is a new method for the determination of four terpenes. Other researchers have developed methods for individual terpene compounds [1, 2].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic grade.*
2. Limonene, reagent grade.*
3. α-Pinene, reagent grade.*
4. β-Pinene, reagent grade.*
5. 3-Carene, reagent grade.*
6. Helium, prepurified.
7. Hydrogen, purified.
8. Air, filtered, dry.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph with flame ionization detector, integrator, and column (p. 1552-1).
4. Vials, 2-mL, glass, PTFE-lined crimp caps.
5. Syringes, 10- and 25-µL, readable to 0.1 µL.
6. Pipets, various sizes for standard preparation.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic, flammable, and explosive (flash point = -30 °C). Terpenes are flammable and are considered irritants. Perform all work in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 30 L.
4. Cap the samplers with plastic caps and pack securely for shipment.
   NOTE: Store samples at 5 °C. Analyze as soon as possible to reduce risk of analyte rearrangement (see EVALUATION OF METHOD).

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range from 0.2 to 1000 µg 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 a calibration graph for each analyte (peak area or peak height vs. µg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards and blanks (steps 11 and 12).

e. Prepare graph of DE vs. μg analyte recovered for each analyte.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1552-1. Inject 1-μL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Sampling and analytical conditions for each terpene were derived from independent methods [1-3]. Recovery was determined by spiking coconut shell charcoal tubes with known amounts of each analyte in CS_2 solution. Six samplers were spiked at each of three levels (20-, 60-, and 100-μg) for each terpene (18 samples for each analyte). Recovery, LOD, and stability data are listed in Table 2. Mean recoveries ranged from 93.4% to 97.6% with precisions, as calculated from the pooled relative standard deviations ($\bar{S}_r$), of <2% for each analyte. The LODs ranged from 0.3 to 0.6 μg per sample. Samples stored at 5 °C were stable for 30 days.

During the development of this method for terpenes, it was found that some terpenes (e.g., camphene, myrcene, γ-terpinene), upon exposure to activated charcoal and CS_2 exhibit rearrangement or decomposition to other terpenes or related compounds. Because γ-terpinene exhibited an acceptable recovery, it was selected for a study to determine the degree of decomposition/rearrangement. The difference between standards aged 21 days and freshly prepared standards was not significant. However, spiked charcoal tubes desorbed with and allowed to stand in CS_2 for 1 day gave a recovery of γ-terpinene of 77.4% with remainder converting to 1-methyl-3-methylethyl benzene. Spiked charcoal tubes aged for 30 days and then desorbed in CS_2 gave a γ-terpinene recovery of 12.4% with 87.6% converting to 1-methyl-3-methylethyl benzene [3].

REFERENCES:

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METHOD WRITTEN BY:

Stephanie M. Pendergrass, MRSB/DPSE

TABLE 1. TERPENES GENERAL INFORMATION

Analyte	CAS #	RTECS #	Properties
limonene (d- & l-)	138-86-3	OS8100000	liquid; d 0.84 g/mL @ 20 °C; BP 175 to 178 °C; FP -95.5 °C; RI 1.474 @ 20 °C; vp 0.280 kPa (2.1 mm Hg) @ 20 °C; vapor density (air=1) 4.7
α-pinene	80-56-8	DT7000000	liquid; d 0.8592 g/mL @ 20 °C; BP 156 to 160 °C; FP -40 °C; RI 1.4663 @ 20 °C
β-pinene	127-91-3	DT5077000	liquid; d 0.8654 g/mL @ 20 °C; BP 164 to 166 °C; RI 1.4739 @ 21 °C
3-carene	13466-78-9	FH8400000	liquid; d 0.8668 g/mL @ 15 °C; BP 168 to 169 °C; RI 1.4723 @ 20 °C

TABLE 2. TERPENE DATA FROM SPIKED SAMPLES

Analyte	n	Recovery (%)	Precision ($\bar{S}_r$)[a]	LOD (µg/sample)	Stability - 30 Day storage (% Recovery)	(S_r)[b]
limonene	18	94.9	0.019	0.4	93.2	0.029
3-carene	18	95.4	0.015	0.3	89.0	0.031
α-pinene	18	93.4	0.016	0.6	92.2	0.093
β-pinene	18	97.6	0.019	0.4	95.4	0.045

[a] Pooled relative standard deviation for 6 samples at each of 3 concentration levels.
[b] Relative standard deviation for 6 samples.

FORMULA see Table 1 MW: see Table 1 CAS: see Table 1 RTECS: see Table 1

METHOD: 2549, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA:
NIOSH: varies with compound
ACGIH:

PROPERTIES: See Table 1

SYNONYMS: VOCs; See individual compounds in Table 1

SAMPLING

SAMPLER: THERMAL DESORPTION TUBE (multi-bed sorbent tubes containing graphitized carbons and carbon molecular sieve sorbents [See Appendix])

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L
-MAX: 6 L

SHIPMENT: Ambient in storage containers

SAMPLE STABILITY: Compound dependent (store @ -10 °C)

BLANKS: 1 to 3 per set

ACCURACY

RANGE STUDIED: not applicable

BIAS: not applicable

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

ACCURACY: not applicable

MEASUREMENT

TECHNIQUE: THERMAL DESORPTION, GAS CHROMATOGRAPHY, MASS SPECTROMETRY

ANALYTE: See Table 1

DESORPTION: Thermal desorption

INJECTION VOLUME: Defined by desorption split flows (See Appendix)

TEMPERATURE-DESORPTION: 300 °C for 10 min.
-DETECTOR (MS): 280 °C
-COLUMN: 35 °C for 4 min; 8 °C/min to 150 °C, 15 °C/min to 300 °C

CARRIER GAS: Helium

COLUMN: 30 meter DB-1, 0.25-mm ID, 1.0-μm film, or equivalent

CALIBRATION: Identification based on mass spectra interpretation and computerized library searches.

RANGE: not applicable

ESTIMATED LOD: 100 ng per tube or less

PRECISION ($\hat{S}_r$): not applicable

APPLICABILITY: This method has been used for the characterization of environments containing mixtures of volatile organic compounds (See Table 1). The sampling has been conducted using multi-bed thermal desorption tubes. The analysis procedure has been able to identify a wide range of organic compounds, based on operator expertise and library searching.

INTERFERENCES: Compounds which coelute on the chromatographic column may present an interference in the identification of each compound. By appropriate use of background subtraction, the mass spectrometrist may be able to obtain more representative spectra of each compound and provide a tentative identity (See Table 1).

OTHER METHODS: Other methods have been published for the determination of specific compounds in air by thermal desorption/gas chromatography [1-3]. One of the primary differences in these methods is the sorbents used in the thermal desorption tubes.

REAGENTS:

1. Air, dry
2. Helium, high purity
3. Organic compounds of interest for mass spectra verification (See Table 1).*
4. Solvents for preparing spiking solutions: carbon disulfide (low benzene chromatographic grade), methanol, etc.(99+% purity)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Thermal sampling tube, ¼" s.s. tube, multi-bed sorbents capable of trapping organic compounds in the C_3-C_{16} range. Exact sampler configuration depends on thermal desorber system used. See Figure 1 for example.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible tubing.
3. Shipping containers for thermal desorber sampling tubes.
4. Instrumentation: thermal desorption system, focusing capability, desorption temperature appropriate to sorbents in tube (~300 °C), and interfaced directly to a GC-MS system.
5. Gas chromatograph with injector fitted with 1/4" column adapter, 1/4" Swagelok nuts and Teflon ferrules (or equivalent).
6. Syringes: 1-µL, 10-µL (liquid); 100-µL, 500-µL (gas tight)
7. Volumetric Flasks, 10-mL.
8. Gas bulb, 2 L

SPECIAL PRECAUTIONS: Some solvents are flammable and should be handled with caution in a fume hood. Precautions should be taken to avoid inhalation of the vapors from solvents as well. Skin contact should be avoided.

SAMPLING:

NOTE: Prior to field use, clean all thermal desorption tubes thoroughly by heating at or above the intended tube desorption temperature for 1-2 hours with carrier gas flowing at a rate of at least 50 mL/min. Always store tubes with long-term storage caps attached, or in containers that prevent contamination. Identify each tube uniquely with a permanent number on either the tube or tube container. Under no circumstances should tape or labels be applied directly to the thermal desorption tubes.

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the caps of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: With a multi-bed sorbent tube, it is extremely important to sample in the correct direction, from least to maximum strength sorbent.
3. For general screening, sample at 0.01 to 0.05 L/min for a maximum sample volume of 6 L. Replace caps immediately after sampling. Keep field blanks capped at all times. Tubes can act as diffusive samplers if left uncapped in a contaminated environment.
4. Collect a "humidity test" sample to determine if the thermal adsorption tubes have a high water background.
   NOTE: At higher sample volumes, additional analyte and water (from humidity) may be collected on the sampling tube. At sufficiently high levels of analyte or water in the sample, the mass spectrometer may malfunction during analysis resulting in loss of data for a given sample.
5. Collect a "control" sample. For indoor air samples this could be either an outside sample at the same location or an indoor sample taken in a non-complaint area.
6. Ship in sample storage containers at ambient temperature. Store at -10 °C.

SAMPLE PREPARATION:

7. Allow samples to equilibrate to room temperature prior to analysis. Remove each sampler from its storage container.
8. Analyze "humidity test" sampler first to determine if humidity was high during sampling (step 10).
9. If high humidity, dry purge the tubes with purified helium at 50 to 100 mL/min for a maximum of 3 L at ambient temperature prior to analysis. .
10. Place the sampler into the thermal desorber. Desorb in reverse direction to sampling flow.

CALIBRATION AND QUALITY CONTROL:

11. Tune the mass spectrometer according to manufacturer's directions to calibrate.
12. Make at least one blank run prior to analyzing any field samples to ensure that the TD-GC-MS system produces a clean chromatographic background. Also make a blank run after analysis of heavily concentrated samples to prevent any carryover in the system. If carryover is observed, make additional blank runs until the contamination is flushed from the thermal desorber system.
13. Maintain a log of thermal desorber tube use to record the number of times used and compounds found. If unexpected analytes are found in samples, the log can be checked to verify if the tube may have been exposed to these analytes during a previous sampling use.
14. Run spiked samples along with the screening samples to confirm the compounds of interest. To prepare spiked samples, use the procedure outlined in the Appendix .

MEASUREMENT:

15. See Appendix for conditions. MS scan range should cover the ions of interest, typically from 20 to 300 atomic mass units (amu). Mass spectra can either be identified by library searching or by manual interpretation (see Table 1). In all cases, library matches should also be checked for accurate identification and verified with standard spikes if necessary.

EVALUATION OF METHOD:

The method has been used for a number of field screening evaluations to detect volatile organic compounds. Estimate of the limit of detection for the method is based on the analysis of spiked samples for a number of different types of organic compounds. For the compounds studied, reliable mass spectra were collected at a level of 100 ng per compound or less. In situations where high levels of humidity may be present on the sample, some of the polar volatile compounds may not be efficiently collected on the internal trap of the thermal desorber. In these situations, purging of the samples with 3 L of helium at 100 mL/min removed the excess water and did not appreciably affect the recovery of the analytes on the sample.

REFERENCES:

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[2] McCaffrey CA, MacLachlan J, Brookes BI [1994]. Adsorbent tube evaluation for the preconcentration of volatile organic compounds in air for analysis by gas chromatography-mass spectrometry. Analyst 119:897-902.

[3] Bianchi AP, Varney MS [1992]. Sampling and analysis of volatile organic compounds in estuarine air by gas chromatography and mass spectrometry. J. Chromatogr. 643:11-23.

[4] EPA [1984]. Environmental Protection Agency Air Toxics Method T01. Rev. 1.0 (April, 1984): Method for the determination of volatile organic compounds in ambient air using Tenax(R) adsorption and gas chromatography/mass spectrometry (GC/MS), Section 13.

METHOD WRITTEN BY:

Ardith A. Grote and Eugene R. Kennedy, Ph.D., NIOSH, DPSE

TABLE 1. COMMON VOLATILE ORGANIC COMPOUNDS WITH MASS SPECTRAL DATA

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Aromatic Hydrocarbons							
Benzene /benzol	71-43-2 CY1400000	C_6H_6	78.11	80.1	95.2	12.7	78*
Xylene /dimethyl benzene	1330-20-7 ZE2100000	C_8H_{10}	106.7				91, 106*, 105
o-xylene				144.4	6.7	0.9	
m-xylene				139.1	8.4	1.1	
p-xylene				138.4	8.8	1.2	
Toluene /toluol	108-88-3 XS5250000	C_7H_8	92.14	110.6	28.4	3.8	91, 92*
Aliphatic Hydrocarbons							
n-Pentane	109-66-0 RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	43, 72*, 57
n-Hexane /hexyl-hydride	110-54-3 MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	57, 43, 86*, 41
n-Heptane	142-82-5 MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	43, 71, 57, 100*,41
n-Octane	111-65-9 RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	43, 85, 114*, 57
n-Decane /decyl hydride	124-18-5 HD6500000	$C_{10}H_{22}$	142.29	174	1.4	0.2	43, 57, 71, 41, 142*
Ketones							
Acetone /2-propanone	67-64-1 AL3150000	C_3H_6O	58.08	56	266	35.5	43, 58*
2-Butanone /methyl ethyl ketone	78-93-3 EL6475000	C_4H_8O	72.11	79.6	100	13	43, 72*
Methyl isobutyl ketone /MIBK, hexone	108-10-1 SA9275000	$C_6H_{12}O$	100.16	117	15	2	43, 100*, 58
Cyclohexanone /cyclohexyl ketone	108-94-1 GW1050000	$C_6H_{10}O$	98.15	155	2	0.3	55, 42, 98*, 69
Alcohols							
Methanol /methyl alcohol	67-56-1 PC1400000	CH_3OH	32.04	64.5	115	15.3	31, 29, 32*
Ethanol /ethyl alcohol	64-17-5 KQ6300000	C_2H_5OH	46.07	78.5	42	5.6	31, 45, 46*
Isopropanol /1-methyl ethanol	67-63-0 NT8050000	C_3H_7OH	60.09	82.5	33	4.4	45, 59, 43

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Butanol /butyl alcohol	71-36-3 EO1400000	C_4H_9OH	74.12	117	4.2	0.56	56, 31, 41, 43
Glycol Ethers							
Butyl cellosolve /2-butoxyethanol	111-76-2 KJ8575000	$C_6H_{14}O_2$	118.17	171	0.8	0.11	57, 41, 45, 75, 87
Diethylene glycol ethyl ether /Carbitol	111-90-0 KK8750000	$C_6H_{14}O_3$	134.17	202	0.08	0.01	45, 59, 72, 73, 75, 104
Phenolics							
Phenol /hydroxybenzene	108-95-2 SJ3325000	C_6H_5OH	94.11	182	47	0.35	94*, 65, 66, 39
Cresol	1319-77-3 GO5950000	C_7H_7OH	108.14				108*, 107, 77, 79
2-methylphenol	95-48-7			190.9	1.9	0.25	
3-methylphenol	108-39-4			202.2	1.0	0.15	
4-methylphenol	106-44-5			201.9	0.8	0.11	
Chlorinated Hydrocarbons							
Methylene chloride /dichloromethane	75-09-2 PA8050000	CH_2Cl_2	84.94	40	349	47	86*, 84, 49, 51
1,1,1-Trichloroethane /methyl chloroform	71-55-6 KJ2975000	CCl_3CH_3	133.42	75	100	13.5	97, 99, 117, 119
Perchloroethylene /hexachloroethane	127-18-4 KX3850000	CCl_3CCl_3	236.74	187 (subl)	0.2	<0.1	164*, 166, 168, 129, 131, 133, 94, 96
o-,p-Dichlorobenzenes		$C_6H_4Cl_2$	147.0				146*, 148, 111, 113, 75
/1,2-dichlorobenzene	95-50-1 CZ4500000			172-9	1.2	0.2	
/1,4-dichlorobenzene	106-46-7 CZ4550000			173.7	1.7	0.2	
1,1,2-Trichloro-1,2,2-trifluoroethane /Freon 113	76-13-1 KJ4000000	CCl_2FCClF_2	187.38	47.6	384	38	101, 103, 151, 153, 85, 87
Terpenes							
d-Limonene	5989-27-5 OS8100000	$C_{10}H_{16}$	136.23	176	1.2		68, 67, 93, 121, 136*
Turpentine (Pinenes)	8006-64-2	$C_{10}H_{16}$	136.23	156 to 170	4 @ 20°		93, 121, 136*, 91
α-pinene	80-56-8			156			
β-pinene	127-91-3			165			

Compound /Synonyms	CAS# RTECS	Empirical Formula	MW[a]	BP[b] (°C)	VP[c] @ 25 °C mm Hg	kPa	Characteristic Ions, m/z
Aldehydes							
Hexanal /caproaldehyde	66-25-1 MN7175000	$C_6H_{12}O$	100.16	131	10	1.3	44, 56, 72, 82, 41
Benzaldehyde /benzoic aldehyde	100-52-7 CU4375000	$C_7H_{12}O$	106.12	179	1.0	0.1	77, 105, 106*, 51
Nonanal /pelargonic aldehyde	124-19-6 RA5700000	$C_9H_{18}O$	142.24	93	23	3	43, 44, 57, 98, 114
Acetates							
Ethyl acetate /acetic ether	141-78-6 AH5425000	$C_4H_8O_2$	88.1	77	73	9.7	43, 88*, 61, 70, 73, 45
Butyl acetate /acetic acid butyl ester	123-86-4 AF7350000	$C_6H_{12}O_2$	116.16	126	10	1.3	43, 56, 73, 61
Amyl acetate /banana oil	628-63-7 AJ1925000	$C_7H_{14}O_2$	130.18	149	4	0.5	43, 70, 55, 61
Other							
Octamethylcyclotetra-siloxane	556-67-2 GZ4397000	$C_8H_{24}O_4Si_4$	296.62	175			281, 282, 283

[a] Molecular Weight
[b] Boiling Point
[c] Vapor Pressure
* Indicates molecular ion

APPENDIX

Multi-bed sorbent tubes: Other sorbent combinations and instrumentation/conditions shown to be equivalent may be substituted for those listed below. In particular, if the compounds of interest are known, specific sorbents and conditions can be chosen that work best for that particular compound(s). The tubes that have been used in NIOSH studies with the Perkin Elmer ATD system are ¼" stainless steel tubes, and are shown in the diagram below:

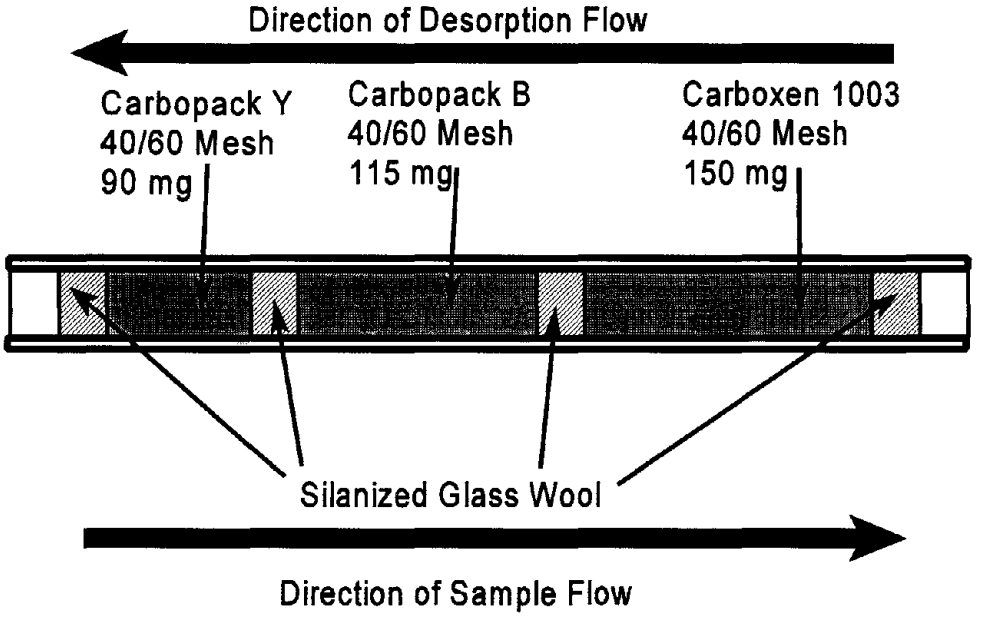

Figure 1

Carbopack™ and Carboxen™ adsorbents are available from Supelco, Inc.

Preparation of spiked samples: Spiked tubes can be prepared from either liquid or gas bulb standards.

Liquid standards: Prepare stock solutions by adding known amounts of analytes to 10-mL volumetric flasks containing high purity solvent (carbon disulfide, methanol, toluene). Solvents are chosen based on solubility for the analytes of interest and ability to be separated from the analytes when chromatographed. Highly volatile compounds should be dissolved in a less volatile solvent. For most compounds, carbon disulfide is a good general purpose solvent, although this will interfere with early eluting compounds.

Gas bulb standards: Inject known amounts of organic analytes of interest into a gas bulb of known volume filled with clean air [4]. Prior to closing the bulb, place a magnetic stirrer and several glass beads are placed in the bulb to assist in agitation after introduction of the analytes. After injection of all of the analytes of interest into the bulb, warm the bulb to 50 °C and place it on a magnetic stirring plate and stir for several minutes to ensure complete vaporization of the analytes. After the bulb has been stirred and cooled to room temperature, remove aliquots from the bulb with a gas syringe and inject into a sample tube as described below.

Tube spiking: Fit a GC injector with a ¼" column adapter. Maintain the injector at 120 °C to assist in vaporization of the injected sample. Attach cleaned thermal desorption tubes to injector with ¼" Swagelok nuts and Teflon ferrules, and adjust helium flow though the injector to 50 mL/min. Attach the sampling tube so that flow direction is the same as for sampling. Take an aliquot of standard solution (gas standards 100 to 500 µL; liquid standards, 0.1 to 2 µL) and inject into the GC injector. Allow to equilibrate for 10 minutes. Remove tube and analyze by thermal desorption using the same conditions as for field samples.

Instrumentation: Actual media, instrumentation, and conditions used for general screening of unknown environments are as follows: Perkin-Elmer ATD 400 (automated thermal desorption system) interfaced directly to a Hewlett-Packard 5980 gas chromatograph/HP5970 mass selective detector and data system.

ATD conditions:

Tube desorption temperature: 300°C
Tube desorption time: 10 min.
Valve/transfer line temperatures: 150°C
Focusing trap: Carbopack B/Carboxen 1000, 60/80 mesh, held at 27°C during tube desorption
Focusing trap desorption temperature: 300°C
Desorption flow: 50-60 mL/min.
Inlet split: off
Outlet split: 20 mL/min.
Helium: 10 PSI

GC conditions:

DB-1 fused silica capillary column, 30 meter, 1-µm film thickness, 0.25-mm I.D.
Temperature program: Initial 35°C for 4 minutes, ramp to 100°C at 8°/min., then ramp to 300°C at 15°/min, hold 1-5 minutes.
Run time: 27 min.

MSD conditions:

Transfer line: 280°C
Scan 20-300 amus, EI mode
EMV: set at tuning value
Solvent delay: 0 min. for field samples; if a solvent-spiked tube is analyzed, a solvent delay may be necessary to prevent MS shutdown caused by excessive pressure.

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

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

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

PROPERTIES: Table 1

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

SAMPLING

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

FLOW RATE: 0.2 to 0.5 L/min

VOL-MIN: 3 L
-MAX: 100 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

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

ACCURACY: ± 12 to ± 23%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

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

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

INJECTION LOOP VOLUME: 50 µL

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

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

CONDUCTIVITY SETTING: 10 µS full scale

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: see EVALUATION OF METHOD

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

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

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

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

REAGENTS:

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

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

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

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

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

SAMPLING:

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

SAMPLE PREPARATION:

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

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

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

CALIBRATION AND QUALITY CONTROL:

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

MEASUREMENT:

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

CALCULATIONS:

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

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

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

EVALUATION OF METHOD:

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

Acid	Range Studied (mg/m³)	Range Studied (µg/sample)	(%)	Measurement Precision ($\bar{S}_r$)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)	Estimated LOD [2] (µg per sample)
HF [7]	0.35 - 6	0.5 - 200	0.7	0.053	0.116	±23.4	0.7
HCl [8]	0.14 - 14	0.5 - 200	0.3	0.025	0.059	±11.9	0.6
H_3PO_4 [1]	0.5 - 2	3 - 100	−0.9	0.029	0.096	±19.7	2.0
HBr [1]	2 - 20	3 - 960	2.0	0.056	0.074	±16.5	0.9
HNO_3 [1]	1 - 10	3 - 500	2.0	0.018	0.085	±18.7	0.7
H_2SO_4 [1]	0.5 - 2	3 - 100	2.4	0.028	0.087	±19.4	0.9

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

REFERENCES:

[1] Cassinelli, M. E. and D. G. Taylor. Airborne Inorganic Acids, ACS Symposium Series 149, 137-152 (1981).

[2] DataChem, Inc. NIOSH Analytical Sequences #7546, #7357, and #7594 (unpublished, 1992).

[3] DataChem Laboratories, NIOSH Sequence #7923-C,D (unpublished, Jan. 25, 1994).

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

[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 7, P&CAM 339, U.S. Department of Health and Human Services, (NIOSH) Publication No. 82-100 (1982).

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

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

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

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

APPENDIX: SAMPLING TUBE PREPARATION

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

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

TABLE 1. GENERAL INFORMATION.

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

*Group I Pesticide

ALKALINE DUSTS

NaOH, KOH, LiOH, and basic salts	MW : 40.00 (NaOH); 56.11 (KOH) 23.95 (LiOH)	CAS: 1310-73-2 1310-58-3 1310-65-2	RTECS: WB490000 (NaOH) TT2100000 (KOH) OJ6307070 (LiOH)

METHOD: 7401, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 mg/m^3 (NaOH)
NIOSH: C 2 mg/m^3/15 min (NaOH); Group I Pesticide
ACGIH: C 2 mg/m^3 (NaOH)

PROPERTIES: basic, hygroscopic, caustic solids and aerosols; VP not significant

SYNONYMS: alkali; caustic soda; lye; sodium hydroxide; potassium hydroxide

SAMPLING

SAMPLER: FILTER (1-μm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 70 L @ 2 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.76 to 3.9 mg/m^3 [1] (360-L samples)

BIAS: 5.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 16.2%

MEASUREMENT

TECHNIQUE: ACID-BASE TITRATION

ANALYTE: OH^- (alkalinity)

EXTRACTION: 5.00 mL 0.01 N HCl, 15 min under nitrogen with stirring

TITRATION: 0.01 N NaOH under nitrogen, endpoint by pH electrode

CALIBRATION: 0.01 N NaOH standardized with 0.01 N HCl

RANGE: 0.14 to 1.9 mg (as NaOH) per sample [1]

ESTIMATED LOD: 0.03 mg per sample (as NaOH) [1] (7 x 10^{-4} moles of alkalinity)

PRECISION ($\hat{S}_r$): 0.033 @ 0.38 to 1.5 mg NaOH per sample [1]

APPLICABILITY: The working range is 0.4 to 5.4 mg/m^3 for a 360-L air sample. The method measures total alkalinity of alkali hydroxides, carbonates, borates, silicates, phosphates, and other basic salts, expressed as equivalents of NaOH.

INTERFERENCES: Carbon dioxide in the air may react with alkali on the filter to produce carbonates but does not interfere when titrated. The carbonates will produce the equivalent amount of strong alkali that was consumed on the filter [1]. Acid aerosols may neutralize the sample, if present, producing a negative interference.

OTHER METHODS: This revises Methods S381 [2] and P&CAM 241 [3].

REAGENTS:

1. Sodium carbonate, primary standard grade.
2. Hydrochloric acid stock solution, 0.1 N. Standardize with sodium carbonate primary standard.
3. Dilute hydrochloric acid, 0.01 N. Dilute 10.0 mL 0.1 N stock HCl to 100 mL in a volumetric flask with distilled water.
4. Water, distilled, CO_2-free. Boil and cool under N_2 or bubble nitrogen through distilled water for 30 min. Store with an Ascarite trap.
5. Nitrogen, compressed.
6. Sodium hydroxide, 50% w/v.* Dissolve 50 g NaOH in CO_2-free distilled water and dilute to 100 mL.
7. Stock sodium hydroxide, 0.1 N. Dilute 8 mL 50% NaOH to 1.0 L with CO_2-free distilled water. Store under Ascarite or other CO_2-absorbing trap.
8. Working sodium hydroxide solution, 0.01 N. Dilute 10 mL stock (0.1 N NaOH) to 100 mL with CO_2-free distilled water.
9. Standard buffer solutions, pH 4 and 7.

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter (Millipore, Fluoropore or equivalent), 1.0-μm pore size, supported by a cellulose backup pad in a cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. pH meter with pH electrode and recorder.
4. Titration vessel, 150 to 200 mL beaker, flask or jar with cover containing openings for the pH electrode and N_2 inlet and outlet.
5. Stirrer, magnetic, and stir bar.
6. Glass rod, ca. 5-mm diameter and 10 cm long to hold filter under liquid surface in titration vessel.
7. Pipets, 5- and 10-mL.
8. Volumetric flasks, 100-mL and 1-L.
9. Burets, 50-mL, readable to 0.1 mL.
10. Tweezers.

SPECIAL PRECAUTIONS: NaOH solutions are corrosive to tissue [4]. Handle with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 70 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer the sample filter to a titration vessel with tweezers. Place the filter face down in the titration vessel.
4. Place the end of a glass rod in the center of the filter to maintain the filter below the liquid surface during the analysis.
5. Cover the titration vessel, add 5.00 mL 0.01 N HCl, start the magnetic stirrer and N_2 purge (ca. 0.1 L/min).
6. Allow to stand 15 min (with stirring).

CALIBRATION AND QUALITY CONTROL:

7. Calibrate the pH meter with pH 4 and pH 7 buffer solutions.
8. Standardize aliquots of the 0.1 N HCl stock solution with sodium carbonate in triplicate [3].
   a. Dry 3 to 5 g primary standard grade Na_2CO_3 at 250 °C for 4 h. Cool in a desiccator.
   b. Weigh ca. 2.5 g Na_2CO_3 to the nearest mg. Dissolve and dilute to exactly 1 L with CO_2-free distilled water. The concentration is ca. 0.05 N Na_2CO_3.
   c. Place 5.00 mL 0.05 N Na_2CO_3 solution into a titration vessel and titrate potentiometrically to a pH of 5.

ALUMINUM and compounds, as Al 7013

Al MW: 26.98 (Al); 101.96 (Al_2O_3) CAS: 7429-90-5 (Al); 1344-28-1 (Al_2O_3) RTECS: BD0330000 BD1200000

METHOD: 7013, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: see table 1
ACGIH: see table 1

PROPERTIES: ductile metal; valence 3; MP 660 °C

SYNONYMS: vary depending upon the compound; alumina (Al_2O_3)

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 10 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

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

ACCURACY: not evaluated

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: aluminum

ASHING: conc. HNO_3, 6 mL; 140 °C

FINAL SOLUTION: 10% HNO_3, 10 mL
1000 μg/mL Cs

FLAME: nitrous oxide-acetylene, reducing

WAVELENGTH: 309.3 nm

BACKGROUND CORRECTION: none used

CALIBRATION: Al^{3+} in 10% HNO_3

RANGE: 50 to 5000 μg per sample [1]

ESTIMATED LOD: 2 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.03 [1,2]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 100-L sample. This is an elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with this ashing procedure. Aliquots of the samples can be analyzed separately for approximately four additional metals.

INTERFERENCES: Cesium at 1000 μg/mL controls ionization in the nitrous oxide-acetylene flame [3]. Iron and HCl at greater than 0.2% (w/w) decrease the sensitivity. Vanadium or H_2SO_4 require 1% (w/w) La as a releasing agent [4].

OTHER METHODS: This is Method P&CAM 173 for Al [1] in a revised format. Method 7300 (ICP-AES) is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 μg Al/mL. Commercially available or dissolve 1.000 g Al wire in minimum volume of (1+1) HCl using small drop of Hg as catalyst. Dilute to 1 L with 1% (v/v) HCl.
4. Cs solution, 50 mg/mL. Dissolve 73.40 g $CsNO_3$ in 100 mL water; dilute to 1 L.
5. Nitrous oxide.
6. Acetylene.
7. Distilled or deionized water.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and aluminum hollow cathode lamp.
4. Regulators, two-stage, for N_2O and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Micropipets, 5 to 500 μL.*
8. Hotplate, surface temperature 100 to 140 °C.

* Clean with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 10 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: Alumina (Al_2O_3) will not be dissolved by this procedure. Lithium borate fusion is necessary to dissolve alumina. The following sample preparation gave quantitative recovery for soluble aluminum compounds (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassettes and transfer the samples and blanks to separate clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 10% HNO_3.
7. Place the beakers on a hotplate and allow to go to a small liquid volume (ca. 0.5 mL).
8. When sample is dry, rinse walls of beaker with 3 to 5 mL 10% HNO_3. Reheat for 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 10-mL volumetric flask containing 0.2 mL 50 mg/mL Cs solution. Dilute to volume with 10% HNO_3.
   NOTE: If vanadium or sulfuric acid are present, add 1% (w/w) La as a releasing agent [1,3].

CALIBRATION AND QUALITY CONTROL:

10. Add known amounts, covering the range 0 to 500 mg Al per sample, of calibration stock solution to 100-mL volumetric flasks containing 2.0 mL 50 mg/mL Cs solution and dilute to volume with 10% HNO_3.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 95% ethanol to each vial. Attach crimp cap to each vial.
7. Agitate 1 h in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.01 to 3 mg analyte per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, in n-hexane to 95% ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 μL) of calibration stock solution, or a dilution thereof, in hexane directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2002-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Use the following conditions as a guide (these were used in development of the methods [1]):

	TEMPERATURES, °C		
COMPOUND	Injection	Column	Detector
Aniline	230	165	245
o-Toluidine	240	180	265
2,4-Xylidine	230	170	235
N,N-Dimethyl-p-toluidine	250	180	250
N,N-Dimethylaniline	150	100 for 4 min, then 8°C/min to 225	250

NOTE: If peak response is above the linear range of the working standards, dilute with 95% ethanol, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area or height.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Precisions, biases and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one and two times the OSHA standard [1]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere. The first three analytes were stable on silica gel for at least one week. Method S164 using collection on activated charcoal was also developed for N,N-dimethylaniline [3].

	Sampling						Measurement		
	Breakthrough volume in dry air at concentration		Range mg/m³	Bias	Overall Precision	Accuracy	Range	Precision	Desorption
Substance	(L)	(mg/m³)	(volume)	(%)	($\hat{S}_{rT}$)	(%)	(mg)	($\hat{S}_r$)	efficiency
Aniline	>44.4	38	9.5-38.2 (20 L)	-4.9	0.060	±15.1	0.20-0.82	0.013	0.980-1.00
o-Toluidine	>221.3	47	11.7-46.9 (50 L)	-1.5	0.060	±12.0	0.55-2.2	0.032	0.970-0.983
2,4-Xylidine	>44.4	50	12.5-50.0 (20 L)	-1.2	0.057	±11.2	0.25-1.01	0.021	0.959-1.015
N,N-Dimethyl-o-toluidine	*	*	9.4-30.0 (100 L)	*	*	*	0.47	0.035	0.88
N,N-Dimethyl-aniline	*	*	*	-7.9	0.090	±16.0	0.05-3.0	*	0.997 (1.9-mg samples)

*Not determined

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] UBTL, Inc., Sequence #2300-S, Aniline (May 15, 1980), and Sequence #2551-M, o-Toluidine (August 28, 1980) (NIOSH, unpublished).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Ibid., Vol. 4, P&CAM 280, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[5] Ibid., Vol. 1, P&CAM 168, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

(1) $HOCH_2CH_2NH_2$	MW: 61.10	CAS:	141-43-5	RTECS: KJ5775000
(2) $(HOCH_2CH_2)_2NH$	105.14		111-42-2	KL2975000
(3) $(HOCH_2CH_2)_3N$	149.19		102-71-6	KL9275000

METHOD: 3509, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

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

PROPERTIES: Table 1

SYNONYMS: (1) 2-aminoethanol; monoethanolamine; MEA
(2) 2,2'-iminodiethanol; diethanolamine; DEA
(3) 2,2',2"- nitrilotriethanol; triethanolamine; TEA

SAMPLING

SAMPLER: IMPINGER
(15 mL 2 mM hexanesulfonic acid)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 5 L
-MAX: 300 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

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

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

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

ANALYTE: MEA, DEA, TEA

INJECTION LOOP VOLUME: 50 µL

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

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

CONDUCTIVITY SETTING: 3 µS full scale

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

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

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD [1] and Table 2

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

INTERFERENCES: Larger amines such as cocomorpholine, 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.

ARSENIC TRIOXIDE, as As 7901

As_2O_3 MW: 197.84 CAS: 1327-53-3 RTECS: CG3325000

METHOD: 7901, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 2:** 15 August 1994

OSHA : 0.01 mg/m^3 (As)
NIOSH: C 0.002 mg/m^3 (As)/15 min; carcinogen
ACGIH: 0.01 mg/m^3; carcinogen

PROPERTIES: solid; MP 275 °C or 313 °C (sublimes); VP 0.0075 Pa (5.6 x 10^{-5} mm Hg; 0.45 μg As/m^3) @ 25 °C

SYNONYMS: arsenous acid anhydride; arsenous sesquioxide; arsenolite; claudetite

SAMPLING

SAMPLER: FILTER (Na_2CO_3-impregnated, 0.8-μm cellulose ester membrane + backup pad)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.01 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.67 to 32 μg/m^3 [1,2] (400-L samples)

BIAS: − 0.55%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.075 [1,2]

ACCURACY: ± 11.9%

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: arsenic

ASHING: 15 mL HNO_3 + 6 mL H_2O_2; 150 °C

FINAL SOLUTION: 10 mL 1% HNO_3, 0.1% Ni^{2+}

WAVELENGTH: 193.7 nm; D_2 or H_2 correction

GRAPHITE TUBE: pyrolytic

GRAPHITE FURNACE: DRY: 100 °C, 70 sec; CHAR: 1300 °C, 30 sec; ATOMIZE: 2700 °C, 10 sec

INJECTION: 25 μL

CALIBRATION: As in 1% HNO_3, 0.1% Ni^{2+}

RANGE: 0.3 to 13 μg per sample

ESTIMATED LOD: 0.06 μg per sample

PRECISION ($\bar{S}_r$): 0.029 [3,4]

APPLICABILITY: The working range is 0.001 to 0.06 mg/m^3 for a 200-L air sample. This method collects particulate arsenic compounds as well as arsenic trioxide vapor. **If only total particulate arsenic is of interest, the use of the treated filter and analysis of the backup pad is not required.** Arsine is not collected by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of a deuterium background corrector. Matrix modification with Ni^{2+} solution allows the use of a higher char temperature in the graphite furnace. Other particulate arsenic compounds will interfere.

OTHER METHODS: This method combines and replaces P&CAM 346 [3], S309 [4], and P&CAM 286 [5]. Method 7300 (ICP-AES) and arsine generation (Method 7900 and the criteria document method [1]) are for particulate arsenic compounds. Other methods (P&CAM 173 [7], P&CAM 180 [8], and P&CAM 188 [9]) have not been revised because of interferences or poor sensitivity.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Dilute 10 mL conc. HNO_3 to 1 L with distilled or deionized water.
3. Hydrogen peroxide, 30% (w/w).
4. Ni^{2+} in 1% HNO_3, 1000 μg/mL. Dilute 4.95 g $Ni(NO_3)_2$ to 1 L with 1% HNO_3.
5. Calibration stock solution*, 1000 μg As/mL, commercially available, or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Dilute to 1 L with 1% HNO_3.
6. 1 M Na_2CO_3:glycerol solution, 20:1. Dissolve 9.5 g sodium carbonate in 100 mL distilled or deionized water. Add 5 mL pure glycerol.
7. Distilled or deionized water.
8. Argon.

* See Special Precautions

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-μm pore size, 37-mm diameter, and cellulose backup pad in cassette filter holder treated as follows:
   a. Remove inlet plug from the loaded cassette.
   b. Add 250 μL 20:1 Na_2CO_3:glycerol solution with a micropipet directly onto filter (wet entire surface).
   c. Attach to vacuum source and draw 30 to 60 L clean air through the filter.
   d. Let dry overnight or dry 8 h @ 120 °C. Replace the inlet plug.
   e. Use within one week.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
   NOTE: The treated filter has a high pressure drop; a personal sampling pump with flow rate control is required.
3. Atomic absorption spectrophotometer with graphite furnace atomizer, arsenic electrodeless discharge lamp, and background correction.
4. Regulator, two-stage for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.*
6. Volumetric flasks, 10-mL.*
7. Assorted volumetric pipets as needed.*
8. Hotplate, surface temperature to 150 °C.
9. Steambath.

* Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Arsenic is a carcinogen [6]. Handle appropriately. Perform all digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer both the treated filter and backup pad to a clean beaker.
4. Add 15 mL conc. HNO_3 and cover with a watchglass.
   NOTE: Start reagent blanks at this step.
5. Heat on a 150 °C hotplate until the liquid volume is reduced to about 1 mL.

ASBESTOS and OTHER FIBERS by PCM 7400

Various MW: Various CAS: Various RTECS: Various

METHOD: 7400, Issue 2 **EVALUATION: FULL** **Issue 1: Rev. 3 on 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 asbestos fiber (> 5 μm long)/cc; 1 f/cc/30 min excursion; carcinogen
MSHA: 2 asbestos fibers/cc
NIOSH: 0.1 f/cc (fibers > 5 μm long)/400 L; carcinogen
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc; carcinogen

PROPERTIES: solid, fibrous, crystalline, anisotropic

SYNONYMS [CAS #]: actinolite **[77536-66-4]** or ferroactinolite **[15669-07-5]**; amosite **[12172-73-5]**; anthophyllite **[77536-67-5]**; chrysotile **[12001-29-5]**; serpentine **[18786-24-8]**; crocidolite **[12001-28-4]**; tremolite **[77536-68-6]**; amphibole asbestos **[1332-21-4]**; refractory ceramic fibers **[142844-00-6]**; fibrous glass.

SAMPLING

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

FLOW RATE*: 0.5 to 16 L/min

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

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.115 to 0.13 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone - collapse/triacetin - immersion method [2]

COUNTING RULES: described in previous version of this method as "A" rules [1,3]

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

CALIBRATION: HSE/NPL test slide

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

ESTIMATED LOD: 7 fibers/mm^2 filter area

PRECISION ($\bar{S}_r$): 0.10 to 0.12 [1]; see EVALUATION OF METHOD

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. The method gives an index of airborne fibers. It is primarily used for estimating asbestos concentrations, though PCM does not differentiate between asbestos and other fibers. Use this method in conjunction with electron microscopy (e.g., Method 7402) for assistance in identification of fibers. Fibers < ca. 0.25 μm diameter will not be detected by this method [4]. This method may be used for other materials such as fibrous glass by using alternate counting rules (see Appendix C).

INTERFERENCES: If the method is used to detect a specific type of fiber, any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This revision replaces Method 7400, Revision #3 (dated 5/15/89).

REAGENTS:

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

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically conductive extension cowl and cellulose ester filter, 0.45- to 1.2-μm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use to check for clarity and background. Discard the filter lot if mean is $\geq$5 fibers per 100 graticule fields. These are defined as laboratory blanks. Manufacturer-provided quality assurance checks on filter blanks are normally adequate as long as field blanks are analyzed as described below.
   NOTE 2: The electrically conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling.
   NOTE 3: Use 0.8-μm pore size filters for personal sampling. The 0.45-μm filters are recommended for sampling when performing TEM analysis on the same samples. However, their higher pressure drop precludes their use with personal sampling pumps.
   NOTE 4: Other cassettes have been proposed that exhibit improved uniformity of fiber deposit on the filter surface, e.g., bellmouthed sampler (Envirometrics, Charleston, SC). These may be used if shown to give measured concentrations equivalent to sampler indicated above for the application.
2. Personal sampling pump, battery or line-powered vacuum, of sufficient capacity to meet flow-rate requirements (see step 4 for flow rate), with flexible connecting tubing.
3. Wire, multi-stranded, 22-gauge; 1", hose clamp to attach wire to cassette.
4. Tape, shrink- or adhesive-.
5. Slides, glass, frosted-end, pre-cleaned, 25 x 75-mm.
6. Cover slips, 22- x 22-mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
7. Lacquer or nail polish.
8. Knife, #10 surgical steel, curved blade.
9. Tweezers.

EQUIPMENT:

10. Acetone flash vaporization system for clearing filters on glass slides (see ref. [5] for specifications or see manufacturer's instructions for equivalent devices).
11. Micropipets or syringes, 5-μL and 100- to 500-μL.
12. Microscope, positive phase (dark) contrast, with green or blue filter, adjustable field iris, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
13. Graticule, Walton-Beckett type with 100-μm diameter circular field (area = 0.00785 mm^2) at the specimen plane (Type G-22). Available from Optometrics USA, P.O. Box 699, Ayer, MA 01432 [phone (508)-772-1700], and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. (see APPENDIX A for the custom-ordering procedure).
14. HSE/NPL phase contrast test slide, Mark II. Available from Optometrics USA (address above).
15. Telescope, ocular phase-ring centering.
16. Stage micrometer (0.01-mm divisions).

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

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. To reduce contamination and to hold the cassette tightly together, seal the crease between the cassette base and the cowl with a shrink band or light colored adhesive tape. For personal sampling, fasten the (uncapped) open-face cassette to the worker's lapel. The open face should be oriented downward.
    NOTE: The cowl should be electrically grounded during area sampling, especially under conditions of low relative humidity. Use a hose clamp to secure one end of the wire (Equipment, Item 3) to the monitor's cowl. Connect the other end to an earth ground (i.e., cold water pipe).
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Handle field blanks in a manner representative of actual handling of associated samples in the set. Open field blank cassettes at the same time as other cassettes just prior to sampling. Store top covers and cassettes in a clean area (e.g., a closed bag or box) with the top covers from the sampling cassettes during the sampling period.
4. Sample at 0.5 L/min or greater [6]. Adjust sampling flow rate, Q (L/min), and time, t (min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 ($3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area A_c = 385 mm^2) for optimum accuracy. These variables are related

to the action level (one-half the current standard), L (fibers/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. The collection efficiency does not appear to be a function of flow rate in the range of 0.5 to 16 L/min for asbestos fibers [7]. Relatively large diameter fibers (>3 μm) may exhibit significant aspiration loss and inlet deposition. A sampling rate of 1 to 4 L/min for 8 h is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If $\geq$ 50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.

NOTE 2: OSHA regulations specify a minimum sampling volume of 48 L for an excursion measurement, and a maximum sampling rate of 2.5 L/min [3].

5. At the end of sampling, replace top cover and end plugs.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE 1: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index $\leq$1.46. This method collapses the filter for easier focusing and produces permanent (1 - 10 years) mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" or similar flash vaporization techniques may be used outside the laboratory [2]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [3,7,8,9]). Unless the effective filtration area is known, determine the area and record the information referenced against the sample ID number [1,9,10,11].

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

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [2].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade surgical steel knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.

b. Insert slide with wedge into the receiving slot at base of "hot block". Immediately place tip of a micropipet containing ca. 250 µL acetone (use the minimum volume needed to consistently clear the filter sections) into the inlet port of the PTFE cap on top of the "hot block" and inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 sec for the filter to clear, remove pipet and slide from their ports.
   CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous use of this device in an unventilated space may produce explosive acetone vapor concentrations.
c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation. Avoid excess pressure and movement of the cover glass.
   NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.
d. Mark the outline of the filter segment with a glass marking pen to aid in microscopic evaluation.
e. Glue the edges of the cover slip to the slide using lacquer or nail polish [12]. Counting may proceed immediately after clearing and mounting are completed.
   NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturers instructions. At least once daily use the telescope ocular (or Bertrand lens, for some microscopes) supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of microscope cleanings and major servicing.
    a. Each time a sample is examined, do the following:
       (1) Adjust the light source for even illumination across the field of view at the condenser iris. Use Kohler illumination, if available. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contract optics.
       (2) Focus on the particulate material to be examined.
       (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
    b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
       (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
       (2) Bring the blocks of grooved lines into focus in the graticule area.
          NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible when centered in the graticule area. Blocks 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.
       (3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.
11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis [13]. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field

and reference samples (e.g., PAT, AAR, commercial samples). The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.

b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter precision. Obtain separate values of relative standard deviation (S_r) for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, >20 to 50 fibers in 100 graticule fields, and >50 to 100 fibers in 100 graticule fields. Maintain control charts for each of these data files.

NOTE: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [9]

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

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

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

13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the absolute value of the difference between the square roots of the two counts (in fiber/mm^2) exceeds 2.77 $(X)S_r'$, where X = average of the square roots of the two fiber counts (in fiber/mm^2) and $S_r' = \frac{S_r}{2}$, where S_r is the intracounter relative standard deviation for the appropriate count range (in fibers) determined in step 11. For more complete discussions see reference [13].

NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data [13].

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

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

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

MEASUREMENT:

16. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.

17. Adjust the microscope (Step 10).

NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 μm) [4].

18. Counting rules: (same as P&CAM 239 rules [1,10,11]: see examples in APPENDIX B).

a. Count any fiber longer than 5 μm which lies entirely within the graticule area.
   (1) Count only fibers longer than 5 μm. Measure length of curved fibers along the curve.
   (2) Count only fibers with a length-to-width ratio equal to or greater than 3:1.

b. For fibers which cross the boundary of the graticule field:

(1) Count as 1/2 fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rule a above.
(2) Do not count any fiber which crosses the graticule boundary more than once.
(3) Reject and do not count all other fibers.

c. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
d. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.

19. Start counting from the tip of the filter wedge and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate or bubble covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

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

NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report <u>total</u> fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters >1 μm), polarized light microscopy (as in NIOSH Method 7403) may be used to identify and eliminate interfering non-crystalline fibers [15].

NOTE 3: Do not count at edges where filter was cut. Move in at least 1 mm from the edge.

NOTE 4: Under certain conditions, electrostatic charge may affect the sampling of fibers. These electrostatic effects are most likely to occur when the relative humidity is low (below 20%), and when sampling is performed near the source of aerosol. The result is that deposition of fibers on the filter is reduced, especially near the edge of the filter. If such a pattern is noted during fiber counting, choose fields as close to the center of the filter as possible [5].

NOTE 5: Counts are to be recorded on a data sheet that provides, as a minimum, spaces on which to record the counts for each field, filter identification number, analyst's name, date, total fibers counted, total fields counted, average count, fiber density, and commentary. Average count is calculated by dividing the total fiber count by the number of fields observed. Fiber density (fibers/mm^2) is defined as the average count (fibers/field) divided by the field (graticule) area (mm^2/field).

CALCULATIONS AND REPORTING OF RESULTS

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

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

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." Other fiber counts outside the 100-1300 fiber/mm^2 range should be reported as having "greater than optimal variability" and as being "probably biased."

21. Calculate and report the concentration, C (fibers/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 (from Step 11) with each set of results.

NOTE: Precision depends on the total number of fibers counted [1,16]. Relative standard deviation is documented in references [1,15-17] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Fig. 1).

EVALUATION OF METHOD:

A. This method is a revision of P&CAM 239 [10]. A summary of the revisions is as follows:
   1. Sampling:
      The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [10].
   2. Sample Preparation Technique:
      The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [2,4,10]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
   3. Measurement:
      a. The Walton-Beckett graticule standardizes the area observed [14,18,19].
      b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [4,14].
      c. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (a total of 78.5 fibers counted in 100 fields, each with field area = .00785 mm^2.) Lower levels generally result in an overestimate of the fiber count when compared to results in the recommended analytical range [20]. The recommended loadings should yield intracounter S_r in the range of 0.10 to 0.17 [21,22,23].

B. Interlaboratory comparability:
   An international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [9]. The relative standard deviations (S_r) varied with sample type and laboratory. The ranges were:

	Intralaboratory S_r	Interlaboratory S_r	Overall S_r
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)**	0.11 to 0.29	0.20 to 0.35	0.25

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

A NIOSH study conducted using field samples of asbestos gave intralaboratory S_r in the range 0.17 to 0.25 and an interlaboratory S_r of 0.45 [21]. This agrees well with other recent studies [9,14,16].

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

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

$$S_r = 1/(N)^{1/2} \quad (1)$$

Thus S_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual S_r found in a number of studies is greater than these theoretical numbers [17,19,20,21].

An additional component of variability comes primarily from subjective interlaboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [15] found this subjective component of intralaboratory S_r to be approximately 0.2 and estimated the overall S_r by the term:

$$\frac{[N + (0.2 \cdot N)^2]^{1/2}}{N} \quad (2)$$

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

In a study of field sample results in 46 laboratories, the Asbestos Information Association also found that the variability had both a constant component and one that depended on the fiber count [14]. These results gave a subjective interlaboratory component of S_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [21]. This value falls slightly above the range of S_r (0.25 to 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH PAT program for laboratory-generated samples [17].

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

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [16].

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

Note that the S_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory S_r is smaller, then it is more correct to use that smaller S_r. However, the estimated S_r of 0.45 is to be used in the absence of such information. Note also that it has been found that S_r can be higher for certain types of samples, such as asbestos cement [9].

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

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

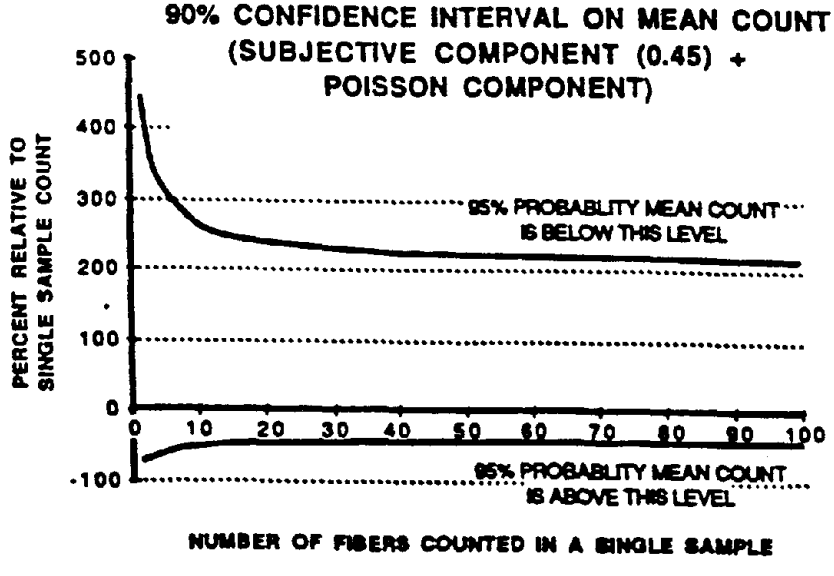

Figure 1. Interlaboratory Precision of Fiber Counts

The curves in Figures 1 are defined by the following equations:

$$UCL = \frac{2X + 2.25 + [(2.25 + 2X)^2 - 4(1 - 2.25 S_r^2) X^2]^{1/2}}{2(1 - 2.25 S_r^2)} \quad (3)$$

$$LCL = \frac{2X + 4 - [(4 + 2X)^2 - 4(1 - 4 S_r^2) X^2]^{1/2}}{2(1 - 4 S_r^2)} \quad (4)$$

where S_r = subjective interlaboratory relative standard deviation, which is close to the total interlaboratory S_r when approximately 100 fibers are counted.
X = total fibers counted on sample
LCL = lower 95% confidence limit.
UCL = upper 95% confidence limit.
Note that the range between these two limits represents 90% of the total range.

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METHOD WRITTEN BY:

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:

$$d_c = \frac{L_a}{L_o} \times D. \qquad (5)$$

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

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

APPENDIX B: COMPARISON OF COUNTING RULES:

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

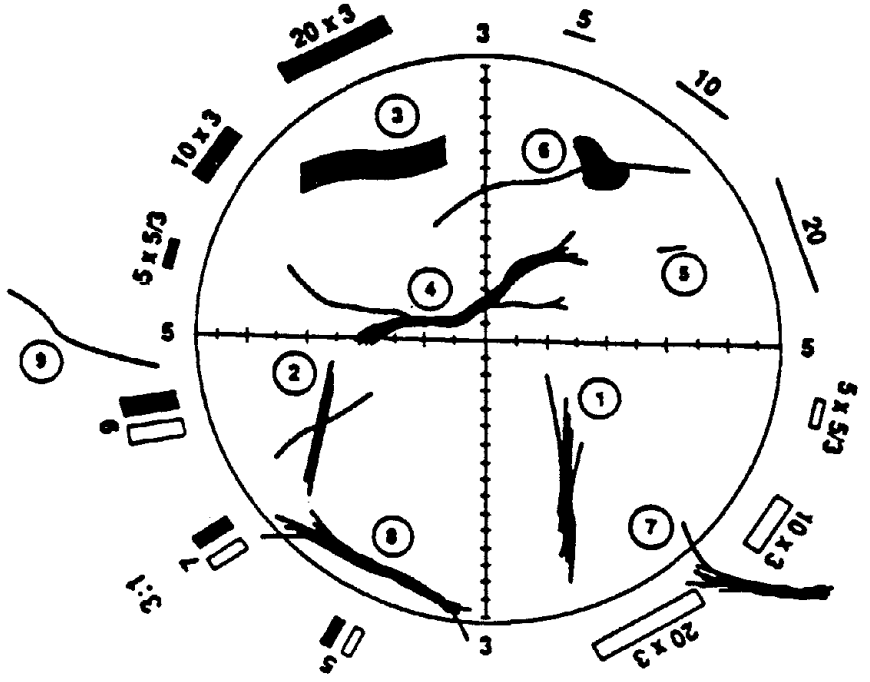

Figure 2. Walton-Beckett graticule with fibers.

These rules are sometimes referred to as the "A" rules.

FIBER COUNT

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

APPENDIX C. ALTERNATE COUNTING RULES FOR NON-ASBESTOS FIBERS

Other counting rules may be more appropriate for measurement of specific non-asbestos fiber types, such as fibrous glass. These include the "B" rules given below (from NIOSH Method 7400, Revision #2, dated 8/15/87), the World Health Organization reference method for man-made mineral fiber [24], and the NIOSH fibrous glass criteria document method [25]. The upper diameter limit in these methods prevents measurements of non-thoracic fibers. It is important to note that the aspect ratio limits included in these methods vary. NIOSH recommends the use of the 3:1 aspect ratio in counting fibers.

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

"B" COUNTING RULES:

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

APPENDIX D. EQUIVALENT LIMITS OF DETECTION AND QUANTITATION

fiber density on filter*		fiber concentration in air, f/cc	
fibers per 100 fields	fibers/mm^2	400-L air sample	1000-L air sample
200	255	0.25	0.10
100	127	0.125	0.05
LOQ.....80.....	.....102.....	.....0.10.....	.....0.04
50	64	0.0625	0.025
25	32	0.03	0.0125
20	25	0.025	0.010
10	12.7	0.0125	0.005
8	10.2	0.010	0.004
LOD.....5.5.....	.....7.....	.....0.00675.....	.....0.0027

* Assumes 385 mm^2 effective filter collection area, and field area = 0.00785 mm^2, for relatively "clean" (little particulate aside from fibers) filters.

ASBESTOS by TEM 7402

FORMULA: Various MW: Various CAS: Various RTECS: Various

METHOD: 7402 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 asbestos fibers (>5 μm long)/cc; 1 f/cc/30 min excursion; carcinogen
MSHA: 2 asbestos fibers/cc
NIOSH: 0.1 f/cc (fibers > 5 μm long)/400 L; carcinogen
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc; carcinogen

PROPERTIES: solid, fibrous, crystalline, anistropic

SYNONYMS [CAS#]: actinolite [77536-66-4] or ferroactinolite [15669-07-5]; amosite [12172-73-5]; anthophyllite [77536-67-5]; chrysotile [12001-29-5]; serpentine [18786-24-8]; crocidolite [12001-28-4]; tremolite [77536-68-6]; amphibole asbestos [1332-21-4].

SAMPLING

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

FLOW RATE: 0.5 to 16 L/min

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

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, TRANSMISSION ELECTRON (TEM)

ANALYTE: asbestos fibers

SAMPLE PREPARATION: modified Jaffe wick

EQUIPMENT: transmission electron microscope; energy dispersive X-ray system (EDX) analyzer

CALIBRATION: qualitative electron diffraction; calibration of TEM magnification and EDX system

RANGE: 100 to 1300 fibers/mm^2 filter area [1]

ESTIMATED LOD: 1 confirmed asbestos fiber above 95% of expected mean blank value

PRECISION ($\bar{S}_r$): 0.28 when 65% of fibers are asbestos; 0.20 when adjusted fiber count is applied to PCM count [2].

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

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

OTHER METHODS: This method is designed for use with Method 7400 (phase contrast microscopy).

REAGENTS:

1. Acetone. (See SPECIAL PRECAUTIONS.)

EQUIPMENT:

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

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

See CHLORINE, Method 6011, for procedure

Br_2 MW: 159.82 CAS: 7726-95-6 RTECS: EF9100000

METHOD: 6011, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.1 ppm
NIOSH: 0.1 ppm; STEL 0.3 ppm
ACGIH: 0.1 ppm; STEL 0.3 ppm
(1 ppm = 6.53 mg/m^3)

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

SYNONYMS: None.

SAMPLING

SAMPLER: PREFILTER + FILTER (PTFE, 0.5-μm + silver membrane, 25-mm, 0.45-μm)

FLOW RATE: 0.3 to 1 L/min

VOL-MIN: 8 L @ 0.1 ppm
-MAX: 360 L

SHIPMENT: routine, protect from light

SAMPLE STABILITY: ≥30 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.07 to 1.42 mg/m^3 (72-L samples)

BIAS: − 1.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069 [1]

ACCURACY: ± 13.6%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY

ANALYTE: bromide ion (Br^-)

EXTRACTION: 3 mL 6 mM $Na_2S_2O_3$, 10 min

INJECTION VOLUME: 50 μL

COLUMN: Dionex HPIC-AG4A guard, HPIC-AS4A separator, MFC-1 precolumn, AMMS anion suppressor

DETECTOR SETTING: 10 μS full scale

ELUENT: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol, 2 mL/min

CALIBRATION: standard solutions of Br^- in deionized water

RANGE: 5 to 150 μg Br^- per sample [1]

ESTIMATED LOD: 1.6 μg Br^- per sample [1]

PRECISION ($\bar{S}_r$): 0.045 @ 5 to 100 μg per sample [1]

APPLICABILITY: The working ranges for Br_2 and Cl_2 are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m^3) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m^3) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference upon a maximum of 15 μg per sample. HBr gives a positive interference as it is sampled continuously [1].

OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 μg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4 °C. Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the frozen samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125 μg 1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the $\bar{S}_r$ of the response was 0.016. Subsequently, simulated samples were exposed to known amounts of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463 μg per sample was 101.6% versus media standards and 91.3% versus standard solutions; the $\bar{S}_r$ of the response was 0.047. At 45.3 μg per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the $\bar{S}_r$ of the response was 0.048. At 4.64 μg per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the $\bar{S}_r$ of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 μg, with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the $\bar{S}_r$ of the response was 0.023. The $\bar{S}_r$ of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision ($\hat{S}_{rT}$) of the total sampling and analytical method was 0.060. For levels at and above 45 μg (0.8 ppm in 25 L), apparent biases may be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed significant breakthrough ($W_b > W_f/10$). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441 μg per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were -0.002 $\pm$ 0.003, 0.000 $\pm$ 0.003, -0.020 ± 0.002, 0.002 $\pm$ 0.002, and -0.019 ± 0.002, respectively. For the media standards, the respective pooled S_r for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 $\pm$ 0.4, 66.4 $\pm$ 0.3, 70.5 $\pm$ 0.2, 86.2 $\pm$ 0.3, and 91.2 $\pm$ 0.2.

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below -4 °C, and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 μg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092, 0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 $\pm$ 0.032, 0.961 $\pm$ 0.014, 0.994 $\pm$ 0.008, 1.029 $\pm$ 0.015, 1.064 $\pm$ 0.021, and 1.074 $\pm$ 0.021. Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the

2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080, 0.005 ± 0.128, -0.003 ± 0.092, 0.060 ± 0.179, 0.249 ± 0.188, and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per μg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable -- the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

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METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., Yvonne T. Gagnon, NIOSH/DPSE and John Palassis, NIOSH/DTMD.

APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [1] is 6 m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C_4 to C_6 hydrocarbons are present, interferences are likely. For the development of this method, a 50 m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al_2O_3/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10 m x 0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

CARBON DIOXIDE 6603

CO_2 MW: 44.01 CAS: 124-38-9 RTECS: FF6400000

METHOD: 6603 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 5000 ppm; STEL 30000 ppm
NIOSH: 5000 ppm; STEL 30000 ppm
ACGIH: 5000 ppm; STEL 30000 ppm
(1 ppm = 1.8 mg/m^3 @ NTP)

PROPERTIES: gas; sublimes @ − 78.5 °C

SYNONYMS: carbonic acid; dry ice

SAMPLING

SAMPLER: GAS SAMPLING BAG

FLOW RATE: 0.02 to 0.1 L/min; fill bag ≤ 80% of capacity; spot samples (step 2.a.) or TWA samples (step 2.b.)

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

FIELD BLANKS: in bag from a non-work area

ACCURACY

RANGE STUDIED: 2270 - 10000 ppm [3] (3.5-L samples)

ACCURACY: ± 5.3% [1]

BIAS: −2.5% [3]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.014 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), TCD

ANALYTE: carbon dioxide

TEMPERATURE-INJECTION: ambient
-DETECTOR: 70 °C
-COLUMN: ambient

CARRIER GAS: He, 100 mL/min

COLUMN: 1.5 m x 6-mm ID stainless steel, packed with 80/100 mesh Poropak QS

DETECTOR: thermal conductivity

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 500 - 15000 ppm [2]

ESTIMATED LOD: 1 ppm

PRECISION ($\hat{S}_r$): 0.005 [1]

APPLICABILITY: The working range is 500 to 15000 ppm (900 to 2700 mg/m^3) in relatively non-complex atmospheres.

INTERFERENCES: Any compound having the same or nearly the same retention time as carbon dioxide on the column in use.

OTHER METHODS: This is method S249 in a revised format [2].

REAGENTS:

1. Carbon dioxide,* 99% or higher purity
2. Nitrogen,* purified
3. Helium,* purified
4. Air*, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with thermal conductivity detector, column (p. 6603-1), and 5-mL gas sampling loop.
2. Strip chart recorder, if appropriate. (Many GCs have built-in data-handling capabilities)
3. Personal sampling pump, 0.02 to 0.1 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
4. Sample bags, five-layer, 2- to 20- L, or other appropriate sizes, fitted with a metal valve and hose bib (Calibrated Instruments, 731 Saw Mill Rd., Ardsley, NY 10502, or equivalent).
5. Gas-tight syringes, 10 mL and other convenient sizes for making standards and GC injections if GC is not equipped with gas sampling loop.
6. Calibrated rotameters, for standards preparation.
7. Label tape and marking pens for labelling bags.

SPECIAL PRECAUTIONS: Shipment of compressed must comply with 49 CFR 171-177, DOT regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC and recorder (if applicable) and allow to warm up according to manufacturer's instructions.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. **Spot sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.
   b. **Integrated air sample for TWA determination.**
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to the outlet port of the personal sampling pump with a minimum length of flexible tubing.
      (3) Pump the air sample into the bag at a rate calculated to fill $\leq$80% of the sample bag capacity over the sampling period.
      NOTE: The flow rate must be known to $\pm$5% throughout the sampling period.
      (4) Within 24 hours after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2a).
3. Obtain the carbon dioxide peak height of the injected sample.
   NOTE: Under these conditions, carbon dioxide elutes at about 2 min, after oxygen and nitrogen.

CHLORINE 6011

Cl_2 MW: 70.91 CAS: 7782-50-5 RTECS: FO2100000

METHOD: 6011, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 1 ppm
NIOSH: 0.5 ppm; STEL 1 ppm
ACGIH: 0.5 ppm; STEL 1 ppm
(1 ppm = 2.90 mg/m^3 @ NTP)

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

SYNONYMS: None.

SAMPLING

SAMPLER: PREFILTER + FILTER (PTFE, 0.5-μm + silver membrane, 25-mm, 0.45-μm)

FLOW RATE: 0.3 to 1 L/min

VOL-MIN: 2 L @ 0.5 ppm
-MAX: 90 L

SHIPMENT: routine, protect from light

SAMPLE STABILITY: ≥30 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.35 to 6.77 mg/m^3 (15-L samples)

BIAS: − 1.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.075 [1]

ACCURACY: ± 14.8%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY

ANALYTE: chloride ion (Cl^-) or bromide ion (Br^-)

EXTRACTION: 3 mL 6 mM $Na_2S_2O_3$, 10 min

INJECTION VOLUME: 50 μL

COLUMN: Dionex HPIC-AG4A guard, HPIC-AS4A separator MFC-1 precolumn, AMMS anion suppressor

DETECTOR SETTING: 10 μS full scale

ELUENT: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol, 2 mL/min

CALIBRATION: standard solutions of Cl^- in deionized water

RANGE: 2 to 50 μg Cl^- per sample [1]

ESTIMATED LOD: 0.6 μg Cl^- per sample [1]

PRECISION ($\hat{S}_r$): 0.067 @ 5.3 to 100 μg per sample [1]

APPLICABILITY: The working ranges for Br_2 and Cl_2 are 0.008 to 0.4 ppm (0.06 to 2.6 mg/m^3) and 0.007 to 0.5 ppm (0.02 to 1.5 mg/m^3) respectively for a 90-L air sample. The method has sufficient sensitivity for STEL samples.

INTERFERENCES: Hydrogen sulfide gives a negative interference. HCl gives a positive interference up to a maximum of 15 μg per sample. HBr gives a positive interference as it is sampled continuously [1].

OTHER METHODS: P&CAM 209 (colorimetric) [2], OSHA Methods ID-101 [3] and ID-108 [4] are alternative methods.

REAGENTS:

1. Sodium thiosulfate, reagent grade.
2. Water, deionized.
3. Extraction solution: 6 mM $Na_2S_2O_3$. Dissolve 0.474 g $Na_2S_2O_3$ in 500 mL deionized water.
4. Eluent: 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol. Dissolve 0.041 g $NaHCO_3$, 0.848 g Na_2CO_3 and 0.186 g p-cyanophenol in 2 L filtered deionized water.
5. Suppressor regenerant, 0.025 N H_2SO_4. Dilute 2.8 mL conc. H_2SO_4 to 4 L with deionized water.*
6. Calibration stock solutions, 1 mg/mL (as anion).
   (1) Dissolve 0.149 g KBr in 100 mL deionized water
   (2) Dissolve 0.21 g KCl in 100 mL deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Silver membrane filter,* 25-mm, 0.45-μm, (Costar/Nuclepore, Poretics, or equivalent) with porous plastic support pad (Costar/Nuclepore); prefilter, PTFE with PTFE support, 0.5-μm (Gelman Zefluor, SKC, or equivalent), or polyester, 0.4-μm (Costar/Nuclepore) with porous plastic support pad; three-piece, 25-mm carbon-filled polypropylene cassette (opaque) with 50-mm extension (Costar/Nuclepore or Gelman) (Fig. 1).
   a. In the outlet piece of cassette, place porous plastic support pad and cleaned silver filter. Insert 50-mm extension (cowl) securely.
   b. At the inlet (top) of the extension, place porous plastic support pad and prefilter. Insert inlet cassette piece securely.
   c. Seal each connection with shrinkable bands or tape.
2. Personal sampling pump, 0.3 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph with Dionex MFC-1, HPIC-AG4A, HPIC-AS4A columns, AMMS anion micromembrane suppressor, conductivity detector and integrator (page 6011-1).
4. Bottles, 30-mL, wide mouth with screw caps, amber or opaque polyethylene.
5. Micropipettes, with disposable tips.
6. Volumetric flasks, 10- and 100-mL.
7. Repipet reagent dispensers, 0 to 10-mL.
8. Syringes, 10-mL, polyethylene, luer-tip.
9. Forceps.

* Silver membrane filters must be cleaned prior to use (see APPENDIX A).
NOTE: Some lots of silver membrane filters contain excessively high chloride background levels. Please screen before field use.

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

SAMPLING:

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

SAMPLE PREPARATION:

NOTE: Silver halides are photosensitive. Protect from light during transfer and desorption.

5. Under very dim or red light, open cassette and transfer the silver filter with forceps to amber bottle. Add 3 mL 6 mM $Na_2S_2O_3$ and cap.
   NOTE: Prefilter may be analyzed for particulate halides, or discarded.
6. Allow samples to stand a minimum of 10 min with occasional swirling.
   NOTE: Once desorbed, samples are no longer photosensitive.
7. Uncap the sample bottles and add 7 mL deionized water for a total solution volume of 10 mL.
8. Pour sample into 10-mL plastic syringe for manual injection or into autosampler vials.

CALIBRATION AND QUALITY CONTROL:

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

MEASUREMENT:

11. Set ion chromatograph according to manufacturer's instructions and to conditions given on page 6011-1.
    NOTE: Excessive amounts of Ag^+ and $Ag(S_2O_3)_2^{3-}$ deteriorate column preformance. Use a metal free column (MFC-1) prior to the chromatographic columns and recondition the column every 100 to 150 analyses (See APPENDIX B).
12. Inject 50-μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from syringe to ensure complete rinse of the sample loop.
13. Measure peak height. If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

The method was evaluated by sampling generated atmospheres of Br_2 and Cl_2 at both high (80%) and low (20%) relative humidities [1]. Samples were taken at four concentration levels ranging from 0.007 to 1.42 mg/m^3 for Br_2 and 0.354 to 6.77 mg/m^3 for Cl_2. Overall recovery for Br_2 was 98.8% with total overall precision, $\hat{S}_{rT}$, of 6.8%. Overall recovery for Cl_2 was 98.6% with total overall precision, $\hat{S}_{rT}$, of 6.7%. Samples for Cl_2 were stable at least 30 days at 25 °C (103 ± 4% Recovery) and up to 60 days at 5 °C (101 ± 3% Recovery). The Br_2 samples were stable up to 60 days at 25 °C (99.2 ± 10.1% Recovery).

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[4] Occupational Safety and Health Administration Analytical Laboratory: OSHA Analytical Methods Manual, (Method No. ID-108). American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1985; Publ. No. ISBN: 0-936712-66-X.

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE

APPENDIX A: CLEANING PROCEDURE FOR SILVER MEMBRANE FILTERS

NOTE: Some lots of silver membrane filters contain extremely high chloride background levels. If excessively high this cleaning procedure will not remove all of the chloride, even if repeated several times. Screening is necessary for each lot before being used for this method. Screening may be done by following this procedure at least twice, or by analyzing by XRD.

1. Place each filter in a 30-mL, wide-mouth bottle, and add 3 mL 6 mM $Na_2S_2O_3$.
2. Allow to stand for a minimum of 10 min with occasional swirling.
3. Discard solution and rinse thoroughly with deionized water. Allow the filters to stand in last rinse for a few minutes.
4. Remove filters from bottles and dry between layers of absorbent laboratory towels.
5. Store cleaned filters between paper disks in manufacturer's container. Filters are stable for at least 8 months.

APPENDIX B: COLUMN RECONDITIONING PROCEDURE

In the following order, pump through the analytical columns at 2 mL/min:

a. 30 mL deionized water to rinse;
b. 60 mL 1 *M* HNO_3 to remove contaminants;
c. 30 mL 0.1 *M* Na_2CO_3 to remove the NO_3^-;
d. Eluent to equilibrate.

Reconditioning is recomended after 100 to 150 analyses.

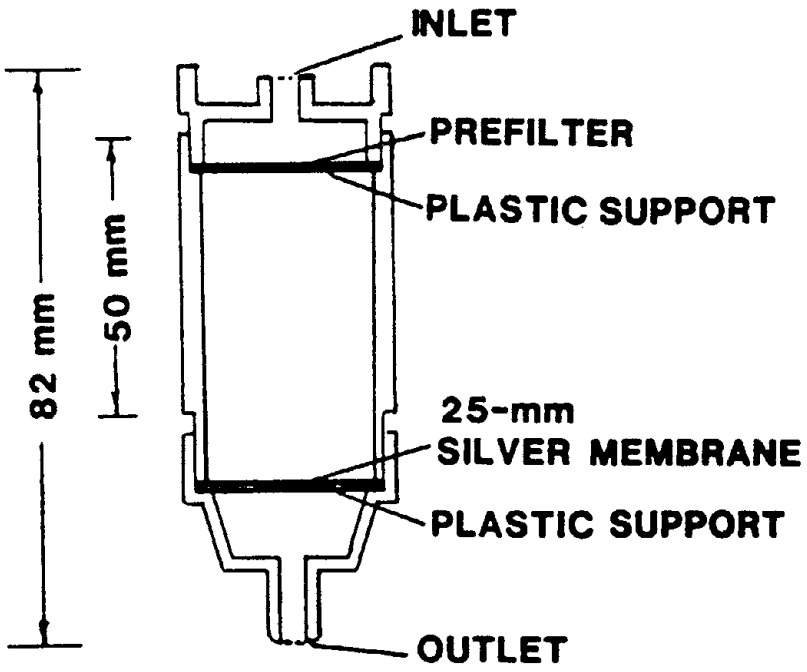

Figure 1. Silver Filter Sampler

CYANIDES, aerosol and gas

HCN and salts	MW: 27.03 (HCN); 65.11 (KCN)	CAS: 74-90-8 (HCN); 151-50-8 (KCN)	RTECS: MW6825000 (HCN); TS8750000 (KCN)

METHOD: 7904, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 11 mg/m^3; skin (HCN)
5 mg/m^3; skin (cyanides, as CN^-)
NIOSH: C 5 mg/m^3/10 min (as CN^-)
ACGIH: C 11 mg/m^3; skin (HCN);
5 mg/m^3; skin (cyanides, as CN)

PROPERTIES: HCN: gas, BP 26 °C; VP 620 mm Hg 20 °C; vapor density 0.94 (air = 1); KCN: solid, d 1.52 g/mL, MP 634 °C

SYNONYMS: HCN: hydrocyanic acid, prussic acid, formonitrile, cyanides.

SAMPLING

SAMPLER:	FILTER + BUBBLER (0.8-μm PVC membrane + 15 mL 0.1 N KOH) [1]
FLOW RATE:	0.5 to 1 L/min
VOL-MIN:	10 L @ 0.5 mg/m^3 (as CN^-)
-MAX:	180 L @ 11 mg/m^3 (as CN^-)
SHIPMENT:	routine
SAMPLE STABILITY:	analyze within 5 days; particulate on filter may liberate HCN gas [2]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	5 to 21 mg/m^3 (HCN) [3]; 2.6 to 10 mg/m^3 (KCN) [2]
BIAS:	− 7.6%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.062 (HCN) [3]; 0.103 (KCN) [2]
ACCURACY:	± 20.0%

MEASUREMENT

TECHNIQUE:	ION-SPECIFIC ELECTRODE
ANALYTE:	cyanide ion (CN^-)
EXTRACT FILTER:	25 mL 0.1 N KOH; 30 min
RINSE BUBBLER:	2 mL 0.1 N KOH; dilute to 25 mL with 0.1 N KOH
MEASURE:	mV reading of cyanide ion electrode vs. reference electrode
CALIBRATION:	solutions of KCN in 0.1 N KOH
RANGE:	0.05 to 2 mg CN^-
ESTIMATED LOD:	2.5 μg CN^- [2]
PRECISION ($\bar{S}_r$):	0.043 (HCN) [3]; 0.038 (KCN) [2]

APPLICABILITY: The working range (as CN^-) is 0.5 to 15 mg/m^3 for a 90-L air sample or 5 to 20 mg/m^3 for a 10-L air sample.

INTERFERENCES: Sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron and mercury interfere. In humid atmospheres, some particulate cyanide collected on the filter will liberate hydrogen cyanide which will be trapped in the bubbler [2]. The method cannot distinguish between HCN formed in this manner and HCN originally present in air.

OTHER METHODS: This method combines and replaces Methods S288 [4], S250 [5], and P&CAM 116 [6]. Method 6010 (Hydrogen Cyanide) uses a soda lime tube as sampler, with colorimetric measurement.

REAGENTS:

1. Deionized water.
2. Potassium cyanide.*
3. Calibration stock solution, 1000 μg/mL CN^-. Dissolve 0.250 g KCN in 0.1 N KOH to make 100 mL solution. Stable for at least 1 week in polyethylene bottle.
4. Potassium hydroxide (KOH), 0.1 N. Dissolve 5.6 g KOH in deionized water; dilute to 1000 mL.
5. Lead acetate paper.
6. Cadmium carbonate (if sulfide present).
7. Hydrogen peroxide, 30% (if sulfide present).
8. Sodium sulfite, 1 M (if sulfide present).

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride membrane filter, 37-mm diameter, 0.8-μm pore size in 2-piece filter cassette holder, followed by a glass midget bubbler containing 15 mL 0.1 N KOH.
2. Personal sampling pump, 0.5 to 1 L/min, with splashover protection and flexible connecting tubing.
3. Vials, polyethylene, with screw caps, 20-mL, and plastic tape for sealing.
4. Cyanide ion electrode, (Orion 94-06 or equivalent).
5. Reference electrode.
6. pH meter, readable to 0.1 mV.
7. Magnetic stirrer and stirring bars.
8. Jars, ointment, 60-mL, squat-form with aluminum-lined screw caps.
9. Pipets, 0.05- to 2 and 25-mL, with pipet bulb.
10. Volumetric flasks, 25-mL.
11. Beakers, 50-mL.
12. Analytical balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hydrogen cyanide gas and the cyanide particulates may be fatal if swallowed, inhaled or absorbed through the skin. Work in a hood.

Amyl nitrite is the antidote for cyanide poisoning [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 0.5 to 1 L/min for a total sample size of 10 to 180 L.
   NOTE: Maintain bubblers in a vertical position during sampling. Do not allow the solution level to fall below 10 mL.
3. Remove the bubbler stem and tap it gently against the inside wall of the bubbler. Rinse the bubbler stem with 1 to 2 mL of unused 0.1 N KOH. Add the rinse to the bubbler.
4. Quantitatively transfer the contents of the bubbler to a 20-mL vial. Close cap tightly and wrap with plastic tape to avoid sample loss during transit. Label each vial.

SAMPLE PREPARATION:

5. Transfer the filter from the cassette filter holder to a 60-mL ointment jar.
6. Pipet 25.0 mL 0.1 N KOH into the jar. Cap and allow to stand for at least 30 min with occasional shaking to complete extraction. Analyze within 2 h after extraction.
7. Empty the contents of the vial into a 25-mL volumetric flask using 0.1 N KOH to rinse the vial. Add rinse to the volumetric flask. Dilute to the mark with 0.1 N KOH.
   NOTE: Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if present. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper; the paper will discolor in the presence of sulfide ion. If this test is positive, remove sulfide by one of the following methods:
   a. Add 1 mL 1 M H_2O_2 and 1 mL 1 M Na_2SO_3 to sample solutions prior to diluting to volume.

$(CH_3)_2NNH_2$ MW: 60.10 CAS: 57-14-7 RTECS: MV2450000

METHOD: 3515, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : C 0.5 ppm (skin)
NIOSH: C 0.06 ppm/120 min; carcinogen
ACGIH: C 0.5 ppm (skin); suspected human carcinogen
(1 ppm = 2.46 mg/m^3 @ NTP)

PROPERTIES: liquid; MP - 58 °C; BP 63 °C; d 0.80 @ 20 °C; VP 157 mm Hg @ 25 °C; vapor density (air = 1) 2.07; flash point - 15 °C (closed cup); flammable range 2 to 95% v/v in air

SYNONYMS: dimazine; unsym-dimethylhydrazine; N,N-dimethylhydrazine.

SAMPLING

SAMPLER: BUBBLER
(0.1 M hydrochloric acid)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 2 L @ 0.5 ppm
-MAX: 100 L

SHIPMENT: remove bubbler stem and rinse with 0.1 M hydrochloric acid; seal bubbles with non-reactive stopper

SAMPLE STABILITY: at least 5 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.506 to 2.22 mg/m^3 [1] (91-L samples)

BIAS: − 1.9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 14.0%

MEASUREMENT

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: complex of phosphomolybdic acid and 1,1-dimethyl hydrazine

PROCEDURE: add phosphomolybdic acid; heat sample solution at 95 °C for 60 min; cool solution under tap water; transfer sample to 1-cm cell; read absorbance at 730 nm

CALIBRATION: standard solutions of 1,1-dimethylhydrazine in 0.1 M hydrochloric acid

RANGE: 2 to 250 μg per sample [1]

ESTIMATED LOD: 1 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.072 [1]

APPLICABILITY: The working range is 0.008 to 1 ppm (0.02 to 2.5 mg/m^3) for a 100-L air sample. This method is also applicable to ceiling measurements.

INTERFERENCES: Other hydrazines, as well as, stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide, may give a positive interference. Negative interferences in the method may occur by oxidation of the 1,1-dimethylhydrazine by halogens, oxygen (especially in the presence of copper (I) ion) and hydrogen dioxide.

OTHER METHODS: This revises Method S143 [2]. Method P&CAM 248 [3] describes an acid-coated silica gel sorbent tube/gas chromatographic method for the determination of hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine. Sample stability problems have been noted with P&CAM 248 [4].

REAGENTS:

1. 1,1-Dimethylhydrazine,* ACS reagent grade.
2. Hydrochloric acid, ACS reagent grade.
3. Collection medium, 0.1 M hydrochloric acid. To 300 mL of distilled water in a 1000-mL volumetric flask, add 8.6 mL of concentrated hydrochloric acid with caution. Mix and bring to volume with distilled water.
4. Phosphomolybdic acid solution. Dissolve 15 g of phosphomolybdic acid in 500 mL distilled water, allow to stand one day, and filter through a fluted paper filter.
5. Water, deionized and distilled.
6. Calibration stock solution, 1 mg/mL. Weigh 500 mg of 1,1-dimethylhydrazine in a 100-mL volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

EQUIPMENT:

1. Sampler: 25-mL bubbler with 10 mL 0.1 M hydrochloric acid.
2. Personal sampling pump, 0.2 to 1.0 L/min, with flexible polyethylene or PTFE tubing.
3. Glass or non-reactive stopper for bubbler.
4. Glass tube, 5 cm long by 6-mm I.D., loosely packed with glass wool.
5. Spectrophotometer, set at 730 nm.
6. 1-cm spectrophotometer cells.
7. Test tube, large.
8. Volumetric flasks, 50-mL, 100-mL, 500-mL, 1000-mL.
9. Pipets, 10-, 15-, 25, and 50-μL; 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 95 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

* See SPECIAL PRECAUTIONS.

SPECIAL PRECAUTIONS: 1,1-Dimethylhydrazine may be fatal if inhaled, swallowed or absorbed through the skin [5]. Contact may cause burns to skin and eyes. Vapor may be irritating to the eyes, skin, and mucous membranes. Handle with caution and use appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 10 mL 0.1 M hydrochloric acid to a bubbler.
3. Connect outlet arm of bubbler to the glass-wool-packed tube (to prevent splashover into the pump) and then to the sampling pump with the flexible tubing.
4. Sample at an accurately known rate of 0.2 to 1.0 L/min for total sample size of 2 to 100 L.
5. Remove bubbler stem and rinse with 2 mL of 0.1 M hydrochloric acid into bubbler body. Seal bubbler with an inert stopper for shipment in a suitable container in order to prevent damage during transit.

SAMPLE PREPARATION:

6. Transfer the liquid from the bubbler, quantitatively, to a volumetric flask.
7. Add 10 mL of phosphomolybdic acid solution and bring volume to 50 mL with 0.1 M hydrochloric acid.
8. Transfer an aliquot of this solution to a large test tube and heat to 95 °C for 60 min. Place test tube under running tap water to cool before measurement.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards to cover the range of 1 to 250 μg 1,1-dimethyl hydrazine per sample.

DIOXANE 1602

$C_4H_8O_2$ MW: 88.11 CAS: 123-91-1 RTECS: JG8225000

METHOD: 1602, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 100 ppm (skin)
NIOSH: 1 ppm/30 min; carcinogen
ACGIH: 25 ppm (skin); carcinogen
(1 ppm = 3.60 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.0337 g/mL @ 20 °C;
BP 101 °C; MP 12 °C
VP 3.9 kPa (29 mm Hg; 3.8% v/v) @ 20 °C;
explosive range 2 to 22% v/v in air

SYNONYMS: dioxan; p-dioxane; 1,4-diethylene dioxide; diethylene ether

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 100 ppm
-MAX: 15 L

SAMPLE STABILITY: >1 week @ 25 °C
>6 weeks @ −10 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 157 to 660 mg/m^3 [1]
(10-L samples)

BIAS: + 9%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.054 [1]

ACCURACY: ± 18.7

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dioxane

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 75 °C

CARRIER GAS: He, 30 mL/min (60 psig)

COLUMN: 6 m x 3-mm stainless steel packed with 10% FFAP on 80/100 mesh Chromosorb W-HP Chromosorb W-HP

CALIBRATION: solutions of dioxane in CS_2 with internal standard

RANGE: 0.2 to 7 mg per sample [1,2]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION ($\hat{S}_r$): 0.017 [1]

APPLICABILITY: The working range is 5.5 to 190 ppm (20 to 700 mg/m^3) for a 10-L air sample.

INTERFERENCES: None known. An alternate GC column is 30 m x 0.32-mm ID fused silica capillary coated with 1 µm DB-5 [3].

OTHER METHODS: This method combines and replaces S360 [4] and P&CAM 127 [5] for dioxane. A similar method appears in the dioxane criteria document [6].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% (v/v) octane, decane, or other suitable internal standard.
2. Dioxane, reagent grade.*
3. Desorption efficiency (DE) stock solution, 0.1 mg/μL. Dilute 1 g dioxane to 10 mL with pentane.
4. Helium, purified.
5. Hydrogen, prepurified.
6. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1602-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1-μL.
6. Volumetric flasks, 10-mL.
7. Pipet, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C).

Dioxane is toxic, causing central nervous system depression and necrosis of liver and kidneys, as well as a skin irritant [6], and a suspect carcinogen [7]. Use personal protective equipment and work only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 15 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 7 mg dioxane per sample.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties		Air Volume, L @ OSHA PEL	
	Atomic Weight	MP, °C	MIN	MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Sodium (Na)	22.99	98	13	2000
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Platinum (Pt)	195.09	1769	1250	2000
Selenium (Se)	78.96	217	13	2000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m^3 (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total) 5 (respirable)	5	10 (dust) 5 (fume)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	--	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.2, C 0.6 (dust) 0.1, C 0.3 (fume)	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05	0.05 (dust, fume)
Chromium (II) (Cr)	22541-79-3	GB6260000	0.5	0.5	0.5
Chromium (III) (Cr)	16065-83-1	GB6261000	0.5	0.5	0.5
Chromium (VI) (Cr)	18540-29-9	GB6262000	C 0.1	0.001 (dust)	0.05 (soluble) 0.05 (insoluble), Ca
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	1309-37-1	NO7400000	10 (dust, fume)	5 (dust, fume)	5 (fume)
Lithium (Li)	--	--	--	--	--
Magnesium (Mg)	1309-48-4	OM3850000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble) 5 (respirable insol.)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.05, Ca
Lead (Pb)	7439-92-1	OF7525000	0.05	<0.1	0.15
Platinum (Pt)	7440-06-4	TP2160000	0.002	1 (metal)	1 (metal)
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti) TiO_2	7440-32-6 13463-67-7	XR1700000 XR2275000	as TiO_2, 15 as TiO_2, 5 (respirable)	lowest feasible, Ca	10
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V) V_2O_5	7440-62-2 1314-62-1	YW240000 YW1355000	C 0.5 (respirable) as V_2O_5 C 0.1 (fume) as V_2O_5	C 0.05	0.05 (respir.) as V_2O_5
Yttrium (Y)	7440-65-5	ZG2980000	1	1	1
Zinc (Zn)	1314-13-2	ZH4810000	5 (ZnO fume) 15 (ZnO dust) 5 (ZnO respirable)	5; STEL 10 (ZnO fume) 5; C 15 (ZnO dust)	5; STEL 10 (ZnO fume) 10 (ZnO dust)
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

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METHOD WRITTEN BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS.

TABLE 1. GENERAL INFORMATION

Element (Formula)	Atomic Weight	CAS#	RTECS
Antimony (Sb)	121.75	7440-36-0	CC4025000
Cadmium (Cd)	112.40	7440-43-9	EU9800000
Cobalt (Co)	58.93	7440-48-4	GF8750000
Chromium (Cr)	52.00	7440-47-3	GB4200000
Copper (Cu)	63.54	7440-50-8	GL5325000
Iron (Fe)	55.85	7439-89-6	NO4565500
Lanthanum (La)	138.91	7439-91-0	--
Lead (Pb)	207.19	7439-92-1	OF7525000
Lithium (Li)	6.94	7439-93-2	OJ5540000
Magnesium (Mg)	24.31	7439-95-4	OM2100000
Manganese (Mn)	54.94	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	7439-98-7	QA4680000
Nickel (Ni)	58.71	7440-02-0	QR5950000
Platinum (Pt)	195.09	7440-06-4	TP2160000
Silver (Ag)	107.87	7440-22-4	VW3500000
Strontium (Sr)	87.62	7440-24-6	--
Thallium (Tl)	204.37	7440-28-0	XG3425000
Vanadium (V)	50.94	7440-62-2	YW1355000
Zinc (Zn)	65.37	7440-66-6	ZG8600000
Zirconium (Zr)	91.22	7440-67-7	ZH7070000

TABLE 2. RECOVERY OF METALS FROM BLOOD [1,2].

Element (Formula)	Wavelength (nm)	Value[a] (µg/100 mL)	Metal "Nonexposed" Added (µg/Sample)	Quantity Recovery (%)	Precision (% s_r) n = 4	Accuracy (±%)
Antimony (Sb)	217.58	0.4	10	106	4.9	15.6
Cadmium (Cd)	226.5	0.5	10	120	1.1	22.2
Cobalt (Co)	231.2	1.0	10	81	21	60.2
Chromium (Cr)	205.6	4.5	10	114	4.7	23.2
Copper (Cu)	324.8	100	10	101	5.8	12.4
Iron (Fe)	45,000	0	--[b]	--[b]		--
Lanthanum (La)	--[c]	10	119	2.4		23.7
Lead (Pb)	220.4	23	10	113	0.85	14.7
Lithium (Li)	670.8	1.0	10	113	1.1	15.2
Magnesium (Mg)	279.6	3,800	110	104	12	27.5
Manganese (Mn)	257.6	4.0	10	98	2.1	6.1
Molybdenum (Mo)	281.6	4.0	10	126	3.1	32.1
Nickel (Ni)	231.6	5.0	10	86	16	45.4
Platinum (Pt)	203.7	--[c]	10	92	14	35.4
Silver (Ag)	328.3	3.5	10	115	0.8	16.6
Strontium (Sr)	421.5	2.8	10	113	0.88	14.7
Thallium (Tl)	190.9	1.0	10	97	8.7	20.0
Vanadium (V)	310.2	1.2	10	131	1.1	33.2
Zinc (Zn)	213.9	700	60	103	17	36.3
Zirconium (Zr)	339.2	1.5	10	71	8.7	46.0

[a]"Nonexposed" value is the average concentration for the respective element in blood of non-occupationally exposed individuals. These values were tabulated from References [6] through [19].

[b]Recovery not determined (blood Fe concentration was above quantitation limit of spectrometer).

[c]Concentration not reported.

ETHYL ACETATE

$CH_3COOC_2H_5$ MW: 88.10 CAS: 141-78-6 RTECS: AH5425000

METHOD: 1457, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 400 ppm
NIOSH: 400 ppm
ACGIH: 400 ppm
(1 ppm = 360 mg/m^3 @ NTP)

PROPERTIES: liquid, d = 0.8945 g/mL @ 25 °C; BP = 77 °C; VP = 9.7 kPa (73 mm Hg) @ 20 °C

SYNONYMS: acetic ether; acetic ester; ethyl ethanoate

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/minute

VOL-MIN: 0.1 L @ 1400 mg/m^3
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 6 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 704 to 2950 mg/m^3 [2] (6-L samples)

BIAS: −2.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.058 [2]

ACCURACY: ±11.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: ethyl acetate

EXTRACTION: 1 mL CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C, 2 min; 10 °C/min to 150 °C

COLUMN: DB-Wax; 30 m, 0.32-mm ID, 1-µm film thickness

CARRIER GAS: He, 1 mL/min

MAKEUP GAS: N_2, 30 mL/min

CALIBRATION: standard solutions of ethyl acetate in CS_2

RANGE: 1.5 to 1,000 µg per sample [1]

ESTIMATED LOD: 0.5 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.019 @ 40.5 to 810 µg per sample [1]

APPLICABILITY: The working range is 0.07 to 790 ppm (0.25 to 2800 mg/m^3) for a 6-L air sample [2]. The method may be adapted for other esters with appropriate changes in chromatographic conditions.

INTERFERENCES: Any compounds with similar retention times.

OTHER METHODS: This revises Method S49 [2]. Improved recovery of analyte may be achieved with the addition of 5% butyl carbitol to the CS_2 desorption procedure [3,4].

REAGENTS:

1. Carbon disulfide,* chrom. grade.
2. Ethyl acetate, reagent grade.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1457-1).
5. Vials, glass, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL and other convenient sizes for preparing standards, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = −30 °C.) Use only in a hood.

SAMPLING:

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

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
   NOTE: Decane or other suitable internal standard at 0.1% v/v may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 8 to 1000 μg analyte per sample.
   a. Add known amounts of analyte to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area of analyte vs. mg ethyl acetate).

FORMALDEHYDE by GC 2541

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2541, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.75 ppm; 2 ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

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

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v HCHO); methylene oxide

SAMPLING

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

FLOW RATE: 0.01 to 0.10 L/min

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

SHIPMENT: routine

SAMPLE STABILITY: 3 weeks @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 10 per sample set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of formaldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

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

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

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

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

CALIBRATION: formalin solution spiked on sorbent

RANGE: 3 to 200 µg per sample [2,3]

ESTIMATED LOD: 1 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.0052 @ 38 to 194 µg per sample [2]

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

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

OTHER METHODS: OSHA Method 52 is similar but uses slightly larger sampling tubes [2]. This method has improved sample stability and ease of personal sampling compared to NIOSH Methods 2502 (which has been withdrawn), 3500 and 3501. However, Method 3500 (chromotropic acid) is the most sensitive.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Formalin solution, 37%*.
4. Formaldehyde* stock solution, 1 mg/mL (see Appendix A).
5. Sulfuric acid, 0.02 N.
6. Sodium hydroxide, 0.01 N.
7. Sodium sulfite (Na_2SO_3), 1.13 M. Prepare fresh immediately before use.
8. Water, deionized, distilled
9. Hydrogen, prepurified.
10. Air, filtered.
11. Helium, purified
12. Magnesium sulfate.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, with flame-sealed ends and plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX B) (front = 120 mg; back = 60 mg) retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 kPa (5.7 mm Hg). Tubes are commercially available (Supelco ORBO-23; SKC 226-118; or equivalent).
2. Personal sampling pump, 0.01 to 0.10 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2541-1).
4. Ultrasonic water bath.
5. Vials, glass, 2-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Syringes, 10-mL (readable to 0.1 mL), 25-, and 50-mL.
9. File.
10. Beakers, 50-mL.
11. pH meter.
12. Magnetic stirrer.
13. Burets, 50-mL.
14. Flasks, round-bottomed, 100-mL.
15. Soxhlet extraction apparatus.
16. Vacuum oven.
17. Distillation apparatus.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen [4,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.10 L/min for a total sample size of 1 to 36 L.
   NOTE: Formaldehyde reacts with 2-(hydroxymethyl)piperidine on the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Sampling above 0.10 L/min may cause appreciable breakthrough owing to incomplete reaction, possibly invalidating the sample. Further discussion of this reaction is included in Ref. [6].
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

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

FORMALDEHYDE by VIS 3500

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 3500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 0.75 ppm; 2ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen;
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

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

SYNONYMS: methanal; formalin (aqueous 30 to 60 % w/v HCHO); methylene oxide

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 day @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.25 to 7.5 mg/m^3 [2] (80-L samples)

BIAS: none identified

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 [2]

ACCURACY: ± 18%

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 [1,2]

ESTIMATED LOD: 0.5 μg per sample [2,3]

PRECISION ($\bar{S}_r$): 0.03 @ 1 to 20 μg per sample [3]

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 of Analytical Methods and is able to measure ceiling levels as low as 0.1 ppm (15-L sample). It is best suited for the determination of formaldehyde in area samples.

INTERFERENCES: Oxidizable organic materials may give a positive interference [2]. Phenol to formaldehyde ratios as low as 0.3 produce a - 15% bias [4]. A method for the removal of the phenol interference has been reported by Hakes et. al. [5]. Ethanol and higher M.W. alcohols, olefins, aromatic hydrocarbons [6] and cyclohexanone also produce small negative interferences [7]. Little interference is seen from other aldehydes [7].

OTHER METHODS: This method was originally adapted from the Intersociety Committee [8] and designated P&CAM 125 [4]. For personal samples or where interferences to this method are present, use Method 2541. Ref [9] is a recent review of formaldehyde methods.

REAGENTS:

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

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

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

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles. Formaldehyde is viewed as a potential carcinogen [9,10] and should be handled in a hood.

SAMPLING:

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

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Record volume of solution from front impinger, V_f (mL) and backup impinger, V_b (mL).

6. Pipette 4-mL aliquots from each sample solution into 25-mL glass-stoppered flasks.
   NOTE: Adjust aliquot size to contain between 2 and 20 μg formaldehyde for optimum absorbance. The calibration graph between becomes non-linear above an absorbance of ca. 1.0. A.U.
7. Add 0.1 mL 1% chromotropic acid to the flask and mix.
   NOTE: This amount of chromotropic acid can react with ca. 40 μg of formaldehyde. Due to this fact, the range of the calibration curve should not exceed 36 μg (90% of theoretical).
8. Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution to mix.
   CAUTION: Mixing of the sample solution with concentrated sulfuric acid is highly exothermic.
9. Heat the solution to 95 °C for 15 min. Allow the solution to cool at room temperature for 2 to 3 hours.
   NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure buildup within the flask.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    a. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock solution to 100 mL 1% sodium bisulfite solution.
    b. Pipet, e.g., 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 mL calibration stock solution into 25-mL glass-stoppered flasks.
    c. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL. Also prepare a reagent blank.
    d. Analyze together with samples and blanks (steps 5 through 9, and steps 11 and 12).
    e. Prepare calibration graph (absorbance vs. μg formaldehyde/mL).

MEASUREMENT:

11. Set spectrophotometer according to manufacturer's recommendations and to conditions given on p. 3500-1. Fill 1-cm cuvette with sample.
12. Read sample absorbance at 580 nm.
    NOTE: If absorbance is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 4 mL with 1% sodium bisulfite solution, and analyze. (Steps 11 and 12). For optimum results, all samples containing over 20 μg formaldehyde should be diluted and reanalyzed.

CALCULATIONS:

13. Calculate the mass, μg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and average reagent blank (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot from step 6) and the total sample volume noted in step 5.
    NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass found in the front impinger. Collection efficiency is ca. 95% for each impinger [15], but may be reduced due to chipped or mismatched impinger parts, or by carryover from the front impinger.
14. Calculate the concentration, C, of formaldehyde in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

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

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

In a study comparing the pararosaniline method [4] and NIOSH P&CAM 125 over the range of 0.021 to 0.5 ppm, the NIOSH method gave better collection efficiency and accuracy [15]. Precision for both methods was equivalent.

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METHOD WRITTEN BY:

Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 6.6 mg/mL)

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

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

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

FORMALDEHYDE ON DUST (TEXTILE OR WOOD) 5700

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: 36172

METHOD: 5700, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 0.75 ppm; 2 ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

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

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v formaldehyde), methylene oxide

SAMPLING

SAMPLER: Institute of Occupational Medicine inhalable dust sampler or equivalent containing a 25-mm PVC filter, 5 μm pore size

FLOW RATE: 2.0 L/min

VOL-MIN: 240 L @ 0.002 mg/m^3
-MAX: 1050 L

SHIPMENT: Place cassette with filter in 30-mL screw-cap low density polyethylene (LDPE) bottle; keep upright. Ship cold.

SAMPLE STABILITY: 21 days (matrix dependent) (cold storage advised)

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.007 to 0.16 mg/m^3 [1] (1050-L sample)

BIAS: − 4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.093 [1]

ACCURACY: ± 22%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone derivative of formaldehyde

EXTRACTION: 10 mL distilled water @ 37 °C, 4 h; 1 mL to 3 mL 2,4-dinitrophenylhydrazine/acetonitrile (1.3 mg/mL DNP/ACN)

INJECTION VOLUME: 15 μL

MOBILE PHASE: 34% acetonitrile/66% methanol/water (1:1, v/v), 1.0 mL/min

COLUMN: Radial Compression Module C_{18} column, 5-μm particle size, 10 cm x 8-mm ID (with a C_{18} guard column) or equivalent

DETECTOR: UV @ 365 nm

CALIBRATION: Standard solutions of formaldehyde in 1.3 mg/mL DNPH/ACN

RANGE: 0.40 to 4000 μg per sample [1]
ESTIMATED LOD: 0.08 μg per sample [1]
PRECISION ($\hat{S}_r$): 0.078 @ 7 to 174 μg per sample [1]

APPLICABILITY: The working range is 0.0004 to 3.8 mg/m^3 for a 1050-L air sample. This method has been used for the determination of formaldehyde in both textile dusts and wood dusts.[1] Caution should be exercised in the way that data collected with this method are interpreted. These results should be reported separately from vapor-phase formaldehyde exposure data until sufficient data has been collected to allow appropriate epidemiological interpretation of formaldehyde-containing particulate exposures.

INTERFERENCES: None identified.

OTHER METHODS: In the absence of phenol or other substances known to interfere with the chromotropic acid analysis of formaldehyde, the analysis procedure described in NIOSH method #3500 [2] can also be used with this extraction technique (See Appendix). The analysis procedure used in this method has also been used for the determination of formaldehyde in automobile exhaust [3]. An alternate analysis [4] may be used in conjunction with this method to determine the amount of "released" formaldehyde from the collected particulate material. NMAM 5700 determines both "released" formaldehyde and formaldehyde equivalents (e.g., small oligomeric pieces of formaldehyde-containing resin) present in the hydrolysis solutions. The use of these two analytical approaches may differentiate between the two forms of formaldehyde present in the sample by the difference in results.

REAGENTS:

1. 2,4-dinitrophenylhydrazine (2,4-DNP) (1.3 g.) in 1 L. acetonitrile; 1.3 mg/mL solution.
2. Formaldehyde stock solution, 1 mg/mL (see Appendix).
3. Methanol, distilled in glass.
4. Acetonitrile, distilled in glass.
5. Water, deionized and distilled.
6. Perchloric acid solution, 1 N.*

* See Special Precautions

EQUIPMENT:

1. Sampler: 25-mm PVC filter (5.0-μm pore size) in a 25-mm Institute of Occupational Medicine inhalable (dust) sampler (Air Quality Research, Berkeley, CA, or equivalent). The sampler should meet the American Conference of Governmental Industrial Hygienists definition for collection of the inhalable fraction of particulate mass. [5]
2. Personal sampling pump, 2.0 L/min, with flexible polyethylene or PTFE tubing.
3. Bottles, screw-cap, low-density polyethylene (Nalgene LDPE or equivalent), 30-mL.
   Note: Do NOT use bottles with 'polycone' liners (source of high formaldehyde blank).
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5700-1).
5. Tweezers.
6. Syringes, 10-, 25-, 50-, and 100-μL.
7. Volumetric flasks, 10-, 100-mL and 1 L.
8. Pipets, 0.1-, 0.5-, 1.0-, and 3-mL glass, delivery, with pipet bulb.
9. Graduated cylinders, glass, 25-mL.
10. Cotton gloves.
11. Equipment for standardizing formaldehyde stock solution, Burets, 50-mL.
12. pH meter.
13. Magnetic stirrer.
14. Beaker, 50-mL.
15. Vials, 5-mL.
16. Filters, 0.45 μm.
17. Scintillation vials, 20-mL.

SPECIAL PRECAUTIONS: Perchloric acid is a strong oxidizing agent, toxic by ingestion and inhalation and is a strong irritant. Use only in a hood. Formaldehyde is a suspect carcinogen [1,6] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. If gravimetric measurements are needed, handle the I. O. M. cassettes only while wearing cotton gloves. Follow NMAM 0500 [7] for pre- and post-collection weighing procedure. Place the cassette containing a 25-mm PVC 5-μm pore filter in the filter holder.
3. Attach outlet of filter holder to the sampling pump.
4. Sample 240 to 1050 L of air at 2.0 L/min flow rate.
5. Transfer cassette from filter holder carefully to a 30-mL LDPE screw-cap bottle while wearing cotton gloves and seal the bottle. Ship in a suitable container in order to prevent damage during transit and keep bottles upright.
6. Collect a bulk sample (ca. 1 g) of the dust/fiber in a glass vial and ship separately.

APPENDIX:

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

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

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

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

ALTERNATE ANALYSIS PROCEDURE FOR THE DETERMINATION OF FORMALDEHYDE LIBERATED FROM DUST/FIBER SAMPLES

Note: This analysis procedure should only be used where interferences to the chromotropic acid analysis are not present. These interferences include phenol, oxidizable organic material, other aldehydes and alcohols.

For formaldehyde determination by the chromotropic acid method, a 4-mL aliquot of the solution resulting from the desorption and incubation of the filter (step 8.) was analyzed by the procedure described in NIOSH Method 3500.[2] The amount of chromotropic acid added to the sample could react with a maximum of 42 μg of formaldehyde per sample aliquot. (Whenever the amount of formaldehyde approached 30 μg per aliquot, the sample was diluted and reanalyzed.) The absorbance of samples at 580 nm was then compared to a calibration curve constructed from results obtained from analysis of calibration standards containing known amounts of formaldehyde. The amount of formaldehyde present in each sample was determined based on the calibration curve.

Calibration standards were prepared by dilution of a standard solution of formalin in distilled water (1 mg/mL) and analyzed in the same manner as the samples. The calibration range usually covered 1 to 25 μg of formaldehyde/4-mL aliquot. A limit of detection of 0.44 μg formaldehyde/filter sampler was determined in laboratory evaluation of this analysis procedure.

FORMIC ACID 2011

HCOOH MW: 46.03 CAS: 64-18-6 RTECS: LQ4900000

METHOD: 2011, Issue 1 **EVALUATION:** PARTIAL **Issue 1:** 15 August 1994

OSHA : 5 ppm
NIOSH: 5 ppm
ACGIH: 5 ppm
(1 ppm = 1.882 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 107 °C; d 1.22 g/mL (90% solution) @ 20 °C; VP 4.7 kPa (33 mm Hg); vapor density (air = 1) 1.6; colorless; pungent odor

SYNONYMS: hydrogencarboxylic acid; methanoic acid

SAMPLING

SAMPLER: FILTER + SOLID SORBENT TUBE (PTFE membrane, 5-μm + washed, silica gel, 400 mg/200 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: formate ion

DESORPTION: 10 mL deionized water; stand 5 minutes

INJECTION VOLUME: 50 μL

ELUENT: 2.5 mM $Na_2B_4O_7 \cdot 10\ H_2O$, 2.0 mL/min

COLUMN: Dionex HPIC-AG4 guard, HPIC-AS4 anion separator, anion micromembrane suppressor

DETECTOR: conductivity, 10 μS full scale

CALIBRATION: standard solutions of formate spiked onto sample media

RANGE: 6 to 100 μg formate per sample [1]

ESTIMATED LOD: 2 μg formate per sample [2,3]

PRECISION($\bar{S}_r$): 0.026 @ 106 to 426 μg per sample [2]
0.097 @ 10 to 80 μg per sample [3]

APPLICABILITY: The working range is 0.13 to 12 ppm (0.25 to 22 mg/m^3) for a 24-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This is a modification of Method 7903 (Acids, inorganic) and revises Method S173 [1,3].

REAGENTS:

1. Acetone, ACS reagent grade.
2. Water, deionized.
3. Eluent: 2.5 mM $Na_2B_4O_7 \cdot 10\ H_2O$. Dissolve 3.82 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 4 liters high purity water. Filter if necessary to remove any particulate matter.
4. Suppressor regenerant, 25 mN H_2SO_4.*
5. Calibration stock solution, 1 mg formate anion per mL. Dissolve 0.1511 g sodium formate (dried @ 110 °C for 4 h, stored in desiccator) in 100 mL deionized water.
6. Formic acid, 88% or 95% (Optional; see Appendix A).
7. Dioxane (Optional; see Appendix A).
8. 0.1 M $Na_2B_4O_7 \cdot 10\ H_2O$. Dissolve 145 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 4 liters deionized water. Filter if necessary to remove particles > 1 μm.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 7-mm OD, 4-mm ID, flamed-sealed ends with plastic 20/40 caps, containing 20/40 mesh washed silica gel (front = 400 mg, back = 200 mg) separated by a 4-mm urethane foam plug. A thick glass fiber filter plug precedes the front section and a 5-mm urethane foam plug follows the back section. Tubes are commercially available (ORBO-53, Supelco, or equivalent) or prepare according to APPENDIX B. Prefilter, PTFE, 25-mm, with porous plastic support pad. Pressure drop across the sampler at 1 L/min airflow must be less than 3.4 kPa.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. Ion chromatograph, with a conductivity detector, chart recorder, integrator, and column.
4. Vials, polyethylene, 20-mL, with plastic caps.
5. Micropipettes, with disposable plastic tips.
6. Volumetric flasks, 100-mL.
7. Pipet, 10-mL, graduated in 0.1-mL intervals.
8. Pipet, volumetric, 20-mL.
9. Syringes, 10-mL, plastic, with luer tip.
10. Filters, luer tip, with membrane filter, 13-mm, 0.45-μm pore size.

SPECIAL PRECAUTIONS: Users of this method should be acquainted with the degree of hazard of each chemical and take the proper precautions. Handle all hazardous chemicals in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach a sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for total volume of 1 to 24 L.
4. Cap the tubes with plastic (not rubber) caps, plug filter cassettes, and pack securely for shipment.
   NOTE: Prefilters may be analyzed for particulate formates, or may be discarded.

SAMPLE PREPARATION:

5. Place the front with glass fiber filter plug and back sorbent sections of the sampler tube (and prefilter, optional) in separate 20-mL plastic vials. A glass rod may be used to push the contents out of the tube. Discard the foam plugs.
6. Add 10 mL deionized water to each plastic vial. Loosely cap.
7. Heat in boiling water for 10 min, cool, and analyze the same day the formic acid is desorbed.
8. Transfer a portion of sample to a syringe fitted with an inline membrane filter, for direct injection or for transfer to autosampler vials.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES.

Name Synonyms	CAS# RTECS	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)
benzene[a] benzol; cyclohexatriene	71-43-2 CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
cyclohexane[a] hexahydrobenzene hexamethylene	110-82-7 GU6300000	C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene[a] tetrahydrobenzene benzene tetrahydride	110-83-8 GW2500000	C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-heptane[b]	142-82-5 MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane[b] hexyl-hydride	110-54-3 MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane[a] cyclohexylmethane	108-87-2 GV6125000	C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-octane[b]	111-65-9 RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane[b]	109-66-0 RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	0.626
toluene[a] methylbenzene; toluol	108-88-3 XS5250000	C_7H_8	92.14	110.6	28.4	3.8	0.867

[a] Properties from [5].
[b] Properties from [6].

TABLE 2. EXPOSURE LIMITS, PPM [7-9].

Substance	OSHA TWA	OSHA C	OSHA Peak	NIOSH TWA	NIOSH C	ACGIH TLV	ACGIH STEL	mg/m³ per ppm @ NTP
benzene*	10	25	50[b]	0.1[d]	1	10[d]		3.19
cyclohexane	300			300		300		3.44
cyclohexene	300			300		300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane[a]	500			50		50		3.52
methylcyclohexane	500			400		400		4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500[b]	100	150[c]	100	150	3.77

[a] The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.
[b] Maximum duration 10 min in 8 h.
[c] STEL
[d] Suspect carcinogen

TABLE 3. SAMPLING FLOWRATE[a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [2-4, 10].

Substance	Sampling Flowrate (L/min)	Sampling Volume (L) MIN	Sampling Volume (L) MAX[b]	Breakthrough Volume at Concentration (L)	Breakthrough Volume at Concentration (mg/m³)	Range at VOL-NOM (mg/m³)	Overall Bias (%)	Overall Precision ($\hat{S}_{rT}$)	Accuracy (%)
benzene	≤0.20	2[c]	30	>45	149.1	41.5-165	0.4	0.059	±11.4
cyclohexane	≤0.20	2.5	5	7.6	1650	510-2010	1.1	0.060[d]	±11.5
cyclohexene	≤0.20	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-heptane	≤0.20	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-hexane	≤0.20	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
methylcyclohexane	≤0.20	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-octane	≤0.20	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-pentane	≤0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6
toluene	≤0.20	2[c]	8	11.9	2294	548-2190	1.6	0.052	±10.9

[a] Minimum recommended flow is 0.01 L/min.
[b] Approximately two-thirds the breakthrough volume.
[c] 10-min sample.
[d] Corrected value, calculated from data in [10].

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

METHOD: 1003, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : See TABLE 1
NIOSH: See TABLE 1
ACGIH: See TABLE 1

PROPERTIES: See TABLE 2

COMPOUNDS:	benzyl chloride	chlorobromomethane	1,1-dichloroethane	1,1,1-trichloroethane
(synonyms	bromoform	chloroform	1,2-dichloroethylene	tetrachloroethylene
in Table 1)	carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	1,1,2-trichloroethane
	chlorobenzene	p-dichlorobenzene	hexachloroethane	1,2,3-trichloropropane

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: see EVALUATION OF METHOD [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD [1]

ACCURACY: see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 μL

TEMPERATURES: Table 4

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 4; alternates are SP-2100, Sp-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: standard solutions of analyte in CS_2

RANGE: Table 4

ESTIMATED LOD: 0.01 mg per sample [2]

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

APPLICABILITY: See Table 3 for working ranges. This method can be used for simultaneous determination of two or more substances suspected to be present by changing gas chromatographic conditions (i.e., temperature program). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interferences.

OTHER METHODS: This method combines and replaces P&CAM 127 [3], S101 [4], S110 [5], S113 [6], S114 [7], S115 [8], S122 [9], S123 [10], S126 [11], S133 [12], S134 [13], S135 [14], S281 [15], S314 [16], S328 [17], S335 [18], S351 [19], and Method 1003 (dated 2/15/84).

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Analyte, reagent grade.
3. Calibration stock solutions:
   a. benzyl chloride, 10 mg/mL in n-heptane.
   b. bromoform, 10 mg/mL in n-hexane.
   c. o-dichlorobenzene, 200 mg/mL in acetone.
   d. p-dichlorobenzene, 300 mg/mL in acetone.
   e. hexachloroethane, 25 mg/mL in toluene.
4. Decane, n-undecane, octane or other internal standards (see step 6).
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available (e.g., SKC #226-01).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (see Table 3).
4. Vials, 2-mL, glass, PTFE-lined septum crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Pipet, TD, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C). Work with it only in a hood. Several of the analytes are suspect carcinogens (Table 1). n-Heptane, n-hexane, and acetone are fire hazards.

SAMPLING:

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

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as decane [16], n-undecane [6,19], or octane [9,13,17] at 0.1% (v/v) may be added at this step and step 8.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (Table 3).
   a. Add known amounts of neat analyte or calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).

HYDROGEN CYANIDE

HCN MW: 27.03 CAS: 74-90-8 RTECS: MW6825000

METHOD: 6010, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: STEL 4.7 ppm
ACGIH: C 10 ppm (skin)
(1 ppm = 1.105 mg/m^3 @ NTP)

PROPERTIES: gas; BP 26 °C; vapor density 0.93 (air = 1.00); d(liq) 0.69 g/mL @ 20 °C; VP 82.7 kPa (620 mm Hg) @ 20 °C; explosive range 5 to 40% v/v in air

SYNONYMS: hydrocyanic acid, prussic acid, formonitrile

SAMPLING

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

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 2 L @ 5 ppm
-MAX: 90 L

SHIPMENT: routine

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

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 15 mg/m^3 [1] (3-L samples)

BIAS: Not significant

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 15.0%

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: cyanide ion complex

DESORPTION: 10 mL deionized water; stand 60 min

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

CALIBRATION: standard solutions of KCN in 0.1 N NaOH

RANGE: 10 to 300 µg CN^- per sample [1]

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

PRECISION ($\bar{S}_r$): 0.041 @ 10 to 50 mg per sample [1]

APPLICABILITY: The working range is 0.3 to 235 ppm (3 to 260 mg/m^3) for a 3-L air sample. This method is applicable to STEL measurements. Particulate cyanides are trapped by the initial glass fiber membrane disk. This method is more sensitive and subject to fewer interferences than NIOSH Method 7904, which uses ion specific electrode analysis. The method was used to determine HCN in firefighting environments [2].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference.

OTHER METHODS: This is based on the method of Lambert, et al. [3]. NIOSH Method 7904 uses an ion specific electrode for measurement. The method has been adapted for use with a Technicon Autoanalyzer [4].

REAGENTS:

1. Potassium cyanide*, reagent grade.
2. Succinimide, reagent grade.
3. N-Chlorosuccinimide, reagent grade.
4. Barbituric acid, reagent grade.
5. Pyridine, spectrophotometric quality.
6. Phenolphthalein, 1% (w/v) in ethanol or methanol, reagent grade.
7. Hydrochloric acid, concentrated, reagent grade.
8. Sodium hydroxide (NaOH), reagent grade.*
9. Sodium lime (CaO + 5-20% NaOH), reagent grade (Aldrich #26,643-4 or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
10. Water deionized-distilled.
11. Sodium hydroxide solution, 0.1 N.*
12. Calibration stock solution. 1 mg /mL CN^-. Dissolve 0.125 g KCN in 0.1 N NaOH in a 50-mL volumetric flask. Dilute to mark with 0.1 N NaOH. Standardize by titration with standard $AgNO_3$ solution (see APPENDIX).
13. Hydrochloric acid solution, 0.15 N.
14. N-Chlorosuccinimide/succinimide oxidizing reagent. Dissolve 10.0 g succinimide in about 200 mL distilled water. Add 1.00 g N-chlorosuccinimide. Stir to dissolve. Adjust volume to 1 liter with distilled water. Stable 6 months when refrigerated.
15. Barbituric acid/Pyridine reagent. Add about 30 mL distilled water to 6.0 g barbituric acid in a 100-mL Erlenmeyer flask. Slowly add 30 mL pyridine with stirring. Adjust the volume to 100 mL with water. Stable 2 months when refrigerated.

EQUIPMENT:

1. Sampler, glass tube, 9 cm long, 7-mm OD, 5-mm ID, with plastic caps, containing two sections (front = 600 mg; back = 200 mg) granular soda lime 10/35 mesh, separated and contained with silanized glass wool plugs, with a 5-mm diameter glass fiber filter disk placed before the plug on inlet side. Tubes are commerically available. (SKC, Inc. 226-28 or equivalent.)
2. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm light path.
3. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
4. Pipets, volumetric 0.1-, 0.5-, 1.0-, 2.0-, 10.0-mL.
5. Vials, glass or plastic, 15-mL with PTFE-lined caps.
6. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers.
7. Pipets, transfer, disposable.
8. Syringes, 10-μL, readable to 0.1 μL.
9. Flask, Erlenmeyer, 100-mL.
10. Syringes, 10-mL, polyethylene with luer tip.
11. Filter cassette, with membrane filter, 13-mm diameter, 0.45-μm pore size, with luer fitting.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [5]. Soda lime and NaOH are very caustic [5]. Use gloves and a fume hood for handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
4. Cap tube. Pack securely for shipment.

APPENDIX: STANDARDIZATION OF CALIBRATION STOCK SOLUTION

Titrate an aliquot of the cyanide standard stock solution (Reagent 12) with standard silver nitrate ($AgNO_3$) solution. The end point is the first formation of a white precipitate, $Ag[Ag(CN)_2]$. Calculate the cyanide concentration with the following equation:

$$M_c = 52.04\ V_a\ (M_a/V_c)$$

Where M_c = cyanide concentration (mg/mL)
V_a = volume (mL) of standard silver nitrate solution
M_a = concentration (moles/L) of standard silver nitrate solution
V_c = volume (mL) of calibration stock solution titrated

HYDROGEN SULFIDE 6013

H_2S MW: 34.08 CAS: 7783-06-4 RTECS: MX1225000

METHOD: 6013, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 20 ppm; P 50 ppm/10 min
NIOSH: C 10 ppm/10 min
ACGIH: 10 ppm; STEL 15 ppm
(1 ppm = 1.39 mg/m^3 @ NTP)

PROPERTIES: gas; d (liq) 1.54 g/mL @ 0 °C; BP - 60 °C; VP 20 atm @ 25 °C; vapor density (air=1) 1.19; explosive range 4.3 to 46% v/v in air

SYNONYMS: sulfuretted hydrogen; hydrosulfuric acid; hepatic gas; stink damp

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SOLID SORBENT TUBE (Zefluor, 0.5 μm; coconut shell charcoal, 400 mg/200 mg)	**TECHNIQUE:**	ION CHROMATOGRAPHY, CONDUCTIVITY
FLOW RATE-RANGE:	0.1 to 1.5 L/min	**ANALYTE:**	sulfate ion
-RECOMMENDED:	0.2 L/min	**DESORPTION:**	2 mL 0.2 M NH_4OH + 5 mL 30% H_2O_2
VOL-MIN:	1.2 L @ 10 ppm	**INJECTION VOLUME:**	50 μL
-MAX:	40 L	**ELUENT:**	40 mM NaOH, 1.5 mL/min
SHIPMENT:	routine	**COLUMN:**	Ion-Pac AS4A separator, AG4A guard
SAMPLE STABILITY:	at least 30 days @ 25 °C [1]	**CALIBRATION:**	SO_4^{2-} in deionized water
BLANKS:	2 to 10 field blanks per set	**RANGE:**	17 to 200 μg per sample
ACCURACY		**ESTIMATED LOD:**	11 μg per sample
RANGE STUDIED:	1.4 to 22.0 mg/m^3 [1] (20-L samples)	**PRECISION ($\bar{S}_r$):**	0.031 [1]
BIAS:	− 0.23% [1]		
OVERALL PRECISION ($\bar{S}_{rT}$):	0.059 [1]		
ACCURACY:	± 11.8%		

APPLICABILITY: The working range is 0.6 to 14 ppm (0.9 to 20 mg/m^3) for a 20-L air sample [1]. The method is applicable to 15-min samples taken at 1 L/min and 10-min samples taken at 1.5 L/min. The upper limit of loading depends on the concentrations of hydrogen sulfide and other substances in the air, including water vapor. High relative humidity (80%) increases the capacity of the sampler four-fold, relative to dry air. Some lots of charcoal have excessively high sulfur backgrounds and/or poor desorption efficiencies; therefore, screening of each lot should be done before field use.

INTERFERENCES: SO_2 is a positive interference, equivalent to H_2S by approximately twice the SO_2 concentration by weight. Methyl and ethyl mercaptans do not interfere [1].

OTHER METHODS: Alternate methods are S4 [2] which uses impinger collection, and P&CAM 296 [3] which uses a molecular sieve sampler but has poor stability.

REAGENTS:

1. Ammonium hydroxide solution, 25%.
2. Hydrogen peroxide, 30%.*
3. Sodium hydroxide, 50% (w/v).*
4. Extraction soln: 0.2 M NH_4OH.
5. Eluent: 40 mM NaOH. Dilute 4.16 mL of 50% NaOH to 2 L with deionized water (degassed).
6. Suppressor regenerant: 0.025 N H_2SO_4. Dilute 1.4 mL concentrated H_2SO_4 to 2 L with deionized water.*
7. Calibration Stock solution: 1 mg/mL (as anion). Dissolve 0.1814 g K_2SO_4 in 100 mL deionized water.
8. H_2S, calibration gas mixture, or permeation device.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg, back = 200 mg) separated by a 6-mm urethane foam plug. A silanized glass wool plug precedes the front section and a 6-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available. Zefluor PTFE prefilter, 0.45-μm, 25-mm, with porous plastic support pad in 25-mm cassette.
   NOTE: Some lots of charcoal have excessively high sulfur backgrounds, and/or desorption efficiencies. Screen each lot before field use.
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Ion chromatograph, conductivity detector, integrator and columns (page 6013-1).
4. Centrifuge tubes, 15-mL, plastic with screw caps.
5. Syringes, 10-mL, polyethylene with luer tip.
6. Syringe filters, 13-mm, 0.45-μm pore size.
7. Vials, autosampler, 4-mL, PTFE-lined caps.
8. Micropipettes, disposable tips.
9. Pipettes, 2-, 3-, 5-mL.
10. Volumetric flasks, 10-, 25-mL.
11. Vortex mixer (optional).

SPECIAL PRECAUTIONS: Hydrogen peroxide is a strong oxidizer causing burns to skin and mucous membranes. Sulfuric acid and sodium hydroxide are extremely corrosive to all body tissue. Wear protective clothing and eye protection. All work should be performed in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler and attach prefilter with a small piece of flexible tubing immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 1.5 L/min for a total sample size of 15 to 40 L.
4. Cap the sorbent tubes with plastic caps and plug prefilter cassettes. Pack securely for shipment.

NOTE: The prefilters may be discarded or analyzed for particulate sulfates by, e.g., Method 6004.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate screw-top centrifuge tubes. Discard the glass wool and foam plugs.
6. Add 2.0 mL of 0.2 M NH_4OH and 5.0 mL H_2O_2 to each centrifuge tube. Attach screw cap and loosen 1/4 turn.
7. Allow to react at least 10 min. Tighten cap and shake for 30 s or vortex 10 s.

8. Dilute to 10 mL with 3 mL of deionized water. Cap and shake vigorously.
9. Transfer sample to 10-mL plastic syringe fitted with in-line filter.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range 0.1 to 20 μg sulfate ion per mL of sample (1 to 200 μg per 10 mL).
    a. Add known amounts of calibration stock solution to deionized water in 10- or 25-mL volumetric flasks and dilute to the mark. Prepare fresh working standards biweekly.
    b. Analyze together with samples and blanks (steps 14 and 15).
    c. Prepare calibration graph (peak height vs. μg SO_4^{2-} per sample).
11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 10). Prepare four tubes at each of three levels plus three media blanks.
    a. Generate concentrations of H_2S from a calibration gas mixture or a permeation device. Mix with dilution air as necessary.
    b. Collect samples at a flow rate of 1 L/min for 30 min.
    c. Cap the tubes and allow to stand overnight.
    d. Desorb (steps 5 through 9) and analyze together with working standards (steps 14 and 15).
    e. Prepare a graph of DE vs. μg sulfate recovered.
12. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6013-1.
14. Inject a 50-μL sample aliquot manually or with autosampler.
15. Measure peak height.
    NOTE: If peak height is above the linear range of the working standards, dilute with deionized water, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, μg (corrected for DE) of sulfate ion found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of hydrogen sulfide in the air volume sampled, V (L), applying the factor 0.3548 (MW H_2S/MW SO_4^{2-}) for the conversion of SO_4^{2-} to H_2S:

$$C = \frac{0.3548\ (W_f + W_b - B_f - B_b)}{V},\ mg/m^3.$$

EVALUATION OF METHOD:

The method was evaluated by sampling generated test atmospheres of H_2S in air [1]. Time-weighted average samples were taken at four concentration levels over a range of 1.4 to 22 mg/m^3 (1 to 16 ppm). For ceiling concentrations or short-term exposure limits, 15-L samples were collected at 1 L/min. Breakthrough was determined for coconut charcoal from a generated atmosphere at a concentration of 20 ppm (2 x PEL) and at both low (~20%) and high (~80%) relative humidity (RH). Breakthrough volumes for low and high RH were 21 L and 84 L, respectively, corresponding to capacities of 588 μg of H_2S (low RH) and 2352 μg of H_2S (high RH). At 1 x PEL, the equivalent breakthrough volume is 42 L (low RH) and 164 L (high RH). Large coconut charcoal tubes have sufficient capacity to collect a 4-h sample at the PEL of 10 ppm, as well as STEL samples (15 ppm for 15 min). H_2S samples are stable for

at least 30 days. Recoveries, based on mass of H_2S found on samples analyzed on day 1, were 97.2% for ambient storage and 98.9% for refrigerated storage. The overall method for H_2S has a limit of detection of 11 μg per sample and a limit of quantitation of 17 μg per sample. A mean bias of -0.17% was determined from the recoveries of six samples generated at each of four concentration levels (0.1, 0.5, 1 and 2 x PEL) with a precision ($\bar{S}_r$) of 0.031. The method had a total precision including pump error ($\bar{S}_{rT}$) of 0.059, and an estimate of overall error of $\pm$11.6%.

REFERENCES:

[1] Cassinelli, ME, Backup Data Report, NMAM 6013, Hydrogen Sulfide. NIOSH/DPSE (1992).

[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S4, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 6, P&CAM 296, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH/DPSE.

		MW:	CAS:	RTECS:
2,4-TDI:	$CH_3C_6H_3(NCO)_2$	174.16	584-84-9	CZ6300000
2,6-TDI:	$CH_3C_6H_3(NCO)_2$	174.16	91-08-7	CZ6310000
MDI:	$CH_2(C_6H_4NCO)_2$	250.26	101-68-8	NQ9350000
HDI:	$OCN(CH_2)_6NCO$	168.20	822-06-0	MO1740000
NDI:	$C_{10}H_6(NCO)_2$	210.20	3173-72-6	NQ9600000

METHOD: 5521, Issue 2 **EVALUATION:** UNRATED **Issue 1:** 15 May 1989 **Issue 2:** 15 August 1994

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

PROPERTIES: Table 1

SYNONYMS: Table 1

SAMPLING

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

FLOW RATE: 1 L/min

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

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

SAMPLE STABILITY: may be unstable; perform steps 7 & 8 as soon as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	not studied
BIAS:	not known
OVERALL PRECISION ($\hat{S}_{rT}$):	not known
ACCURACY:	not determined

MEASUREMENT

TECHNIQUE: HPLC, ELECTROCHEMICAL AND UV DETECTION

ANALYTE: urea derivatives of isocyanates

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

INJECTION VOLUME: 10 μL

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

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

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

CALIBRATION: standard solutions of ureas in methanol

RANGE: 2,4-TDI: 0.5 to 8 μg per sample [1]
2,6-TDI: 0.7 to 10 μg per sample [1]
MDI: 0.3 to 4 μg per sample [1]
HDI: 1 to 15 μg per sample [1]
NDI: 0.2 to 13 μg per sample

ESTIMATED LOD: ca. 0.1 μg diisocyanate per sample [1]

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

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

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

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

REAGENTS:

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

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Midget impinger, 25-mL
2. Personal sampling pump, 1.0 L/min, with flexible connecting tubing free of phthalate plasticizer.
   NOTE: Avoid collection of plasticizer in the toluene during sampling. Fluran™ tubing is an acceptable, PVC tubing is not.
3. Liquid chromatograph (HPLC) with electrochemical (ECHD) detector (+0.80 V vs. Ag/AgCl), recorder, integrator and column (page 5521-1)
4. Ultrasonic water bath.
5. Vials, 4-mL glass, with screw caps and 20-mL glass, screw caps with cone-shaped polyethylene liner and shrinkable sealing bands.
6. Pasteur pipets, 7-cm glass, disposable.
7. Flasks, volumetric, glass, 10-mL
8. Syringes, sizes appropriate for preparing standard solutions.
9. Pipets, 5- and 15-mL glass, delivery, with pipet bulb.
10. Hot plate, spark free, 60 °C.
11. Evaporator, Mini-Vap, 6-port or equivalent.
12. pH meter.
13. Vacuum oven.
14. Buchner funnel, fritted glass, medium porosity, 100-mL.
15. Vacuum pump.
16. Flask, filtration, 500-mL.

SPECIAL PRECAUTIONS: Preparation of urea derivatives, samples, and standards should be done in a hood to avoid exposure to isocyanate and solvent vapors. Isocyanates are known respiratory irritants.[4] Toxicity of 1-(2-methoxyphenyl)piperazine is unknown.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL sampling medium to an impinger.
3. Connect the assembled impinger to a sampling pump.
4. Sample 5 to 500 L of air at 1.0 L/min.
   NOTE 1: Toluene evaporates during sampling; when level of solution drops below 10 mL, restore volume to 15 mL with toluene.
   NOTE 2: The reagent in the sampling medium reacts with isocyanates to form ureas:
   $$CH_3OC_6H_4NC_4H_8NH + R\text{-}N{=}C{=}O \rightarrow CH_3OC_6H_4NC_4H_8NC(=O)NHR$$
5. Prepare blank samples by transferring 15 mL sampling medium to 20-mL vials.
6. Transfer the sample solution to a 20-mL vial for shipment. Rinse both impinger parts with 2 to 3 mL toluene and add rinsings to the sample. Secure vial's screw cap with sealing band. Refrigerate samples as soon as possible. If samples are to be shipped, carefully pack the vials to avoid breakage or spillage of sample.

LEAD by GFAAS

Pb MW: 207.19 (Pb); 223.19 (PbO) CAS: 7439-92-1 (Pb); 1317-36-8 (PbO) RTECS: OF7525000 (Pb); OG1750000 (PbO)

METHOD: 7105, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 μg/100 g
ACGIH: 0.15 mg/m^3

PROPERTIES: soft metal; d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING

SAMPLER: FILTER (0.8-μm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 1 L @ 0.05 mg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION SPECTROPHOTOMETER, GRAPHITE FURNACE

ANALYTE: lead

ASHING: conc. HNO_3, 3 mL; 30% H_2O_2; 1 mL; 140 °C

FINAL SOLUTION: 10 mL 5% HNO_3

WAVELENGTH: 283.3 nm

GRAPHITE TUBE: pyrolytic coated

INJECTION: 20 μL + 10 μL matrix modifier,
DRY: 110 °C, 70 sec;
CHAR: 800 °C, 30 sec;
ATOMIZE: 1800 °C, 5 sec.

BACKGROUND CORRECTION: D_2, H_2, or Zeeman

CALIBRATION: Pb^{2+} in 5% HNO_3

RANGE 0.05 to 100 μg per sample [1]

ESTIMATED LOD: 0.02 μg per sample [1]

PRECISION ($\bar{S}_r$): 0.049 [1]

APPLICABILITY: The working range is 0.002 to >1 mg/m^3 for a 200-L air sample. If high concentrations are expected, the samples should be analyzed by flame AAS. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the sample may be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control molecular absorption. High concentrations of calcium, sulfate, carbonate, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be offset by an additional sample treatment step.

OTHER METHODS: This revises and replaces P&CAM 214 (2). Method 7300 (ICP-AES) is an alternate analytical method. Method 7505 is specific for lead sulfide by X-ray diffraction. Method 7082 is a flame AAS method, with a higher working range.

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 5% (v/v). Add 50 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O (w/w), reagent grade.*
4. Calibration stock solution, 1000 μg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of HNO_3 and dilute to 1 L with 1% (v/v) HNO_3. Store in a polyethylene bottle.
5. Matrix Modifier. Place 0.2 g $NH_4H_2PO_4$ and 0.3 g $Mg(NO_3)_2$ in a 100-mL volumetric flask. Add 2 mL conc. HNO_3 and bring to volume with distilled or deionized water.
6. Argon, prepurified.
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-μm, 37-mm, in 2-piece cassette.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace atomizer and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for Argon.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140 °C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Conc. nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 1 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: Some matrices, especially bulk samples containing epoxy-based paint, may require a different digestion procedure for complete recovery of lead. See the Appendix of Method 7082 (Lead by Flame AAS) for a microwave digestion procedure which can be used for this purpose.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Rinse the watchglass and walls of the beaker with 3 to 5 mL 5% HNO_3. Allow the solution to evaporate to 0.5 mL.
7. Cool each beaker.
8. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare a series of six working standards covering the range 0.002 to 0.1 μg/mL Pb (0.02 to 1.0 μg Pb per sample).
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 5% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.

CH_3SH	MW: 48.11	CAS: 74-93-1	RTECS:	PB4375000
CH_3CH_2SH	62.13	75-08-1		KI9625000
$CH_3CH_2CH_2CH_2SH$	90.19	109-79-5		EK6300000

METHOD: 2542, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

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

PROPERTIES: Table 1

SYNONYMS: Methyl mercaptan: methanethiol; mercaptomethane; methyl sulfhydrate
Ethyl mercaptan: ethanethiol; mercaptoethane; ethyl sulfhydrate
n-Butyl mercaptan: butanethiol; 1-mercaptobutane; 1-butanethiol

SAMPLING

SAMPLER: FILTER (glass fiber, 37-mm, impregnated with mercuric acetate)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 10 L @ 0.5 ppm
-MAX: 150 L

SHIPMENT: protect samples from light [1,2]

SAMPLE STABILITY: at least 3 weeks @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 2

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Table 2

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD SULFUR MODE

ANALYTE: methyl, ethyl and n-butyl mercaptans

EXTRACTION: 20 mL HCl (25% v/v) plus 5 mL 1,2-dichloroethane, 2 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 250 °C
-COLUMN: 30 °C 2 min, 15 °C/min, 200 °C

COLUMN: narrow-bore, fused-silica capillary, 30 cm x 0.25-mm ID, 1 µm DB-1

CARRIER GAS: He, 1.0 mL/min; makeup gas: N_2, 20 mL/min

CALIBRATION: standard solutions of mixed mercaptans in 1,2-dichloroethane

RANGE: Table 2

ESTIMATED LOD: Table 2

PRECISION ($\bar{S}_r$): Table 2

APPLICABILITY: The working ranges are 0.2 to 10 ppm for a 20-L air sample for all three mercaptans [1-4].

INTERFERENCES: Dimethyl disulfide, diethyl disulfide and dibutyl disulfide may interfere [2-4].

OTHER METHODS: This is a modification of OSHA Method 26 for methyl mercaptan with the addition of ethyl- and n-butyl mercaptan [2].

REAGENTS:

1. Methyl mercaptan*
   gas, lecture bottle, 99.5+%.
2. Ethyl mercaptan,* 99+%.
3. n-Butyl mercaptan,* 99+%.
4. Mercuric acetate, ACS reagent grade.
5. Hydrochloric acid, ACS reagent grade.
6. 1,2-Dichloroethane, ACS reagent grade.
7. Methyl mercaptan calibration stock solution, 0.394 mg/mL. Pipet 5.0 mL methylene chloride into a vial and attach PTFE-lined cap. Add 1.0 mL pure methyl mercaptan gas (measured at 25 °C, 1 atm) to the liquid using gas-tight syringe.
8. Ethyl mercaptan calibration stock solution, 2.52 mg/mL. Dissovle 30 μL ethyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
9. n-Butyl mercaptan calibration stock solution, 3.34 mg/mL. Dissolve 40 μL n-butyl mercaptan in methylene chloride in a 10-mL volumetric flask and dilute to the mark.
10. Helium, purified.
11. Hydrogen, prepurified.
12. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass fiber filters impregnated with mercuric acetate. The filters are prepared by immersing 37-mm Gelman Metrigard (or equivalent) glass fiber filters with acrylic binder in 5% (w/v) aqueous solution of mercuric acetate, dried in the air, and then assembled in two-piece filter cassettes without backup pads. The filters exhibit yellowish color, but it does not affect their collection efficiency.
2. Personal sampling pump, 0.10 to 0.20 mL/min, with flexible polyethylene or PTFE tubing.
3. Gas chromatograph with a flame photometric detector, capillary column, integrator.
4. Vials, glass, 2-mL and 5-mL, PTFE-lined crimp caps.
5. Syringes, 10-, 50, and 250-μL.
6. Volumetric flasks, 10-mL.
7. Pipets, 5- and 20-mL glass, delivery, with pipet bulb.
8. Separatory funnel, 30-mL.

SPECIAL PRECAUTIONS: Store methyl-, ethyl-, and n-butyl-mercaptans from flammable and oxidizing materials [5,6]. The analytes are highly flammable and irritating to the eyes. Work in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the plugs from the filter cassette immediately before sampling. Connect the cassette to the sampling pump with flexible tubing. Air being sampled should not pass through any hose or tubing before entering filter cassette.
3. Sample at an accurately known flow rate between 0.1 and to 0.2 L/min for a total sample size of 10 to 150 L.
4. Replace the plugs in the filter cassette immediately after sampling. Store protected from light.

SAMPLE PREPARATION:

5. Add 20 mL of 25% (v/v) hydrochloric acid and 5 mL of 1,2-dichloroethane to a 30-mL separatory funnel. Fold sample filter and insert into the neck of a separatory funnel, without allowing the filter to become wet. While seating the stopper, push filter into funnel.
6. Shake funnel for 2 min without venting.
7. Let stand at least 5 min, until the phases completely separate. Then drain the 1,2-dichloroethane into a vial and seal with a PTFE-lined cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of the samples:
   a. Add known amounts of calibration stock solution to 1,2-dichloroethane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. prepare calibration graphs: either quadratic curves, i.e., peak area vs. concentration of mercaptans, or linear curves, i.e., ln (peak area) vs. ln (concentration)^2 can be used for calibration.
9. Determine recovery (R) for each lot of glass fiber filters impregnated with mercuric acetate in the concentration range of interest. Prepare four filters at each of three concentrations plus three media blanks.
   a. Apparatus for preparing and sampling gas spikes is shown in Figure 1. The apparatus is composed of glass and Teflon.
   b. Sample at a rate of 0.2 L/min for 100 min.
      NOTE: Protect the samples from light.
   c. Extract the samples (steps 5 through 7) and analyze (steps 10 and 11).
   d. Prepare separate recovery graphs for each mercaptan (R vs. μg analyte).

MEASUREMENT:

10. Set gas chromatograph to conditions given on page 2542-1. Set air and hydrogen flow rates on the flame photometric detector to manufacturer's specification. Inject 1-μL sample aliquot via the split injection mode. Retention times: methyl mercaptan, 2.4 min; ethyl mercaptan, 3.2 min; n-butyl mercaptan 6.9 min.
11. Measure peak area.

CALCULATIONS:

12. Determine the mass, μg, of methyl-, ethyl-, and n-butyl-mercaptans found in the samples (W) and in the average media blanks (B).
13. Calculate concentration, C, of the mercaptans in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method modifies OSHA Method 26, Methyl Mercaptan [2], and further develops and evaluates the procedure for ethyl- and n-butyl mercaptans, as well as methyl mercaptan [1]. The method was evaluated for recovery and extraction efficiency with gas spikes, 18 samples (6 at each level, 0.5, 1, and 2 x PEL)(Figure 1). Recoveries were 82.7% for methyl mercaptan, 89.3% for ethyl mercaptan, and 93.0% for n-butyl mercaptan. Test atmospheres of methyl- and ethyl mercaptans were generated with permeation tubes as the analyte source. Six samples at one level (1 x PEL) were collected and analyzed. Recoveries for generated samples, corrected for extraction efficiency, were 98.6 ± 8.9% for methyl mercaptan and 102 ± 7.8% for ethyl mercaptan. Samples of n-butyl mercaptan were not generated. Samples prepared by spiking impregnated filters with a solution of mixed mercaptans were found to be stable for at least three weeks at ambient temperatures when protected from light. The evaluation data are summarized in Table 2.

REFERENCES:

[1] Xue, Zhi-Lun, Backup Data Report for Methyl, Ethyl, and n-Butyl Mercaptans (NIOSH/DPSE, unpublished, October, 1991).
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[3] Knarr, R. and Rapport, S.M., Determination of Methanethiol at Parts-per-Million Air Concentration by Gas Chromatography, Anal. Chem., 52, 733-736 (1980).
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[5] Material Safety Data Sheet, #504 Butyl Mercaptan, General Electric, Schenectady, NY 12305 (1982).
[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Pratima Shah, NIOSH/DPSE, and Zhi-Lun Xue.

TABLE 1. GENERAL INFORMATION

Compound	Exposure Limits (ppm) OSHA	NIOSH	ACGIH	1 ppm = mg/m³ @ NTP	Density @ 20 °C (g/mL)	BP (°C)	kPa (mm Hg)
Methyl mercaptan	C 10	C 0.5/15 min	0.5 ppm	2.0	0.866	6.2	> 1 atm
Ethyl mercaptan	C 10	C 0.5/15 min	0.5 ppm	2.6	0.839	35	58.9 (442)
n-Butyl mercaptan	10 ppm	C 0.5/15 min	0.5 ppm	3.7	0.834	98.4	4.7 (35)

TABLE 2. EVALUATION DATA

Compound	Range Studied* (mg/m³)	Measurement Range (µg/sample)	Measurement Precision $\bar{S}_r$	LOD (µg/sample)	Overall Precision $\hat{S}_{rT}$
Methyl mercaptan	1.0 to 4.0	10 to 50	0.055	4	0.091
Ethyl mercaptan	1.3 to 5.6	10 to 50	0.059	5	0.097
n-Butyl mercaptan	1.8 to 7.4	20 to 70	0.063	7	0.086

* 180-L samples

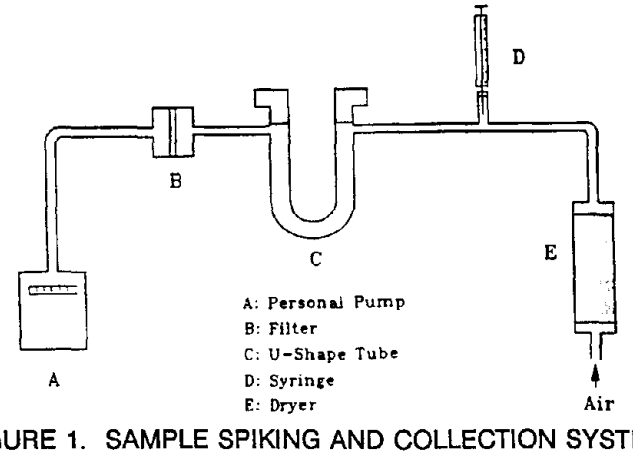

FIGURE 1. SAMPLE SPIKING AND COLLECTION SYSTEM

Hg MW: 200.59 CAS: 7439-97-6 RTECS: OV4550000

METHOD: 6009, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 0.1 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin)
ACGIH: 0.025 mg/m^3 (skin)

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; HP −39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C; Vapor Density (air=1) 7.0

SYNONYMS: quicksilver

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Hopcalite in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.5 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [2] (10-L samples)

BIAS: not significant

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{2+} in 1% HNO_3

RANGE: 0.1 to 1.2 μg per sample

ESTIMATED LOD: 0.03 μg per sample

PRECISION ($\bar{S}_r$): 0.042 @ 0.9 to 3 μg per sample [4]

APPLICABILITY: The working range us 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [3].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [4,5,6]. This method is based on the method of Rathje and Marcero [7] and is similar to the OSHA method ID 145H [2].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg^{2+}, 1000 μg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 μg/mL. Place 0.1 mL 1000 μg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v). Dilute 14 mL conc. HNO_3 to 1 L with deionized water.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hopcalite held in place by glass wool plugs (SKC, Inc., Cat. #226-17-1A, or equivalent).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the sorbent may be used if particulate mercury is to be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder, or integrator.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-μL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and contact with the skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known rate of 0.15 to 0.25 L/min for a total sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hopcalite sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 h or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards, a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in

NOTE: Steps 5 to 10 of Method 7300 (Elements by ICP), an $HNO_3/HClO_4$ digestion, may be substituted for the low temperature oxygen plasma ashing. Use a final solution volume of 5.0 mL (step 11).

10. Add 0.5 mL dissolution acid and warm on a hotplate (15 min at 50 °C).
11. Transfer solutions quantitatively to 5-mL volumetric flasks and dilute to volume with distilled deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to manufacturer's recommendations.
    NOTE: Typically, an acid blank and 10 μg/mL multi-element solutions are used.
13. Analyze a standard for every 10 samples.
14. Check measurement recoveries with at least three spiked unexposed urine samples per 10 samples.
    NOTE: For urine spikes, split a 100-mL control urine sample and analyze 50 mL without spiking. Subtract the metal quantity found in the unspiked portion from the metal quantity found in the spiked portion in order to determine measurement recovery.

MEASUREMENT:

15. Set the spectrometer to conditions specified by the manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the sample solutions with 1 volume dissolution acid plus 9 volumes deionized water, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentration for the sample, C_s (μg/mL), and the average blank, C_b (μg/mL), from the analyses data.
18. Using the solution volumes of sample, V_s (mL), and blank, V_b (mL), calculate the concentration, C (μg/mL), of each element in the volume of urine collected, V (L):

$$C = \frac{(C_sV_s - C_bV_b)}{V}, \text{ mg/m}^3.$$

19. Report the results as μg metal/g creatinine.

GUIDELINES TO INTERPRETATION:

Acceptable and unacceptable levels for metals have not been determined by this method. Lauwerys [4] discusses metals and can be consulted for guidance and interpretation.

EVALUATION OF METHOD:

Recovery of these 16 metals from spiked urine samples are shown in Table 2 (recoveries ranged from 77 to 100%). The precisions determined for the various elements are also given in Table 2 [1].

REFERENCES:

[1] Hull, R. D. Analysis of Trace Metals for Occupationally Exposed Workers, Morbidity and Mortality Weekly Report, 33, (1984).

[2] Hull, R. D. ICP-AESMulti-element Analysis of Industrial Hygiene Samples, NTIS Publication No. PB85-221414, 1985.

[3] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., pp. 994-997, W. B. Saunders Co., Philadelphia, PA (1976).

[4] Lauwerys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, CA (1983).

[5] Hackett, D. S. and S. Siggia. Selective Concentration and Determination of Trace Metals Using Polydithiocarbamate Chelating Ion-Exchange Resins, Environmental Analysis, p. 253, (G. W. Ewing, ed.), Academic Press, NY (1977).

[6] Bray, J. T. and F. J. Reilly. Extraction of Fourteen Elements from a Sea Water Matrix by a Polydithiocarbamate Resin, Jarrell-Ash Plasma Newsletter, 4, 4 (1981).

METHOD WRITTEN BY:

R. DeLon Hull, Ph.D., NIOSH/DBBS.

TABLE 1. GENERAL INFORMATION

Element (Formula)	Atomic Weight	CAS #	RTECS
Aluminum (Al)	26.98	7429-90-5	BD0330000
Barium (Ba)	137.34	7440-39-3	CQ8370000
Cadmium (Cd)	112.40	7440-43-9	EU9800000
Chromium (Cr)	52.00	7440-47-3	GB4200000
Copper (Cr)	63.54	7440-50-8	GL5325000
Iron (Fe)	55.85	7439-89-6	NO4565500
Lead (Pb)	207.19	7439-92-1	OF7525000
Manganese (Mn)	54.94	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	7439-98-7	QA4680000
Nickel (Ni)	58.71	7440-02-0	QR5950000
Platinum (Pt)	195.09	7440-06-4	TP2160000
Silver (Ag)	107.87	7440-22-4	VW3500000
Strontium (Sr)	87.62	7440-24-6	
Tin (Sn)	118.69	7440-31-5	XP7320000
Titanium (Ti)	47.90	7440-32-6	XR1700000
Zinc (Zn)	65.37	7440-66-6	ZG8600000

METHYLENE CHLORIDE

CH_2Cl_2 MW: 84.94 CAS: 75-09-2 RTECS: PA8050000

METHOD: 1005, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 500 ppm; C 1000 ppm; P 2000 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.323 g/mL @ 20 °C; BP 40 °C; MP −95 °C; VP 47 kPa (349 mm Hg; 46% v/v) @ 20 °C; not flammable

SYNONYMS: dichloromethane; methylene dichloride.

SAMPLING

SAMPLER: SOLID SORBENT TUBES (2 coconut shell charcoal tubes, 100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2.5 L

SHIPMENT: separate front and backup tubes

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1700 to 7097 mg/m^3 (1-L samples) [1]

BIAS: − 4.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: ± 14.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylene chloride

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 to 225 °C
-DETECTOR: 250 °C
-COLUMN: 60 to 90 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3-mm ID stainless steel, 10% SP-1000 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of CH_2Cl_2 in CS_2 with internal standard

RANGE: 0.03 to 10 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [3,4]

PRECISION ($\bar{S}_r$): 0.026 @ 1.3 to 5.3 mg per sample [1]

APPLICABILITY: The working range is 9 to 3000 ppm (30 to 10,400 mg/m^3) for a 1-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. The method was validated using a 6 m x 3-mm ID stainless steel column packed with 10% FFAP on 100/120 mesh Supelcoport. Alternate chromatographic columns are 10% TCEP on 80/100 Chromosorb PAW, SP-2100, SP-2100 with 0.1% Carbowax 1500, or DB-1 fused silica capillary column.

OTHER METHODS: This revises Methods S329 [2], 1005 (dated 2/15/84), P&CAM 127 [3], and the criteria document method [5]. OSHA Method 59 uses larger (350 mg) sorbent sections and has been evaluated for 10-L air samples at 1 ppm methylene chloride [6].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% v/v decane, benzene, or other suitable internal standard.
2. Methylene chloride.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: separate front and backup glass tubes with plastic caps, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg). A silylated glass wool plug is placed at each end of each tube. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: Two commercially available tubes, each containing 150 mg charcoal in two beds, may be used in tandem.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1005-1).
4. Vials, 2-mL, PTFE-lined septum crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = −30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.5 to 2.5 L.
4. Separate the front and backup tubes and cap each tube to prevent migration of methylene chloride between tubes. Pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

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

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1005-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Method S329 [2] was issued on June 6, 1975, and validated over the range 1700 to 7100 mg/m^3 at 25 °C and 763 mm Hg using a 1-L sample [1]. Overall precision, $\hat{S}_{rT}$, was 0.073 with average recovery 95.3%, representing a non-significant bias. The concentration of methylene chloride was independently verified by calibrated syringe pump. Desorption efficiency was 0.97 in the range 1.3 mg to 5.3 mg methylene chloride per sample. Breakthrough (5% on back section) occurred at 18.5 min when sampling an atmosphere containing 6726 mg/m^3 methylene chloride at 0.187 L/min at 0% RH. The stability of methylene chloride on charcoal was not determined. The method was used in NIOSH Sequences #7745 (4/8/93), #7620N (2/16/93), #7716M (1/22/93), and #7716F (1/21/93) [7].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, NIOSH, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] User check, UBTL, NIOSH Sequence #3990-R (unpublished, November 3, 1983).

[5] Criteria for a Recommended Standard...Occupational Exposure to Methylene Chloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-138 (1976).
[6] OSHA Method 59.
[7] NIOSH Sequences (unpublished) (1993).

METHOD REVISED BY:

G. David Foley and Y. T. Gagnon; NIOSH/DPSE; S329 originally validated under NIOSH Contract CDC-99-74-45.

SAMPLE PREPARATION:

6. Agitate the samples for 1 hour in an ultrasonic water bath.
7. Filter the sample solution through a 0.45-μm PTFE filter and a disposable syringe into a clean vial.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Make serial dilutions as needed to obtain MDA concentrations in the range 0.025 to 1 μg/mL.
   b. Analyze together with samples and blanks (steps 11 through 13).
   c. Prepare a calibration graph (peak area vs. concentration of MDA, μg per sample) for each detector (UV and ECHD).
9. Determine the recovery at least once for each lot of filters used for sampling in the range of interest. Prepare six filters at each of three concentration levels plus three media blanks.
   a. Add known amounts of MDA in methanol to the filters, using a microliter syringe.
   b. Cover filters. Allow to stand overnight for solvent evaporation.
   c. Extract with 4.0 mL extracting solutions, prepare samples (steps 6 and 7) and analyze (steps 11 through 13) together with standards and blanks.
   d. Determine recovery (R). Construct a graph of R vs. μg MDA recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

11. Set liquid chromatograph to manufacturer's recommendations and parameters given on page 5029-1.
12. Inject sample aliquot manually or with autosampler.
13. Measure peak areas for UV and ECHD responses.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

A calibration curve for the UV absorption detector was constructed from 8 standards over the range 0.03 μg/mL to 1.22 μg/mL [1]. The curve was linear over this region and the LOD was determined to be 0.03 μg/mL. A calibration curve for the ECHD over the range 0.001 μg/mL to 0.12 μg/mL was linear and the LOD was determined to be 0.002 μg/mL. Test samples were prepared by spiking acid-impregnated filters with known amounts of MDA from a solution in methanol. Samples were prepared in triplicate at levels between 0.009 μg per filter and 3.7 μg per filter. (See Table 1 for results):

a. To evaluate extraction efficiency, the filters were analyzed immediately.
b. To assess storage stability, spiked filters were stored in glass scintillation vials for 1 month prior to analysis.

c. To investigate the stability of MDA on the filter during sampling, spiked filters were attached to a sampling pump and 1000 L of laboratory air was drawn through them at 2.5 L/min before analysis.

Table 1: Average Percent Recovery (n=3) of 4,4'-Methylenedianiline From Filter Media

Spiked Amount (μg)	Extraction Efficiency (S.D.) (%)	Storage Stability[a] (%)	Sampling Stability (%)
3.71	94.5 (0.8)	94.4 (1.0)	94.4 (1.0)
1.80	91.3 (0.2)	91.1 (0.4)	90.8 (1.7)
0.93	85.9 (0.8)	86.4 (0.9)	85.5 (0.4)
0.37	84.8 (0.9)	86.0 (0.7)	84.9 (1.0)
0.09	82.0 (2.7)	82.0 (3.8)	77.0 (3.5)
0.037	80.0 (4.1)	83.0 (4.1)	77.0 (3.1)

[a] - Stored in glass scintillation vial for 1 month.

Nine spiked filters were prepared independently and submitted for analysis as a single blind test. Recoveries were 80 to 95% when spiked with 0.012 to 1.2 μg per filter.

During method ruggedization, recoveries were observed to drop significantly during shipment in cassettes. The reason has not been determined but stability has been achieved by field extraction of the filter with methanolic KOH. Solutions and extracted filters were prepared, shipped, stored for 60 days, and analyzed. The data are shown in Table 2.

Table 2: Stability of Extracted Filter Solutions

Spiked Amount (μg)	N	% Recovery (S.D.)
9.9	4	92.1 (0.017)
5.1	4	90.4 (0.042)
1.0	4	100.0 (0.050)
0.0	2	NA

WIPE SAMPLING-This analytical method was used to analyze environmental samples collected on gauze pads and smear tabs. MDA was spiked onto acid-treated gauze pads, plain gauze pads, and smear tabs at 92, 9.2, and 0.92 μg per sample. Sets of each concentration were extracted immediately after allowing the spiking solution to evaporate, one day, one week, and one month after spiking. The extraction solution consisted of 10 mL 0.1 N methanolic KOH for the gauze pads and 2 mL for the smear tabs. The best recovery was obtained when the media were extracted immediately after the methanol evaporated. The same-day samples were reanalyzed at various times to determine if MDA would react with the medium when in solution. Recoveries are given in Table 3.

$C_{10}H_{14}N_2$ MW: 162.26 CAS: 54-11-5 RTECS: QS5250000

METHOD: 2544, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 0.5 mg/m^3 (skin)
NIOSH: 0.5 mg/m^3 (skin); Group I Pesticide
ACGIH: 0.5 mg/m^3 (skin)

PROPERTIES: liquid, BP 245.5 °C; density 1.009 g/mL (20 °C)

SYNONYMS: 3-(1-methyl-2-pyrrolidinyl) pyridine

SAMPLING

SAMPLER: SOLID SORBENT TUBE XAD-2 (100 mg/50 mg)

FLOW RATE: 1.0 L/min

VOL-MIN: 60 L @ 0.5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days at 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.3 to 1.2 mg/m^3 [1] (100-L samples)

BIAS: not determined [2]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [2]

ACCURACY: ± 12%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY-NITROGEN PHOSPHOROUS DETECTOR

ANALYTE: nicotine

DESORPTION: 1 mL ethyl acetate, stand 30 min

INJECTION VOLUME: 2.0 µL

TEMPERATURE-INJECTION: 235 °C
-DETECTOR: 260 °C
-COLUMN: 165 °C

CARRIER GASES: He, 25 mL/min; fuel, H_2

COLUMN: glass, 2 m x 2-mm ID, packed with 3% OV-101 on 100/120 mesh Supelcoport

CALIBRATION: solutions of nicotine in ethyl acetate

RANGE: 0.03 - 0.13 mg per sample

ESTIMATED LOD: not determined [2]

PRECISION ($\bar{S}_r$): 0.015 [1]

APPLICABILITY: The working range is 0.3 to 2 mg/m^3 for a 100-L air sample. The probable useful range of this method is likely to extend to lower concentrations than the analytical range specified above. Desorption efficiency must be determined over the range evaluated.

INTERFERENCES: None identified.

OTHER METHODS: This is method S293 [2] in a revised format.

REAGENTS:

1. Nicotine, reagent grade.*
2. Ethyl acetate, chromatographic quality.
3. Calibration solution, 5 mg/mL:
   Add 5 mg (5 μL) of nicotine to a 1.0 mL volumetric flask. Dilute to the mark with ethyl acetate.
4. Nitrogen, purified.
5. Hydrogen, pre-purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass tube, 7 cm long, 6-mm OD, 4-mm ID; two sections of 20/50 mesh pre-extracted XAD-2 (front = 100 mg, back = 50 mg separated by a plug of silylated glass wool and held in place with plugs of silylated glass wool, flame-sealed with plastic caps. The pressure drop across the tube should be 0.133 kPa at $\leq$1.0 L/min. Tubes are commercially available.
2. Personal sampling pump, 1.0 L/min with flexible connecting tubing.
3. Gas chromatograph, NPD, integrator, and column (p-2544-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-μL and 25-μL, readable to 0.1 μL.
6. Volumetric flasks, 1.0-mL.
7. Pipets, delivery-type, 1.0-mL.
8. File.

SPECIAL PRECAUTIONS: Nicotine is a vasoconstrictor. Perform all work with these chemicals in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Before sampling, score the ends of each sampling tube with a file, and break open. Attach the sampler to personal sampling pump with flexible tubing.
3. Sample at 1.0 L/min to obtain the recommended sample volume of 60 to 400 L.
4. Cap the tubes with plastic (not rubber) caps immediately following sampling and pack securely for shipment.

SAMPLE PREPARATION:

5. Transfer the front (larger) section of XAD-2 with glass wool plug to a 2-mL vial. Transfer the backup sorbent section along with the separating section of glass wool to another vial. Discard the back glass wool plug.
6. Pipet 1.0 mL of ethyl acetate into each vial. Seal the vials with a teflon-lined crimp-cap.
7. Allow to stand 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the analytical range 0.005 to 0.13 mg nicotine per sample.
   a. Add 1 to 25 μL or other convenient aliquots of the calibration solution to 1.0 mL of ethyl acetate in separate vials. Correct the volume of ethyl acetate in each vial to account for volume of the aliquot of calibration solution added. Seal the vials with septum-lined crimp-caps.
   b. Analyze the standards together with the samples (steps 11 through 13).
   c. Prepare a calibration graph of peak area vs. mg of analyte.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards to cover the range of 1 to 18 μg nitrite ion per 10-mL sample.
    a. Analyze the working standards together with blanks and samples (steps 8 through 10 and steps 12 through 14).
    b. Prepare a calibration graph [absorbance vs. μg NO_2^- per sample].

MEASUREMENT:

12. Set wavelength on the spectrophotometer to 540 nm.
13. Set to zero with reagent blank.
14. Transfer some of the sample solution from step 10 to a cuvette and record the absorbance.

CALCULATIONS:

15. From the calibration graph, determine the mass of NO_2^- in each Tube A, W_A (μg), and in the corresponding average blank, B_A (μg). Similarly, determine the mass of NO_2^- in each Tube C, W_c (μg), and average blank, B_c (μg).
16. Calculate the concentration, C_{NO2} (mg/m^3) of NO_2 in the volume of air sampled, V (L), applying the conversion factor 0.63:

$$C_{NO_2} = \frac{(W_A - B_A)}{0.63\ V},\ \text{mg/m}^3.$$

NOTE: The conversion factor 0.63 represents the number of moles of nitrite ion produced by 1 mole of nitrogen dioxide gas. For NO or NO_2, gas concentrations above 10 ppm, use 0.5 as the conversion factor [7].

17. Calculate the concentration, C_{NO} (mg/m^3), of NO in the air volume sampled, V (L), applying the factor 0.652 (MW NO/MW NO_2^-) and the conversion factor 0.63:

$$C_{NO} = \frac{(W_c - B_c) \cdot 0.652}{0.63\ V},\ \text{mg/m}^3.$$

EVALUATION OF METHOD:

Method S321, Nitric Oxide, was evaluated over the range of 11.1 to 47.7 ppm (13.8 to 58.5 mg/m^3) for 1.5-L samples, collected from dynamically generated test atmospheres [1,8]. The test concentration was verified with a direct reading instrument, Energetic Sciences Enolyzer. The 1.2 g oxidizer section was found adequate for a 60-min sampling time. NO samples had a mean recovery of 99.5% after 7 days storage at ambient temperature.

Method S320, Nitrogen Dioxide, was evaluated over the range 3.0 - 11.6 ppm (5.8 to 21.6 mg/m^3) using 3.9-L samples [2,7]. When an atmosphere at 84% RH containing 11.59 ppm NO_2 was sampled at 0.064 L/min, 1.0% breakthrough occurred after 60 min and 2.4% breakthrough occurred after 180 min. Quantitative recovery was obtained for samples containing 47 μg NO_2 which were stored for 12 days at ambient conditions.

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METHOD REVISED BY:

W. J. Woodfin and M. E. Cassinelli, NIOSH/DPSE; Method S321 validated under NIOSH Contract No. 210-76-0123.

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

METHOD: 2522, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PELs; N-nitrosodimethylamine is a carcinogen
NIOSH: no RELs; N-nitrosodimethylamine is suspect carcinogen
ACGIH: no TLVs; N-nitrosodimethylamine is suspect carcinogen

PROPERTIES: Table 1

SYNONYMS: Table 1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Thermosorb/N™ air sampler)

FLOW RATE: 0.2 to 2 L/min

VOL-MIN: 15 L @ 10 $\mu g/m^3$
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 weeks @ 20 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, TEA [1]

ANALYTE: nitrosamines (Table 1)

DESORPTION: 2 mL 3:1 (v/v) dichloromethane/methanol; stand 30 min

INJECTION VOLUME: 5 μL

COLUMN: stainless steel (10 in x ⅛ in); 10% Carbowax 20M + 2% KOH on Chromosorb W-AW

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 550 °C to 600 °C
-COLUMN: 110 °C to 200 °C programmed @ 5°/min

GASES: N_2 carrier, 25 mL/min; oxygen, 5 mL/min; ozone, 0.2 mL/min

CALIBRATION: standard solutions of analytes in methanol/dichloromethane

RANGE: 0.15 to 0.5 μg per sample [2]

ESTIMATED LOD: 0.05 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.014 @ 0.05 to 0.4 μg per sample [2]

APPLICABILITY: The working range is 0.003 to 10 mg/m^3 for a 50-L air sample. If high ambient concentrations of nitrosamines are expected, another Thermosorb/N tube should be used as a back-up in sampling.

INTERFERENCES: When the thermal energy analyzer (TEA) is operated in the nitrosamine mode, it is highly specific for N-nitroso compounds. Because of the TEA's selectivity and sensitivity, it is possible to chromatograph and quantitate N-nitroso compounds, even in the presence of other co-eluting compounds. Therefore, there is little or no interference from other compounds.

OTHER METHODS: This replaces NIOSH methods P&CAM 252 [3] and P&CAM 299 [4].

REAGENTS:

1. Dichloromethane, reagent grade.
2. Methanol, reagent grade.
3. Nitrogen, purified.
4. Oxygen, purified, 99.99%.
5. Standard solutions of N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodibutylamine, N-nitrosodipropylamine, N-nitrosomorpholine, N-nitrosopiperidine, N-nitrosopyrrolidine.
6. Eluent, 3:1 (v/v) dichloromethane/methanol.
7. Air, filtered, compressed.
8. Ozone, purified 99.99%.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Commercially available tubes (Thermedics Detection, Inc., 220 Mill Rd., Chelmsford, MA 01824, 508/251-2000).
2. Personal sampling pump, 0.2 to 2 L/min, with flexible tubing.
3. Gas chromatograph equipped with thermal energy analyzer (TEA), integrator and column (page 2522-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Pipets, various sizes for preparing standards.
6. Syringes, 1-, 5-, 10-, 25-, and 100-μL readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Gloves for safe handling of toxic chemicals.
9. Syringe, glass, 5.0-mL, with male Luer adapter.
10. Needle, industrial blunt, 20-gauge with female luer adapters.

SPECIAL PRECAUTIONS: N-nitrosodimethylamine is an OSHA-regulated carcinogen. Other nitrosamines are suspected carcinogens and are very toxic. Handle samples and standards in a well-ventilated hood or glove box.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the Thermosorb/N tube from the foil pouch. Save the pouch.
3. Remove the red end caps from the inlet and outlet ports. Store red caps on the Thermosorb/N tube in the brackets under the "AIR IN" sign.
4. Label the Thermosorb/N tube with the peel-off "AIR SAMPLER" label provided on the foil pouch.
5. Attach the Thermosorb/N tube to the sampling pump with flexible tubing.
6. Sample at an accurately known flow rate between 0.2 and 2 L/min for a total sample size of 15 to 1000 L.
7. After sampling, detach the sampler from the pump.
8. Replace the red end caps on the inlet and outlet ports of the sampler.
9. Replace the Thermosorb/N tube in the foil pouch. Fold the pouch and seal it with the clip provided and pack securely for shipment.

SAMPLE PREPARATION:

10. Remove the sampler from the foil pouch.
11. Label analysis vial with the label from the Thermosorb/N air sampler.
12. Remove the red end-caps, store them in the bracket provided with the tube.
13. Attach a syringe needle to the male Luer fitting of the Thermosorb/N tube.
14. Attach a syringe barrel containing eluent to the female Luer fitting of the Thermosorb/N tube.
15. Elute by "backflushing" the Thermosorb/N tube with 2.0 mL of eluent. Collect the effluent in the labeled vial.
    NOTE: The optimum elution rate is 0.5 mL/min.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4-μm median cut point

CAS: None RTECS: None

METHOD: 0600, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA: 5 mg/m^3
NIOSH: no REL
ACGIH: 3 mg/m^3

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates the non-ciliated portions of the lung

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm cyclone or Higgins-Dewell (HD) cyclone + tared 5-μm PVC membrane)

FLOW RATE: nylon cyclone: 1.7 L/min
HD cyclone: 2.2 L/min

VOL-MIN: 20 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: indefinitely

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 10 mg/m^3 (lab and field)

BIAS: depends on dust size distributions [1]

OVERALL PRECISION ($\hat{S}_{rT}$): depends on size distributions [1,2]

ACCURACY: depends on dust size distributions [1]

MEASUREMENT

TECHNIQUE: GRAVIMETRIC (FILTER WEIGHT)

ANALYTE: mass of respirable dust fraction

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights

RANGE: 0.1 to 2 mg per sample

ESTIMATED LOD: 0.03 mg per sample

PRECISION: <10 μg with 0.001 mg sensitivity balance
<68 μg with 0.01-mg sensitivity balance [3]

APPLICABILITY: The working range is 0.5 to 10 mg/m^3 for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. Besides inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust (e.g., $\approx +7\%$ bias for non-diesel, coal mine dust)[5].

INTERFERENCES: Larger than respirable particles (over 10 μm) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in the sample are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
   a. Filter: 5.0-μm pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive).
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD)[7], or equivalent.
2. Personal sampling pump, 1.7 L/min ± 5% for nylon cyclone or 2.2 ± 5% L/min for HD cyclone, with flexible connecting tubing.
   NOTE: Pulsation in the pump flow must be within ± 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Static neutralizer, e.g., Po-210; replace nine months after the production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance, e.g., 20 °C ± 1 °C and 50% ± 5% RH.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps (nylon forceps if further analyses will be done).
   c. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette.
4. Remove the cyclone's grit cap before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
   NOTE: Because of its square inlets, the nylon cyclone must be calibrated within a large vessel with inlet and outlet ports. The vessel inlet is connected to a calibrator (e.g., a bubble meter); whereas the outlet is connected to the sampling pump. The HD cyclone, on the other hand, can have the calibrator connected directly to the cyclone inlet. Note that even if the flowrate shifts by a known amount between calibration and use, the nominal flowrates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed approximately 2 mg dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3, \ mg/m^3.$$

where: W_1 = tare weight of filter before sampling (mg)
W_2 = post-sampling weight of sample-containing filter (mg)
B_1 = mean tare weight of blank filters (mg).
B_2 = mean post-sampling weight of blank filters (mg)
V = volume as sampled at the nominal flowrate (i.e., 1.7 L/min or 2.2 L/min)

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as −0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias is less than -0.02 for most dust size distributions encountered in the workplace.

Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.029 mg.

   Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

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METHOD REVISED BY:

David L. Bartley, Ph.D., NIOSH/DPSE.

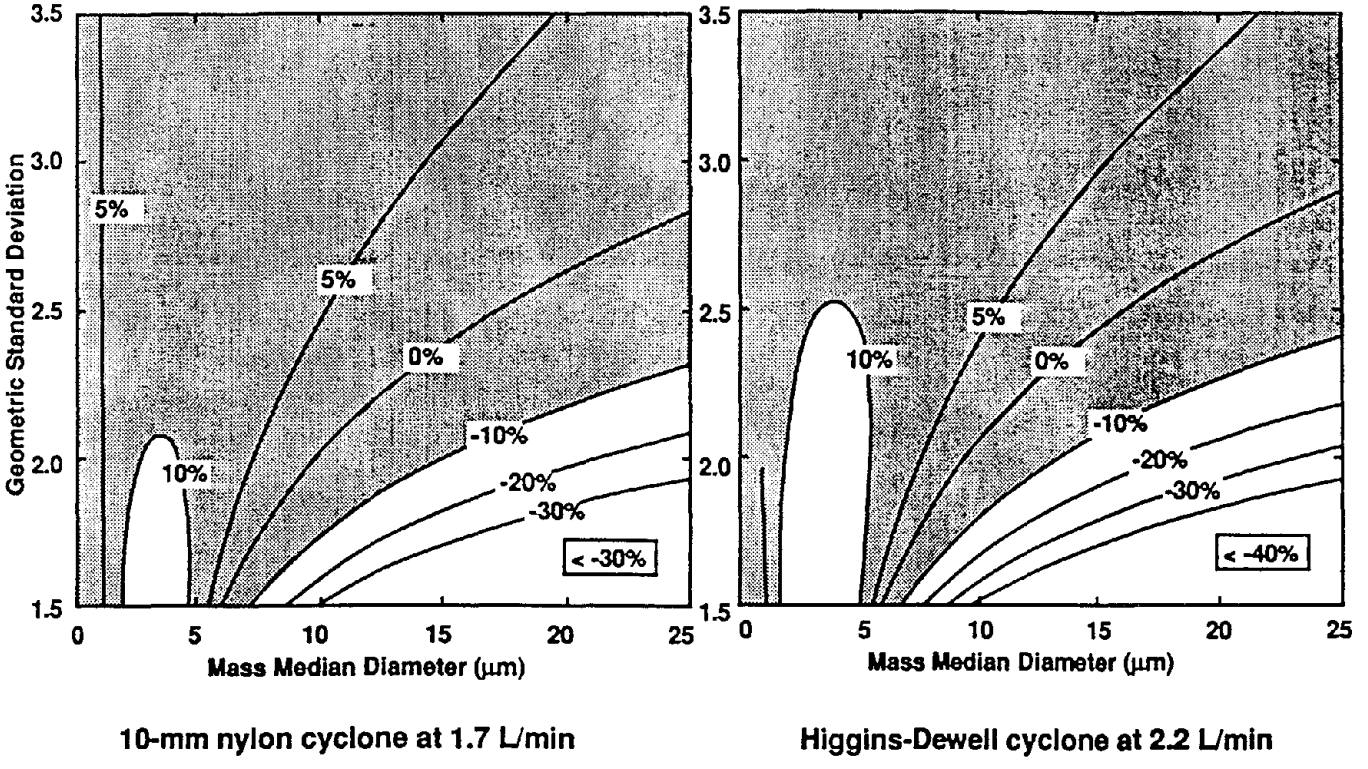

Figure 1. Bias in respirable dust determination.

PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500

DEFINITION: total aerosol mass CAS: NONE RTECS: NONE

METHOD: 0500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 15 mg/m^3
NIOSH: no REL
ACGIH: 10 mg/m^3, total dust less than 1% quartz

PROPERTIES: contains no asbestos and quartz less than 1%

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (tared 37-mm, 5-μm PVC filter)	**TECHNIQUE:**	GRAVIMETRIC (FILTER WEIGHT)
FLOW RATE:	1 to 2 L/min	**ANALYTE:**	airborne particulate material
VOL-MIN:	7 L @ 15 mg/m^3	**BALANCE:**	0.001 mg sensitivity; use same balance before and after sample collection
-MAX:	133 L @ 15 mg/m^3		
SHIPMENT:	routine	**CALIBRATION:**	National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights
SAMPLE STABILITY:	indefinitely	**RANGE:**	0.1 to 2 mg per sample
BLANKS:	2 to 10 field blanks per set	**ESTIMATED LOD:**	0.03 mg per sample
BULK SAMPLE:	none required	**PRECISION ($\hat{S}_r$):**	0.026 [2]

ACCURACY

RANGE STUDIED:	8 to 28 mg/m^3
BIAS:	0.01%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.056 [1]
ACCURACY:	± 11.04%

APPLICABILITY: The working range is 1 to 20 mg/m^3 for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [3] in addition to the other ACGIH particulates not otherwise regulated [4].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [3].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [3] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

EQUIPMENT:

1. Sampler: 37-mm PVC, 2- to 5-μm pore size membrane or equivalent hydrophobic filter and supporting pad in 37-mm cassette filter holder.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Microbalance, capable of weighing to 0.001 mg.
4. Static neutralizer: e.g., Po-210; replace nine months after the production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance (e.g., 20 °C ± 1 °C and 50% ± 5% RH).

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
   NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 7 to 133 L. Do not exceed a total filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust.
   NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.

c. Prepare a calibration graph of peak area vs. amount (μg) of pentachlorophenol per 25 mL of sample.

11. Determine recovery for each lot of filters used for sampling in the concentration range of interest. Prepare four filters at each of five levels plus three media blanks.
    a. Spike aliquot of calibration solution onto each filter.
    b. After air-drying, extract filters in 15 mL ethylene glycol.
    c. Just before analysis, add 10 mL methanol and analyze (steps 13 through 15).
    d. Prepare graph of recovery vs. μg pentachlorophenol.
12. Check recovery at two levels for each sample set. Repeat recovery graph determination if checks do not agree to within 5% of recovery graph.

MEASUREMENT:

13. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5512-1.
14. Inject 20-μL sample aliquot.
    NOTE: If sample peak area exceeds the linear calibration range, dilute, and apply appropriate dilution factor in calculations.
15. Measure peak area.

CALCULATIONS:

16. Determine mass, μg (corrected for recovery), of pentachlorophenol (W) found in the sample and the average media blank (B).
17. Calculate concentration of pentachlorophenol in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was validated over the range 0.265 to 1.31 mg/m^3 at 24 °C and pressure of 761 mm Hg using 180-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.072, with average recovery of 105%, representing a non-significant bias. The concentration of pentachlorophenol was independently verified by direct UV analysis of sample solutions. Recovery of pentachlorophenol from filters was 101% in the range 45 to 180 μg per sample. Sample stability during storage was evaluated at 100 μg pentachlorophenol per sample. Samples showed 95.3% recovery after eight days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Pentachlorophenol, prepared under NIOSH Contract 210-76-0123 (1977).

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S297, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[3] Analysis of NIOSH Samples for Pentachlorophenol and Tetrachlorophenol, NIOSH/MRSB Sequence #4492, Utah Biomedical Research Laboratory, Salt Lake City, UT (unpublished, 1984).

[4] Vulcan Materials Co. Analytical Backup Report #1. Determination of Pentachlorophenol in Air, Birmingham, AL 35255 (1982).

[6] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[7] CCINFO Database, Release 93-3, Record No. 41. Canadian Centre for Occupational Health and Safety, Hamilton, Ontario, Canada (1993).

METHOD REVISED BY:

M.J. Seymour, NIOSH/DPSE.

PHENYL ETHER

$(C_6H_5)_2O$ MW: 170.22 CAS: 101-84-8 RTECS: KN8970000

METHOD: 1617, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: STEL 2 ppm
(1 ppm = 6.96 mg/m^3)

PROPERTIES: solid, geranium-like odor; MP 27 °C; BP −257 °C; d 1.072 g/mL @ 22 °C; VP 2.7 Pa (0.02 mm Hg) @ 25 °C; vapor density 5.86 (air = 1); flash pt. 115 °C; flammable limits in air 0.8 to 1.5%

SYNONYMS: diphenyl ether; diphenyl oxide; 1,1'-oxybisbenzene.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 1 ppm
-MAX: 50 L

SHIPMENT:

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 3.0 to 13.0 mg/m^3 [1] (10-L samples)

BIAS: 0.06%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 [1,2]

ACCURACY: ± 13.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: phenyl ether

EXTRACTION: 0.5 mL carbon disulfide, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 230 °C
-DETECTOR: 265 °C
-COLUMN: 215 °C

COLUMN: 10 ft x 1/8-in. ID stainless steel column packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W

DETECTOR: flame ionization detector

CALIBRATION: standard solutions of phenyl ether in hexane

RANGE: 7 to 210 µg per sample [1,2]

ESTIMATED LOD: 0.7 µg per sample [1,2]

PRECISION ($\hat{S}_r$): 0.048 [1,2]

APPLICABILITY: The working range is 0.1 to 9 ppm (0.7 to 60 mg/m^3) for a 10-L air sample. Better sensitivity may be achieved with a capillary column with appropriate adjustment in the instrumental conditions. A DB-wax (polyethelyene glycol) or equivalent is similar to the FFAP packed column.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S72 [3].

REAGENTS:

1. Phenyl ether*, ACS reagent grade.
2. Carbon disulfide*, ACS reagent grade.
3. Hexane, distilled in glass.
4. Calibration stock solution, 17.3 mg/mL, of phenyl ether in hexane.
5. Prepurified nitrogen.
6. Prepurified hydrogen.
7. Filtered compressed air.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tubes, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg)separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube a 1 L/min airflow must be less than 4.3 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 1-mL with PTFE-lined caps.
5. Gas chromatograph with a flame ionization detector, recorder, integrator and column (page 1617-1).
6. Tweezers.
7. Syringes, 5-, 10- and 100-μL; other sizes as needed.
8. Volumetric flasks, 10- and 25-mL.
9. Pipets, 0.5-, 1-, and 10-mL glass, delivery, with pipet bulb, graduated to 0.1-mL increments.
10. Graduated cylinders, glass, 25-mL.
11. File.

SPECIAL PRECAUTIONS: Phenyl ether is toxic by inhalation. All work with carbon disulfide should be performed in a hood because of its high toxicity and flammability (flash point = −30 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm). Attach sampler to personal sampling pump with flexible tubing.
3. Sample 1 to 50 L of air at an accurately known flow rate between 0.01 and 0.2 L/min.
4. Record the humidity temperature, and pressure of the atmosphere being sampled, if pressure reading is not available, record the elevation.
5. Cap each tube with plastic plugs and pack securely for shipment.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Place front and back sections of the sampler in separate 1-mL vials. Discard the glass wool and foam plugs.
8. Add 0.5 mL carbon disulfide to each sample vial and attach the crimp cap.
9. Allow to stand 30 min with occasional agitation.

PHENYL ETHER-DIPHENYL MIXTURE 2013

$(C_6H_5)_2O$ & $C_6H_5C_6H_5$ MW: 166 (average) CAS: 8004-13-5 RTECS: DV1500000

METHOD: 2013, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: no TLV
(1 ppm = 6.79 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 257 °C; MP 12 °C; d = 1.06 g/mL @ 25°C; VP = 10 Pa (0.08 mm Hg) @ 25 °C; vapor density (air = 1) 5.7.; flammable limits in air 0.5 to 6.2% v/v

SYNONYMS: None. This is a liquid eutectic, prepared by dissolving 26.5 parts by weight solid diphenyl in 73.5 parts melted phenyl ether.

SAMPLING

SAMPLER: SORBENT TUBE (silica gel, 150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

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

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required

ACCURACY

RANGE STUDIED: 3.86 to 15.7 mg/m^3 [1] (10-L samples)

BIAS: − 0.35%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.089 [1]

ACCURACY: ± 17.2%

MEASUREMENT

TECHNIQUE: gas chromatography, FID

ANALYTE: phenyl ether-diphenyl mixture

EXTRACTION: 0.5 mL benzene for 30 min

INJECTION VOLUME: 5 µL

CARRIER GAS: nitrogen, 50 mL/min

COLUMN: 10-ft x 1/8-in stainless steel column packed with 5% OV-17 on 80/100 mesh, acid washed DMCS Chromosorb W

DETECTOR: flame ionization detector

CALIBRATION: standard solutions of eutectic mixture in hexane

RANGE: 7 to 210 µg per sample [1]

ESTIMATED LOD: 4 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.073 @ 38 to 156.7 µg per sample [1]

APPLICABILITY: The working range is 0.1 to 10 ppm (0.7 to 70 mg/m^3) for a 10-L air sample. Better sensitivity may be achieved with a capillary column in place of a packed column; a DB-17 column (50% methyl, phenyl-50% dimethyl-polysiloxane) with appropriate instrumental conditions is recommended.

INTERFERENCES: None identified.

OTHER METHODS: This is Method S73 [2] in fourth edition format.

REAGENTS:

1. Diphenyl*, reagent grade.
2. Phenyl ether*, reagent grade.
3. Phenyl ether-biphenyl mixture: dissolve 2.65 g solid diphenyl in 7.35 g melted phenyl ether (10 g mixture, liquid eutectic).
4. Benzene*, reagent grade.
5. Hexane, reagent grade.
6. Calibration stock solution, analyte mixture in hexane, 17.5 mg/mL.
7. Hydrogen, prepurified.
8. Air filtered, compressed.
9. Nitrogen, purified.

* See Special Precautions

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; with plastic caps; containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg; back = 75 mg). A silylated glass wool plug proceeds the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.20 L/min, with flexible polyethylene or PTFE tubing.
3. PTFE plugs and/or tubing.
4. Vials, glass, 1-mL with PTFE-lined crimp caps.
5. Gas chromatograph, flame ionization detector, recorder, integrator and column (page 2013-1).
6. Tweezers.
7. File.
8. Syringes, 5-, 50- and 100-μL, other sizes if needed.
9. Volumetric flasks, 10-mL.
10. Pipets, 0.5-, and 1.0-mL glass, delivery, graduated in 0.1-mL increments, with pipet bulb.
11. Graduated cylinders, glass, 10-mL.

SPECIAL PRECAUTIONS: Benzene is a carcinogen, toxic and is flammable. Phenyl ether is toxic by inhalation. Diphenyl is toxic. Work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2-mm). Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample volume of 1 to 40 L.
4. After the sample is collected, cap each tube with plastic plugs and pack securely for shipment.
5. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

6. Place front and back sorbent sections of the sampler tube in separate vials. Discard the glass wood and foam plugs.
7. Add 0.5 mL benzene to each sample vial and attach the crimp cap.
8. Allow to stand for 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 0.5 mL benzene.
   b. Analyze with samples and blanks (steps 12 and 13).

$C_6H_5NHNH_2$ MW: 108.14 CAS: 100-63-0 RTECS: MV8925000

METHOD: 3518, Issue 1 **EVALUATION:** FULL **Issue 1:** 15 August 1994

OSHA : 5 ppm (skin)
NIOSH: C 0.14 ppm/120 min (skin)
ACGIH: 5 ppm, STEL 10 ppm, suspect carcinogen
(1 ppm = 4.42 mg/m^3 @ NTP)

PROPERTIES: solid; MP 19.5 °C; d 1.098 g/mL @ 20 °C; VP 5 Pa (0.04 mm Hg; 50 ppm) @ 25 °C

SYNONYMS: hydrazinobenzene, hydrazine-benzene

SAMPLING

SAMPLER: GLASS MIDGET BUBBLER (containing 15 mL 0.1 M hydrochloric acid)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 25 L @ 5 ppm
-MAX: 120 L

SHIPMENT: hand delivery or use of bubbler shipping cases

SAMPLE STABILITY: at least 5 days at room temperature [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: [1] 10.4 to 44.8 mg/m^3 (100-L samples)

BIAS: 4.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.060 [1]

ACCURACY: ± 16.6%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: phenylhydrazine hydrochloride/ phosphomolybdic acid complex

SAMPLE WORKUP: transfer bubbler solution, two 5-mL rinses, and 10 mL phosphomolybdic acid to 50-mL volumetric flask

DILUTION: 3-mL aliquot diluted to 10 mL

COLORIMETRY: absorbance @ 730 nm

CALIBRATION: phenylhydrazine hydrochloride in 0.1 M hydrochloric acid

RANGE: 0.5 to 4.4 mg per sample [1]

ESTIMATED LOD: 0.2 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.023 [1]

APPLICABILITY: The working range is 1.1 to 11 ppm (5 to 45 mg/m^3) for a 100-L air sample.

INTERFERENCES: Other hydrazines may interfere in the analysis; reducing agents such as ferrous salts may interfere also [2].

OTHER METHODS: This is Method S160 [2] in a revised format. Feinsilver et al. [3] provided the basis for this method. Murty et al. [4] used photometry and photometric titrations with cacotheline as a reagent to determine phenylhydrazine in the range of 0.1 to 2 mg. Hasan [5] determined phenylhydrazine spectrophotometrically over a range of 0.1 to 3.0 mg using copper (II) nitrate.

REAGENTS:

1. Phenylhydrazine hydrochloride*.
2. Hydrochloric acid, concentrated*.
3. Phosphomolybdic acid.
4. Distilled water.
5. Collection medium, 0.1 M HCl. Fill a 1-L volumetric flask with approximately 300 mL distilled water, add 8.6 mL concentrated HCl, mix and dilute to the mark.
6. Phosphomolybdic acid solution (PMA). Dissolve 15 g PMA in 500 mL distilled water, allow to stand one day, and filter before use through a fluted paper filter.
7. Phenylhydrazine hydrochloride stock solution. Weigh accurately 0.1 g phenylhydrazine hydrochloride into a 100-mL volumetric flask and fill to the mark with 0.1 M HCl.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass, standard midget bubbler with a stem that has a fritted glass end. The fritted end should have a maximum pore diameter of approximately 170 to 220 μm.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm ID and 8-mm OD) glass tube loosely packed with glass wool and inserted between the exit arm of the bubbler and the pump.
3. Spectrophotometer, visible, 730 nm, with cuvettes, 1-cm.
4. Volumetric flasks, 1000-, 100-, 50-, and 10-mL.
5. Pipets, glass, 1-, 2-, 3-, 6-, 9-, and 10-mL, delivery, with pipet bulb.
6. Graduated cylinders, glass, 10- and 25-mL.

SPECIAL PRECAUTIONS: Concentrated hydrochloric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron, and full face shield with goggles. Phenylhydrazine is viewed as a potential carcinogen [6,7] and should be handled in a hood. Exposure to phenylhydrazine has caused hemolytic anemia [6,7]. Phenylhydrazine is a highly reactive reducing agent, and contact with oxides of copper or iron and manganese, lead, copper, or their alloys can cause fires and explosions [7]. Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL 0.1 M HCl into each bubbler. Connect the bubbler to trap and trap to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 25 to 120 L.
4. After sampling, tap bubbler stem gently against inside wall of bubbler bottle to recover as much sampling solution as possible. Wash stem with 5 mL distilled water and add wash to bubbler. Prior to shipping, seal bubblers with a hard, non-reactive stopper (preferably PTFE or glass).

SAMPLE PREPARATION:

5. Transfer liquid from bubbler to a 50-mL volumetric flask.
6. Rinse bubbler twice with 5 mL distilled water. Add rinses to volumetric flask.
7. Add 10 mL phosphomolybdic acid solution to volumetric flask and dilute to mark with distilled water.
8. Pipet a 3-mL aliquot into a 10-mL volumetric flask and dilute to mark with distilled water.

PHOSPHORUS TRICHLORIDE 6402

PCl_3 MW: 137.33 CAS: 7719-12-2 RTECS: TH3675000

METHOD: 6402, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.5 ppm
NIOSH: 0.2 ppm; STEL 0.5 ppm
ACGIH: 0.2 ppm; STEL 0.5 ppm
(1 ppm = 5.61 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.574 g/mL @ 21 °C; BP 76 °C; MP −112 °C; VP 13 kPa (100 mm Hg; 13% v/v) @ 21 °C

SYNONYMS: phosporous chloride.

SAMPLING

SAMPLER: BUBBLER (15 mL H_2O)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 11 L @ 0.5 ppm
-MAX: 100 L

SHIPMENT: ship in sealed bubblers

SAMPLE STABILITY: unknown

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: ca. 3.1 mg/m^3 [1]

BIAS: not significant [1]

OVERALL PRECISION ($\hat{S}_{rT}$): unknown

ACCURACY: not determined

MEASUREMENT

METHOD: VISIBLE SPECTROPHOTOMETRY

ANALYTE: molybdenum blue

COLOR DEVELOPMENT: 3 mL Br_2 water + 5 mL Na_2MoO_4 + 2 mL hydrazine sulfate → molybdenum blue

WAVELENGTH: 830 nm

CALIBRATION: KH_2PO_4 solutions

RANGE: 0.03 to 0.5 mg PCl_3 per sample

ESTIMATED LOD: 3 μg PCl_3 per sample

PRECISION ($\bar{S}_r$): 0.06 @ 0.03 to 0.14 mg PCl_3 per sample [1]

APPLICABILITY: The working range is 0.2 to 14 ppm (1.2 to 80 mg/m^3) for a 25-L air sample.

INTERFERENCES: Phosphorus (V) compounds do not interfere. The sample solutions are stable to oxidation by air during sampling [1].

OTHER METHODS: This revises P&CAM 305 [2].

REAGENTS:

1. Potassium dihydrogen phosphate stock solution, 100 μg H_3PO_4/mL. Dissolve 0.1389 g KH_2PO_4 in distilled H_2O and dilute to 1 L.
2. Calibration stock solution, 10 μg/mL H_3PO_4. Dilute 100 mL KH_2PO_4 stock solution to 1 L with distilled water.
3. Sulfuric acid, 10 N. Slowly add 279 mL conc. H_2SO_4 to 500 mL distilled water. Dilute to 1 L when cool.
4. Sodium molybdate solution. Dilute 25.0 g $Na_2MoO_4 \cdot 2H_4O$ to 1 L with 10 N surfuric acid.
5. Bromine water, saturated.* Add sufficient liquid Br_2 to saturate distilled water with stirring.
6. Hydrazine sulfate solution, 1.5 g/L. Dissolve 1.5 g $N_2H_6SO_4$ in distilled water to make 1 L solution.
7. Hydrazine sulfate, saturated. Add sufficient hydrazine sulfate to distilled water with stirring to saturate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget bubbler* with non-rubber (e.g., PTFE) stopper and fritted glass inlet (Corning EC or 170- to 220-μm max pore); 5-cm glass tube with glass wool plug for protection of pump from splashover.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Spectrophotometer, reading at 830 nm, with matched glass cuvettes, 1-cm path length.
4. Waterbath, boiling.
5. Pipets, 0.1-, 1-, 2-, 3-, 5- and 25-mL.*
6. Volumetric flasks, 50-mL and 1-L.*
7. Beakers, 50-mL.*
8. Cold water bath.

* Boil all glassware contaminated by phosphate detergent in 1:1 HCl. Rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Liquid bromine causes severe eye and skin burns. Bromine vapor is a severe irritant of the eyes and respiratory tract. Permanent breathing difficulty may result [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Add 15 mL distilled water to the bubbler. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 11 to 100 L.
   NOTE: The bubbler must be kept in a vertical position during sampling. If the bubbler solution spills into the trap, discard the sample.
3. Remove the bubbler stem and tap gently against the inside wall of the bubbler to recover as much of the sample solution as possible. Rinse the stem with several mL distilled water, collecting the rinse in the bubbler.
4. Seal the bubbler bottom with a stopper. Alternatively, connect the inlet of the bubbler top to the outlet with PTFE tubing and seal the top to the bottom with tape.

SAMPLE PREPARATION:

5. Transfer contents of the bubbler quantitatively to a 50-mL volumetric flask. Dilute to mark with distilled water and mix.
   NOTE: Start reagent blanks at this step.
6. Pipet 25 mL of the diluted sample into a 50-mL beaker.
7. Pipet 3 mL saturated bromine water into the beaker. Let stand 60 sec for oxidation to occur.
   NOTE: The purpose of the bromine water is to oxidize PCl_3, present in water as H_3PO_3, to H_3PO_4.

8. Add saturated hydrazine sulfate dropwise until the orange-yellow color of excess bromine is gone; add one drop in excess. Transfer the solution to a second 50-mL volumetric flask. Wash the beaker several times with a few mL of distilled water, adding the wash to the second volumetric flask.
9. Pipet 5 mL sodium molybdate solution and 2 mL of 1.5 g/L hydrazine sulfate solution into the second volumetric flask (containing the oxidized sample). Add identical amounts of reagents to the unoxidized 25-mL sample in the volumetric flask from step 5. Dilute both solutions to the mark with distilled water and shake well.
10. Immerse the volumetric flasks in a boiling water bath for 10 min. Remove and cool rapidly to room temperature in cold water bath. Proceed immediately with the measurement (steps 12 through 14).

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range 3 to 500 μg PCl_3 (2 to 360 μg H_3PO_4) per sample.
    a. Pipet aliquots of calibration stock solution into 50-mL volumetric flasks.
    b. Prepare (steps 5 through 10) and measure (steps 12 through 14) together with the samples and blanks.
    c. Construct calibration graph (absorbance vs. μg phosphoric acid).

MEASUREMENT:

12. Set the spectrophotometer according to manufacturer's directions to read at 830 nm.
13. Transfer several mL of the sample or standard solution to a cuvette and place in the spectrophotometer.
14. Record the absorbance reading vs. reagent blank.

CALCULATIONS:

15. Determine from the calibration graph the mass (μg) of phosphoric acid present in each oxidized sample (M_o) and unoxidized sample (M_u) and the average media blank (M_b).
16. Calculate the concentration (C) of PCl_3 in the air volume sampled, V (L):

$$C = \frac{(2 \cdot M_o - 2 \cdot M_u - M_b) \cdot 1.4}{V}, \text{ mg/m}^3.$$

where: 1.4 = M.W. PCl_3/M.W. H_3PO_4 = 137.3/98.0.

EVALUATION OF METHOD:

This method is based on P&CAM 305 [1,2]. In that work, recoveries were determined for samples spiked at 0.5, 1, and 2 times the OSHA standard to be 0.992, 1.04, and 1.05. The overall precision and accuracy have not been completely determined. In one experiment, the efficiency of bubbler collection of PCl_3 was found to be 0.99 $\pm$0.06 based on six pairs of bubblers sampling from a 3.1 mg/m^3 atmosphere generated using a diffusion cell. At the concentrations studied, PCl_3 tended to react with water vapor in the air to produce fogs of H_3PO_3. Attempts to separate the H_3PO_3 aerosol from PCl_3 vapor by means of polyvinyl chloride membrane filters were unsuccessful because of reaction between the filters and PCl_3. The reactions for the molybdenum blue color development are:

(1) $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
(2) $H_3PO_3 + Br_2 + H_2O \rightarrow H_3PO_4 + 2HBr$
(3) $H_3PO_4 + Na_2MoO_4 + N_2H_6SO_4 \rightarrow$ molybednum blue

REFERENCES:

[1] Arthur D. Little, Inc. Development of Methods for the Determination of Phosphoric Acid, PCl_3, PCl_5 and P_4S_{10} in Air, Final Report of NIOSH Contract 210-76-0038 (unpublished, May 10, 1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 305, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

METHOD REVISED BY:

Martin Abell, NIOSH/DPSE; P&CAM 305 originally developed under NIOSH Contract 210-75-0038.

POLYCHLOROBIPHENYLS

mixture: $C_{12}H_{10-x}Cl_x$ [where x = 1 to 10] MW: ca. 258 (42% Cl ; $C_{12}H_7Cl_2$); ca. 326 (54% Cl ; $C_{12}H_5Cl_5$) CAS: Table 1 RTECS: Table 1

METHOD: 5503, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Revision #1: 15 August 1987
Issue 2: 15 August 1994

OSHA : 1 mg/m^3 (42% Cl); 0.5 mg/m^3 (54% Cl)
NIOSH: 0.001 mg/m^3/10 h (carcinogen)
ACGIH: 1 mg/m^3 (42% Cl) (skin); 0.5 mg/m^3 (54% Cl) (skin)

PROPERTIES: 42% Cl: BP 325 to 366 °C; MP −19 °C; d 1.38 g/mL @ 25 °C; VP 0.01 Pa (8 x 10^{-5} mm Hg; 1 mg/m^3) @ 20 °C
54% Cl: BP 365 to 390 °C; MP 10 °C; d 1.54 g/mL @ 25 °C; VP 0.0004 Pa (3 x 10^{-6} mm Hg; 0.05 mg/m^3) @ 20 °C

SYNONYMS: PCB; 1,1'-biphenyl chloro; chlorodiphenyl, 42% Cl (Aroclor 1242); and 54% Cl (Aroclor 1254)

SAMPLING

SAMPLER: FILTER + SOLID SORBENT (13-mm glass fiber + Florisil, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min or less

VOL-MIN: 1 L @ 0.5 mg/m^3
-MAX: 50 L

SHIPMENT: transfer filters to glass vials after sampling

SAMPLE STABILITY: unknown for filters; 2 months for Florisil tubes [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD (^{63}Ni)

ANALYTE: polychlorobiphenyls

DESORPTION: filter + front section, 5 mL hexane; back section, 2 mL hexane

INJECTION VOLUME: 4-μL with 1-μL backflush

TEMPERATURE-INJECTION: 250 to 300 °C
-DETECTOR: 300 to 325 °C
-COLUMN: 180 °C

CARRIER GAS: N_2, 40 mL/min

COLUMN: glass, 1.8 m x 2-mm ID, 1.5% OV-17/1.95% QF-1 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard PCB mixture in hexane

RANGE: 0.4 to 4 μg per sample [2]

ESTIMATED LOD: 0.03 μg per sample [2]

PRECISION ($\bar{S}_r$): 0.044 [1]

APPLICABILITY: The working range is 0.01 to 10 mg/m^3 for a 40-L air sample [1]. With modifications, surface wipe samples may be analyzed [3,4].

INTERFERENCES: Chlorinated pesticides, such as DDT and DDE, may interfere with quantification of PCB. Sulfur-containing compounds in petroleum products also interfere [5].

OTHER METHODS: This method revises methods S120 [6] and P&CAM 244 [1]. Methods S121 [7] and P&CAM 253 [8] for PCB have not been revised.

REAGENTS:

1. Hexane, pesticide quality.
2. Florisil, 30/48 mesh sieved from 30/60 mesh. After sieving, dry at 105 °C for 45 min. Mix the cooled Florisil with 3% (w/w) distilled water.
3. Nitrogen, purified.
4. Stock standard solution of the PCB in methanol or isooctane (commercially available).*

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter without binders in a Swinnex cassette (Cat. No. SX 0001300, Millipore Corp.) followed by a glass tube, 7 cm long, 6-mm OD, 4-mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. (SKC 226-39, Supelco ORBO-60, or equivalent) Join the cassette and Florisil tube with PVC tubing, 3/8" L x 9/32" OD x 5/32" ID, on the outlet of the cassette and with another piece of PVC tubing, 3/4" L x 5/16" OD x 3/16" ID, complete the union.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Tweezers.
4. Vials, glass, 4- and 7-mL, with aluminum or PTFE-lined caps
5. Gas chromatograph, electron capture detection (^{63}Ni), integrator and column (page 5503-1).
6. Volumetric flasks, 10-mL and other convenient sizes for preparing standards.
7. Syringe, 10-μL.

SPECIAL PRECAUTIONS: Avoid prolonged or repeated contact of skin with PCB and prolonged or repeated breathing of the vapor [9-11].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the Florisil tube immediately before sampling. Connect Florisil tube to Swinnex cassette and attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 50 L.
   NOTE: At low PCB concentrations, the sampler was found to be efficient when operated at flow rates up to 1 L/min, for 24 hours [4]. Under these conditions, the limit of detection was 0.02 $\mu g/m^3$.
4. Transfer the glass fiber filters to 7-mL vials. Cap the Florisil tubes with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and 100-mg Florisil bed in the same 7-mL vial in which the filter was stored. Add 5.0 mL hexane.
6. In a 4-mL vial, place the 50-mg Florisil bed including the two urethane plugs. Add 2.0 mL hexane.
7. Allow to stand 20 min with occasional agitation.

$C_{12}H_{10-x}Cl_x$ (x = 1 to 10) MW: 188 to 498 CAS: Varies RTECS: Varies

METHOD: 8004, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

BIOLOGICAL INDICATOR OF: exposure to PCB.

SYNONYMS: Aroclor; PCB; chlorodiphenyl

BIOLOGICAL SAMPLING		MEASUREMENT	
SPECIMEN:	serum	**TECHNIQUE:**	GAS CHROMATOGRAPHY, ECD
VOLUME:	10 mL	**INJECTION VOLUME:**	3 µL, Grob type splitless
PRESERVATIVE:	none	**COLUMN:**	capillary, 15 m x 0.2-mm ID, WCOT SE-54
SHIPMENT:	polyethylene shippers @ 10 °C	**CARRIER GAS:**	5% methane in argon, 1 mL/min
STABILITY:	indefinite if serum is kept frozen	**TEMPERATURE-INJECTOR:**	260 °C
CONTROLS:	collect 3 specimens from unexposed populations per study or 1 per 10 unknowns for studies exceeding 30 specimens	**-COLUMN:**	100 °C for 2 min; 20 °C/min to 260 °C for 4 min
BULK:	submit a bulk sample of material to which workers were exposed	**-DETECTOR:**	350 °C
		CALIBRATION:	hexane solutions of Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260
		QUALITY CONTROL:	pooled or spiked serum
		RANGE:	0.005 to 1.0 µg/mL
		ESTIMATED LOD:	0.001 µg/mL
		RECOVERY:	greater than 80%
		PRECISION ($\bar{S}_r$):	0.16
		ACCURACY:	> ± 30%

APPLICABILITY: Since PCBs are rapidly absorbed from the lung, GI tract, and skin, this procedure is useful for estimating acute and chronic exposures to PCB, assuming (a) no metabolism of PCB, (b) all isomers of PCB are extracted with equal efficiency, and (c) similar ECD response for all PCBs. PCBs have high biological and chemical stability. They accumulate in adipose tissue and may present a serious latent health threat. Metabolism involves hydroxylation and conjugation with glucose and sulfates.

INTERFERENCES: Chlorinated hydrocarbons, phthalate based plasticizers, dibenzofurans, and chlorinated naphthalenes interfere.

OTHER METHODS: This replaces P&CAM 329 [1]. Other methods include a screening method for Aroclor 1254 in whole blood [2].

REAGENTS:

1. Methanol, hexane, ethyl ether, and acetone (pesticide grade).
2. Potassium hydroxide, KOH.
3. Calibration stock solutions, 0.1 mg/mL.* Dissolve 10 mg of the bulk sample or other suitable standard, e.g., Aroclor 1016, 1221, 1232, 1242, 1248, 1254, and 1260 in 100 mL n-hexane (standards available from EPA).
4. Silica gel, activity grade I.
   a. Heat to 130 °C for 24 h.
   b. Cool and add 3 g water per 100 g silica gel. Mix for 2 h in a sealed container.
5. Sodium sulfate (anhydrous).
6. 1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) solution, 50 ng/mL, in hexane.
7. Methanol KOH, 2% (w/v). Dissolve 2 g KOH in methanol to make 100 mL solution.
8. Methanol-water, 1:1 (v/v).
9. Hexane-ethyl ether, 1:1 (v/v).
10. Nitrogen, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Gas-liquid chromatograph equipped with an electron capture detector.
2. Syringes, glass, 30-mL.**
3. Culture tubes, 16- x 150-mm, organic-free, with PTFE-lined screw caps.**
4. Rotary mixer, variable speed.
5. Centrifuge.
6. Kuderna-Danish concentrator tubes, 25-mL.**
7. Micro-Synder Columns.**
8. Tube heater.
9. Chromatography column, 7-mm ID x 200 mm, with 50-mL reservoir and PTFE stopcock.**
   a. Put a small plug of glass wool in the bottom of the column.
   b. Pour a suspension of 3 g silica gel in 50 mL hexane into the column.
   c. Let the suspension settle and add 5 to 7 g sodium sulfate.
10. Syringes, 10-μL, glass.
11. Graduated cylinder, 25-mL.**
12. Pipet, Pasteur.

** Clean all glassware, including that used in sampling as follows: Wash in detergent. Rinse with tap water. Soak in chromic acid. Rinse with, in order, tap water, distilled water, acetone and hexane.

SPECIAL PRECAUTIONS: Samples of blood collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle blood specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

PCBs have potential carcinogenicity in humans. They are microsomal enzyme inducers and liver toxins; therefore, use extreme caution when handling these substances [3].

SAMPLING:

1. Collect 20 to 25 mL whole blood samples by venipuncture via 30-mL glass syringe.
2. After the blood has clotted, centrifuge for 10 min at 2000 rpm. Transfer the serum to a 16 x 150-mm culture tube with a PTFE-lined screw cap.
3. Ship the serum in an insulated container with bagged refrigerant to keep the samples at 4 °C.
4. Freeze the samples upon arrival at the laboratory.

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 μL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg pyridine recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1613-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CH_2Cl_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Method S161 was issued on August 1, 1975 [3], and validated with atmospheres generated by calibrated syringe pump and confirmed using a total hydrocarbon analyzer [2]. Average recovery was 109% $\pm$3.6% (18 samples) in the range 7.6 to 30.4 mg/m^3 for 100-L samples. Breakthrough (effluent concentration = 5% of test concentration) was not observed after sampling for 240 min at 0.93 L/min from an atmosphere containing 30.4 mg/m^3 pyridine in dry air. Carbon disulfide and methanol were tested and rejected as possible desorbing solvents. Carbon disulfide gave an average DE of 0.734; methanol, 0.201. Desorption efficiency using methylene chloride for 18 spiked samples in the range 0.8 to 3.1 mg pyridine per sample averaged 0.81 with S_r = 0.013.

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[2] UBTL, Inc. Report, NIOSH Sequences 4949-K (unpublished, May 24, 1985) and 3030-K (unpublished, July 20, 1981).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S161, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[5] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
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METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.

NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and net intensities should be normalized to the most recently measured reference intensity.

14. Remove the PVC filter from the XRD holder, fold the filter carefully and place it in a platinum crucible in the furnace. Raise the temperature of the furnace slowly (ca. 50 °C/min) to 500 °C to ash the filter. When ashing is completed (ca. 0.5 h), raise the temperature to 1500 °C and maintain at 1500 °C for 2 h (for fumed amorphous silica) or to 1100 °C and maintain at 1100 °C for 6 h (for other amorphous silicas). Turn the furnace off and let the crucibles cool overnight in the furnace.
15. Place ca. 10 mg NaCl in the crucible and mix with the ash in the crucible. Transfer contents of the crucible to an agate mortar and grind to a fine powder using an agate pestle. Add distilled water from a polyethylene squeeze bottle to the mortar. Use a rubber policeman to stir. When the NaCl is dissolved, transfer the solution to a 100-mL beaker (hold the rubber policeman at the edge of the mortar to guide the flow into the beaker). Rinse mortar, pestle, crucible, and rubber policeman, collecting rinsings in the beaker. Cover the beaker with a watchglass and place in an ultrasonic bath for 2 to 3 min.
    NOTE 1: Use extreme care to avoid air currents when working with the dry sample, as it is easily lost in the form of an aerosol.
    NOTE 2: Use uniform grinding techniques to produce similar particle size in standards and samples.
16. Wash the underside of the watchglass and collect rinsings in the beaker. Place a silver membrane filter in the filtration apparatus and filter the contents of the beaker (step 5).
17. Mount the silver membrane filters in the XRD instrument and:
    a. Analyze for the three silica polymorphs (step 13); and
    b. Determine the net intensity, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure.
        NOTE: Scan times should be shorter for the silver peak (e.g., about 5% of scan times for analyte peaks) and consistent throughout the method.

CALCULATIONS:

18. Calculate normalized intensities for the cristobalite peak on the PVC filter before heating, $\hat{I}_x$ (step 13); the cristobalite peak on the Ag filter, $\hat{I}'_x$ (step 17.a.); the silver peak on the Ag filter, $\hat{I}_{Ag}$ (step 17.b.); and the average silver peak on six media blank Ag filters, $\hat{I}_{Ag}$ (step 11).
19. Calculate the transmittance of each sample: $T = \hat{I}_{Ag}/\hat{I}_{Ag}$.
20. Calculate the matrix absorption correction factor for each sample, $f(T) = -R\ln T/(1-T^R)$, where $R = \sin(\Theta_{Ag})/\sin(\Theta_x)$ (or use Table 1).
21. Calculate the concentration of amorphous silica, C (mg/m^3), in the air sample as the difference in cristobalite concentrations measured before and after heat treatment using the slope, m, and intercept, b, of the calibration graph and the air volume sampled, V (L):

$$C = \frac{[\,(\hat{I}'_x - b)/m\,]\,f(T) - [\,(\hat{I}_x - b)/m\,]\cdot 10^3}{V},\ mg/m^3.$$

NOTE: Compute the applicable OSHA standard using the formulae on page 7501-1 and the % crystalline silica found in the air sample before heat treatment.

EVALUATION OF METHOD:

This method is based on NIOSH P&CAM 316 [3,4] which was further evaluated with field samples in July, 1982 [1]. The relative standard deviation was determined to be related to the type of amorphous silica; gelled, fumed, and precipitated amorphous silica yielded 4.4%, 8.2%, and 4.7%, respectively, over

the range of 0.5 to 5 mg. The method was further evaluated using 11 different types of gelled, precipitated, and fumed amorphous silicas and diatomaceous earth [5], with the following conclusions:

1. Not all fumed silicas converted to cristobalite at 1100 °C. A higher temperature (1500 °C) was needed to convert all the fumed silicas to cristobalite.
2. The moisture content of the gelled and precipitated silicas was ca. 7%; of diatomaceous earth, ca. 4%; and of fumed, from 0.5 to 3%.
3. The calibration curves from the four different types of amorphous silicas indicated very similar slopes (S_r = ± 6.6%).
4. Comparing the four slopes to a slope of a pure respirable cristobalite material, they were running approximately 30% lower in slope value. Therefore, field samples of amorphous silicas must be compared only to standards prepared from amorphous silicas.
5. Precision studies at 0.2-, 1-, and 2.5-mg levels (six samples per level) of gelled, precipitated, diatomaceous earth, and fumed silicas indicated a pooled precision, $\bar{S}_r$, of 8.8, 10.5, 5.6, and 21.5%, respectively, for the above silicas.
6. Recovery studies of the same silicas and concentration levels indicated average recoveries of 82, 115, 95, and 111%, respectively, with pooled $\bar{S}_r$ equal to 18.2, 13.1, 12.9, and 15.3%, respectively, for the gelled, precipitated, and fumed silicas, and diatomaceous earth.

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[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 316, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
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METHOD REVISED BY:

C.D. Lorberau, NIOSH/DPSE.

TABLE 1. CAS Numbers, RTECS Numbers, and Exposure Limits for Amorphorous Silica Forms

Amorphous Forms	CAS#	RTECS	OSHA PEL (mg/m^3)	NIOSH REL (mg/m^3)	ACGIH TLV (mg/m^3)
diatomaceous earth, <1% crystalline SiO_2	61790-53-2	HL8600000	80/% SiO_2	6	10 (total)
precipitated, and gel	7699-41-4, 112926-00-8	VV8850000	80/% SiO_2	6	10 (total)
fumed	112945-52-5	VV7310000	80/% SiO_2	--	2 (respir)

SILICA, CRYSTALLINE in coal mine dust, by IR 7603

SiO_2 MW: 60.08 CAS: 14808-60-7 RTECS: VV7330000

METHOD: 7603, Issue 2 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

quartz (respirable):
OSHA : 10 mg/m^3/(%SiO_2 + 2)
NIOSH: 0.05 mg/m^3 (suspect carcinogen)
ACGIH: 0.1 mg/m^3

PROPERTIES: solid; crystalline transformations: quartz to tridymite @ 867 °C: tridymite to crystobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + PREWEIGHED FILTER (10-mm cyclone, nylon, or Higgins-Dewell (HD), and PVC filter, 37-mm, 5-μm)

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 300 L @ 0.1 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required for OSHA standard calculations; area respirable or settled dust

ACCURACY

RANGE STUDIED: 25 to 160 μg/sample [1]
(2 mg quartz/m^3 atmosphere)

BIAS: unknown

OVERALL PRECISION ($\hat{S}_{rT}$): 0.13 to 0.22 (varies with sample loading and matrix)

ACCURACY: ±25.6 to 43.4%

MEASUREMENT

TECHNIQUE: INFRARED SPECTROPHOTOMETRY (IR)

ANALYTE: quartz

WEIGH: dust cassette

ASH: muffle furnace or RF plasma asher

REDEPOSIT: 0.45-μm acrylic copolymer membrane filter

IR: scan, 1000 to 650 cm^{-1}, absorbance mode with blank filter in reference beam

CALIBRATION: standard suspension of quartz in 2-propanol

RANGE: 30 to 250 μg quartz per sample [1]

ESTIMATED LOD: 10 μg quartz per sample [1]

PRECISION ($\hat{S}_r$): 0.098 @ 100 to 500 μg per sample (varies with sample matrix) [1]

APPLICABILITY: The working range is 0.03 to 2 mg/m^3 for a 1000-L sample. The method was specifically developed for respirable coal mine dust samples [2]. The precisions ($\hat{S}_r$ & $\hat{S}_{rT}$) stated above are based on ruggedization data [1].

INTERFERENCES: Calcite is used as a dusting agent in coal mines and interferences by reacting with quartz during muffle furnace treatment resulting in low quartz assay. Kaolinite is sometimes present in coal dust and interferes by absorbing radiation at the quartz analytical wavelength of 800 cm^{-1}. These interferences are corrected by procedures given in this method. Muscovite does not interfere. Cristobalite and tridymite have absorbance peaks at 800 cm^{-1}. Cristobalite and tridymite have not been detected in coal mine dust.

OTHER METHODS: This method was based on an unpublished Bureau of Mines method that was collaboratively tested [1]. Quartz can also be determined by NIOSH Methods 7500 (XRD), 7602 (IR), and 7601 (UV-VIS) and MSHA Method P7 [3].

REAGENTS:

1. Quartz (SRM 1878, available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards Technology, Gaithersburg, MD 20899).
2. 2-Propanol, reagent grade.
3. Calibration stock solution, 15 μg/mL. Suspend 7.5 mg of quartz in 2-propanol in a 500-mL volumetric flask and dilute the suspension to the mark with 2-propanol (See CALIBRATION AND QUALITY CONTROL).
4. Kaolinite (Hydrite UF from Georgia Kaolin), for standard samples, 100 μg/mL. Suspend 50 mg of dried kaolinite in a 500-mL volumetric flask with 2-propanol and dilute the suspension to the mark with 2-propanol.
   NOTE: This is not required if muffle furnace is used to ash samples (see step 5).
5. Hydrochloric acid solution. 25% v/v conc. HCl in distilled water. Required if calcite is present and samples are ashed with a muffle furnace.
6. Dessicant (Drierite).
7. Oxygen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-μm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area air sampler: PVC membrane filter, 37-mm, 5-μm pore size in two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps for: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Filters for standards and redeposition, 47-mm diameter, 0.45-μm pore size, vinyl chloride-acrylonitrile copolymer membrane (DM-450 Gelman Sciences, or equivalent).
5. Glass fiber filters, 25-mm diameter, for backup during filtration.
6. Filtration apparatus for redepositing sample after ashing, consisting of fritted support (Millipore XX1002502), side-arm vacuum flask and special funnel similar to Millipore XX1002514 but with an internal diameter of 1.0 cm. The funnel is glass with a bakelite base and should seal to the fritted support to make the fit liquid-tight.**
7. Funnel for treating filters to remove calcite (required only if using a muffle furnace): Millipore XX1002514 with apparatus in item 5 above except with funnel internal diameter ca. 1.6 cm; 0.5-μm pore size PVC filters, 37-mm diameter to recollect residue.**
8. Double-beam infrared spectrophotometer, with sample holders for infrared instrument: metal (preferably steel) plates with a center hole to match the diameter of the sample deposit (1 cm), and small ring magnets to hold the filter in position on the plate.
9. Low-temperature radio frequency asher (LTA) or muffle furnace (600 °C).
10. Ultrasonic bath.
11. Porcelain crucibles with covers, 10-mL.**
12. Beakers, 50-mL.**
13. Analytical balance, 0.01-mg; dessicator cabinet.
14. Magnetic stirrer with thermally insulated top, and stirring bars.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    NOTE: Standards should be spiked onto charcoal tubes as follows to avoid high recoveries seen with liquid standards [3].
    a. Add known amounts of calibration stock solution onto charcoal tubes (5.0 to 80 μg F^-) and desorb in the same manner as field samples (steps 5 through 9).
    b. Analyze working standards together with samples and blanks (steps 12 through 14).
    c. Prepare a calibration graph of peak height vs. amount (μg) of fluoride per 20 mL of sample.
11. (Optional). Determine recovery (R) for each lot of tubes used for sampling in the concentration range of interest. Prepare four tubes at each of five levels plus three media blanks.
    a. Collect a known amount of SO_2F_2 gas onto each charcoal tube (steps 1 through 9).
    b. Analyze samples in the same manner as field samples (steps 12 through 14).
    c. Prepare graph of recovery vs. μg sulfuryl fluoride.

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 6012-1.
13. Re-filter sample if necessary, then inject a sample aliquot into the ion chromatograph.
14. Measure peak height.

CALCULATIONS:

15. Determine mass (μg) of fluoride found on the front (W_f) and back (W_b) sections, and in the average media blank front (B_f) and back (B_b) sorbent section.
16. Calculate concentration C of sulfuryl fluoride (mg/m^3) in the actual air volume, V(L), applying the conversion factor 2.686 (MW SO_2F_2/MW F^-; the reaction is $SO_2F_2 + 4NaOH \rightarrow 2NaF + Na_2SO_4 + 2H_2O$):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.686}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 20 to 420 mg/m^3. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.070 [1]. The average recovery of SO_2F_2 from charcoal was 99% when sampling atmospheres prepared in aluminized gas bags (Calibrated Instruments, Inc., Hawthorne, NY 10532). Recovery of fluoride from sampling media was 97% in the range 10 to 160 μg F^- per sample. Sample stability during storage was evaluated at 417 mg/m^3 SO_2F_2 per sample. Samples showed 101% recovery after twelve days of storage at 0-5 °C compared to one-day old samples.

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METHOD WRITTEN BY:

George Y. Williamson, MRSB, DPSE.

(1) 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and (2) 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

1016

(1): CCl_3CClF_2 MW: 203.83 CAS: (1) 76-11-9 RTECS: (1) KI1425000
(2): CCl_2FCCl_2F (2) 76-12-0 (2) KI1420000

METHOD: 1016, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 500 ppm
NIOSH: 500 ppm
ACGIH: 500 ppm
(1 ppm = 8.34 mg/m^3 @ NTP)

PROPERTIES: solids; MP (1) 40.6 °C; (2) 25 °C; BP (1) 91.5 °C, (2) 93 °C; VP 5.3 kPa (40 mm Hg; 5.2% v/v) @ 20 °C; not combustible

SYNONYMS: (1): Refrigerant 112a.
(2): Refrigerant 112.

SAMPLING

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

FLOW RATE: 0.01 to 0.035 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2 L

SHIPMENT: routine

SAMPLE STABILITY: not tested

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: (1): 2160 to 9020 mg/m^3 [1]
(2): 1880 to 8060 mg/m^3 [1]

BIAS: (1) 0.17%
(2) 2.0%

OVERALL PRECISION ($\hat{S}_{rT}$): (1): 0.069;
(2): 0.054 [1]

ACCURACY: (1) ± 32.4%
(2) ± 11.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,1,2-tetrachloro-2,2-difluoroethane; 1,1,2,2-tetrachloro-1,2-difluoroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

	(1)	(2)
TEMPERATURE-INJECTION:	185 °C	50 °C
-DETECTOR:	250 °C	240 °C
-COLUMN:	50 °C	50 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions in CS_2

RANGE: 2 to 20 mg per sample

ESTIMATED LOD: 0.3 mg per sample

PRECISION ($\bar{S}_r$): (1): 0.27 @ 4 to 17 mg per sample [1];
(2): 0.005 @ 4 to 17 mg per sample [1]

APPLICABILITY: The working range for either analyte is 120 to 1400 ppm (1000 to 12,000 mg/m^3) for a 2-L air sample. These compounds are used as degreasing solvents, refrigerants, foaming agents and corrosion inhibitors. Capillary columns may be used (DB-Wax or Nukol on fused silica, 3 m x 0.32-mm, 0.5 µm film) with appropriate changes in instrumental conditions.

INTERFERENCES: None reported.

OTHER METHODS: This combines and revises Methods S131 and S132 [2].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,1,2-Tetrachloro-2,2-difluoroethane and 1,1,2,2-tetrachloro-1,2-difluoroethane, reagent grade.*
3. Hexane, chromatographic quality.
4. Calibration stock solution, 0.2 mg/μL. Dissolve 2 g analyte in CS_2 to prepare 10 mL solution. Prepare in duplicate.
5. DE stock solution, 1 mg/μL. Dissolve 10 g analyte in hexane to prepare 10 mL solution. Prepare in duplicate.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.035 L/min, with flexible connecting tubing.
3. File, triangular.
4. Gas chromatograph, flame ionization detector, integrator and column (page 1016-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10-μL, readable to 0.1 μL.
7. Volumetric flasks, 10-mL.
8. Pipets, 10- to 1000-μL.

SPECIAL PRECAUTIONS: Tetrachloro-1,2-difluoroethane has been determined to be a carcinogen [3]. Both analytes react with chemically-active metals such as sodium, potassium and beryllium or with powdered magnesium, aluminum and zinc.

Hazardous products such as hydrogen chloride, hydrogen fluoride and carbon monoxide may be released when either analyte decomposes. Both analytes will attack some forms of plastics, rubber and coatings.

Carbon disulfide is toxic and flammable; work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.035 L/min for a total sample size of 0.5 to 2 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

TRICHLOROETHYLENE by portable GC 3701

$Cl_2C=CHCl$ MW: 131.39 CAS: 79-01-6 RTECS: KX4550000

METHOD: 3701, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 100 ppm; C 200 ppm; P 300 ppm
NIOSH: 25 ppm; C 2 ppm/1 h; carcinogen
ACGIH: 50 ppm; 200 ppm STEL; suspect carcinogen
(1 ppm = 5.37 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.46 g/mL @ 20 °C; BP 87 °C; MP −86 °C; VP 7.7 kPa (58 mm Hg; 7.6% v/v) @ 20 °C; explosive range 11 to 41% v/v in air

SYNONYMS: trichloroethene; ethylene trichloride; triclene

SAMPLING

SAMPLER: AIR BAG (Tedlar)

FLOW RATE: 0.02 to 0.05 L/min or higher; fill bag to ≤80% of capacity; spot samples possible (step 2.1.)

SAMPLE STABILITY: bags should be analyzed as soon after collection as possible (≤4 h)

BLANKS: clean air, either in bag or from a non-work area

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: trichloroethylene (TCE)

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 10 to 1000 ppm

ESTIMATED LOD: 0.25 ng per injection (0.1 ppm for a 1-mL injection

PRECISION ($\hat{S}_r$): 0.078

ACCURACY

RANGE STUDIED: 25 to 100 ppm

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): 0.078

ACCURACY: > ± 15%

APPLICABILITY: The working range is 10 to 1000 ppm (54 to 5400 mg/m^3) in relatively non-complex atmospheres where trichloroethylene is known to be present (see EVALUATION OF METHOD).

INTERFERENCES: None found.

OTHER METHODS: Method 1022 [1] uses activated charcoal sampler tubes.

REAGENTS:

1. Trichloroethylene (TCE)* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure trichloroethylene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 0.05 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
3. Bags, Tedlar, 2- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC, and for preparation of bag standards.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labelling bags.

SPECIAL PRECAUTIONS: TCE is a suspect carcinogen [2]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A straight line baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. **Spot sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections, if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration; and
      (4) set conditions such that peaks are at least 50% of full scale.
   b. **Integrated air sample for TWA determination.**
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
         NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to a personal sampling pump suitable for bag filling with a minimum length of flexible tubing.
      (3) Pump the air to be sampled into the sample bag at a rate calculated to fill $\leq$ 80% of the sample bag capacity over the sampling period.
         NOTE: The flow rate must remain within $\pm$ 5% of the initial setting throughout the sampling period.

VINYL CHLORIDE

$CH_2=CHCl$ MW: 62.50 CAS: 75-01-4 RTECS: KU9625000

METHOD: 1007, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1 ppm; C 5 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 5 ppm; carcinogen
(1 ppm = 2.56 mg/m^3 @ NTP)

PROPERTIES: BP −14 °C; vapor density 2.2 (air = 1); lower explosive limit = 4% v/v in air

SYNONYMS: chloroethylene; chloroethene.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m^3 [1]

BIAS: − 6%

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

ACCURACY: ± 17.8%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 μL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 2 to 200 μg per sample [1]

ESTIMATED LOD: 0.04 μg per sample [1]

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

APPLICABILITY: The working range is 0.4 to 40 mg/m^3 (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [2].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
3. Calibration stock solutions 0.26 mg/mL.
   a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 and add the washings to the flask.
   d. Dilute to the mark with CS_2.
4. Helium, purified.
5. Hydrogen, purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two tandem glass tubes, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
   NOTE: A pair of two-section (100 mg/50 mg) tubes may be used. (SKC ST226-01, or equivalent).
2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
4. File.
5. Bent wire for removing plugs from sampling tube.
6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
7. Volumetric flasks, 10-mL, with polyethylene stoppers.
8. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
9. Air sampling bags, Tedlar, 10-L.
10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
11. Syringe, 10-μL, with 0.1-μL graduations.

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

Vinyl chloride is a human carcinogen [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
4. Separate the primary and backup tubes and cap each tube for shipment.

VINYLIDENE CHLORIDE

$CH_2=CCl_2$ MW: 96.94 CAS: 75-35-4 RTECS: KV9275000

METHOD: 1015, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: lowest feasible; carcinogen
ACGIH: 5 ppm; STEL 20 ppm; carcinogen
(1 ppm = 3.96 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.213 g/mL @ 20 °C;
BP 31.7 °C; MP −122.5 °C; flammable

SYNONYMS: 1,1-dichloroethene; 1,1-dichloroethylene.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2.5 L @ 1 ppm
-MAX: 7 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C
21 days @ 5 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 7.6 to 10 mg/m^3 [2]

BIAS: − 0.05

OVERALL PRECISION ($\hat{S}_{rT}$): 0.069

ACCURACY: ± 18.6%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinylidene chloride

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 200 °C
-COLUMN: 65 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: silanized glass, 3 m x 6-mm OD packed with Durapak OPN 100/120 mesh or equivalent

CALIBRATION: standard solutions of vinylidene chloride in CS_2

RANGE: 10 to 100 µg per sample

ESTIMATED LOD: 7 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.048 @ 12 to 85 µg per sample [2]

APPLICABILITY: The working range is 0.5 to 5 ppm (2 to 20 mg/m^3) for a 5-L air sample. The capacity of charcoal for vinylidene chloride decreased rapidly with increasing relative humidity and was also found to be a function of concentration.

INTERFERENCES: The GC column will not separate vinyl chloride and carbon disulfide. Other GC packings that separate vinyl chloride and CS_2 may not separate vinylidene chloride and CS_2. If determination of both of these monomers is to be performed, a capillary column such as a 105 meter Rtx® 502.2 would be required.

OTHER METHODS: The revises P&CAM 266 [1].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. Vinylidene chloride, 99%.*
3. Cyclohexane.
4. Calibration stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in CS_2 to make 10 mL solution. Prepare in duplicate.
5. DE stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in cyclohexane to make 10 mL solution. Prepare in duplicate.
6. Nitrogen or helium, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1015-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-μL, readable to 0.1 μL.
6. Volumetric flasks, 10-mL.
7. Pipets, volumetric, 10- to 100-μL, and 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Vinylidene chloride is a suspect carcinogen [3]. Carbon disulfide and vinylidene chloride are toxic and severe fire and explosion hazards (flash point = −30 °C for CS_2 and −10 °C for vinylidene chloride). Work with both compounds only in a hood. Vinylidene chloride polymerizes above 0 °C, especially in the presence of oxygen or catalysts; explosive reaction products may result [4].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2.5 to 7 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Refrigerated shipment will decrease migration of vinylidene chloride to back sorbent section.

SAMPLE PREPARATION:

5. Allow samples to equilibrate to room temperature before uncapping. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL CS_2 to each vial. Cap vial immediately.
7. Allow to stand 30 min with occasional agitation.

VOLUME

cm^3	liters	m^3	in^3	ft^3	oz (fl, U.S.)
1	0.001	0.000001	0.061024	0.000035315	0.033814
1000	1	0.001	61.024	0.035315	33.814
1000000	1000	1	61024.	35.315	33814.
16.387	0.016387	0.000016387	1	0.0005787	0.55411
28317	28.317	0.028317	1728.	1	957.51
29.574	0.029574	0.000029574	1.8047	0.0010444	1

PRESSURE

atm	mm Hg, 0 °C	in. water, 20 °C	lb/in^2	kg/cm^2	kPa
1	760.	407.51	14.696	1.0333	101.33
0.0013158	1	0.53620	0.019337	0.0013595	0.13332
0.0024539	1.8650	1	0.036062	0.0025354	0.24864
0.068046	51.715	27.730	1	0.070307	6.8947
0.96784	735.56	394.41	1.4223	1	98.066
0.0098692	7.5006	4.0219	0.14504	0.010197	1

CONCENTRATION IN AIR

Gas or Vapor			Aerosol		
parts per million	% by volume	mg/m^3	mg/m^3	particles per cm^3	MPPCF
1	0.0001	$M.W./V_m$	1	S/1000	S/35310
10000	1	$M.W.\cdot 10^4/V_m$	1000/S	1	0.02832
$V_m/M.W.$	$V_m/M.W.\cdot 10^4$	1	35310/S	35.31	1

where V_m, the volume of 1 mole of gas, is:

V_m (L) = 62.36 (t, °C + 273.15)/(P, mm Hg)

V_m as a function of t and P

	p, mm Hg			
	640	680	720	760
40	30.51	28.72	27.12	25.70
30	29.54	27.80	26.26	24.87
25	29.05	27.34	25.82	24.46
t, °C 20	28.56	26.88	25.39	24.05
10	27.59	25.97	24.52	23.23
0	26.62	25.05	23.66	22.41

where S, specific mass in particles/μg, is:

$S = 1/[(4\pi/3)(D_s/2)^3\ d\cdot 10^6]$

where: D_s = Stokes diam., μm
d = particle density, g/cm^3

EXAMPLES (assumes monodisperse aerosol):

Aerosol	D_s, μm	d, g/cm^3	S, p/μg
Steel	10	7.5	250
Quartz	10	2.65	720
Fe_2O_3	5	5.2	2900
Quartz	5	2.65	5800
Quartz	2	2.65	$9\cdot 10^4$
PbO fume	1	9.5	$2\cdot 10^5$
PbO fume	0.2	9.5	$2.5\cdot 10^7$

APPENDIX B. Air Concentration Calculations for Comparison to OSHA Standards

OSHA Permissible Exposure Limits (PEL) are set on the basis of mass of toxic substance per unit volume of air at ambient conditions. Therefore, the OSHA PEL in mg/m^3 is absolutely fixed and not subject to corrections for temperature and pressure. This constraint implies that volume concentration of gases in parts per million (ppm) must be with reference to some defined temperature and pressure; these are NTP (25 °C and 760 mm Hg) in the OSHA PEL limit.

The following formulae, therefore, must be used in calculations comparing analytical results to OSHA PEL. Each of the methods in this Manual uses a similar calculation.

Physical Form of Substance Sampled	Unit of Air Concentration	Formula for Direct Comparison With OSHA PEL Table
Gas	ppm	$C_v = \frac{m \cdot 10^3}{V} \cdot \frac{24.46}{MW}$
Gas	mg/m3	$C = \frac{m \cdot 10^3}{V}$
Aerosol	mg/m^3	$C = \frac{m \cdot 10^3}{V}$

where: m = actual mass of substance, in mg, found on the sampling device
V = air volume, L, taken at the sampling site, ambient temperature and pressure
24.46 = the volume (L) of 1 mole of gas at 25 °C and 760 mm Hg
C_v = air concentration, ppm by volume, at 25 °C and 760 mm Hg
C = air concentration, mg/m^3
MW = molecular weight, grams/mole

Example: A personal sampling pump is calibrated at 25 °C and 630 mm Hg, and then used to sample air at 20 °C and 660 mm Hg for 60 min at a flow rate of 1.00 L/min. The analytical lab reports 0.188 mg of allyl chloride (MW 76.5) in the sample. What is the air concentration relative to the OSHA PEL?

NOTE: If the sampling pump uses a rotometer for flow rate indication, the calibrated flow rate must be corrected for the actual air pressure and temperature during sampling. (See formula on p. 26.) In this example the pump does not use a rotameter, so the calibrated flow rate is used.

Solution: Concentration of allyl chloride, for comparison with the OSHA PEL, is:

$$C_v = \frac{0.188 \cdot 1000}{60} \cdot \frac{24.46}{76.5} = 1.0 \text{ ppm}$$

or

$$C = \frac{0.188 \cdot 1000}{60} = 3.13 \text{ mg/m}^3$$

These values indicate that the concentration of allyl chloride is at the OSHA PEL.

V. A. INDEX OF THIRD AND FOURTH EDITION METHOD NUMBERS

XX = Discontinued Method

0500 PARTICULATES NOT OTHERWISE REGULATED, TOTAL (Grav)
0600 PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE (Grav)
0700 see 9100

1000 ALLYL CHLORIDE (GC)
1001 METHYL CHLORIDE (GC)
1002 CHLOROPRENE (GC)

1003 HYDROCARBONS, HALOGENATED (GC)
- benzyl chloride
- bromoform
- carbon tetrachloride
- chlorobenzene
- chlorobromomethane
- chloroform
- o-dichlorobenzene
- p-dichlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethylene
- ethylene dichloride
- hexachloroethane
- methylchloroform
- tetrachloroethylene
- 1,1,2-trichloroethane
- 1,2,3-trichloropropane

1004 DICHLOROETHYL ETHER (GC)
1005 METHYLENE CHLORIDE (GC)
1006 FLUOROTRICHLOROMETHANE(GC)
1007 VINYL CHLORIDE (GC)

1008 ETHYLENE DIBROMIDE (GC)
1009 VINYL BROMIDE (GC)
1010 EPICHLOROHYDRIN (GC)
1011 ETHYL BROMIDE (GC)
1012 DIFLUORODIBROMOMETHANE(GC)
1013 PROPYLENE DICHLORIDE (GC)
1014 METHYL IODIDE (GC)
1015 VINYLIDENE CHLORIDE (GC)
1016 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE (GC)
1017 BROMOTRIFLUOROMETHANE (GC)
1018 DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, CHLORODIFLUOROMETHANE (GC)
1019 1,1,2,2-TETRACHLOROETHANE (GC)

1020 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE (GC)
1022 TRICHLOROETHYLENE (GC)
1024 1,3-BUTADIENE (GC)
1300 KETONES I (GC)
- acetone
- cyclohexanone
- diisobutyl ketone
- 2-hexanone
- methyl isobutyl ketone
- 2-pentanone

1301 KETONES II (GC)
- camphor
- ethyl butyl ketone
- mesityl oxide
- 5-methyl-3-heptanone
- methyl-(n-amyl)-ketone

1400 ALCOHOLS I (GC)
- tert-butyl alcohol
- isopropyl alcohol
- ethanol

1401 ALCOHOLS II (GC)
- n-butyl alcohol
- sec-butyl alcohol
- isobutyl alcohol
- n-propyl alcohol

1402 ALCOHOLS III (GC)
- allyl alcohol
- cyclohexanol
- isoamyl alcohol
- diacetone alcohol
- methyl isobutyl carbinol

1403 ALCOHOLS IV (GC)
- 2-butoxyethanol
- 2-ethoxyethanol
- 2-methoxyethanol

1404 METHYLCYCLOHEXANOL (GC)
1450 ESTERS I (GC)
- n-amyl acetate
- sec-amyl acetate
- n-butyl acetate
- sec-butyl aetate
- tert-butyl acetate
- 2-ethoxyethyl acetate
- ethyl acrylate
- isoamyl acetate
- isobutyl acetate
- methyl isoamyl acetate
- n-propyl acetate

1451 METHYL CELLOSOLVE ACETATE (GC)
1452 ETHYL FORMATE (GC)
1453 VINYL ACETATE (GC)

1454 ISOPROPYL ACETATE (GC)
1455 XX- Triphenyl phosphate
1456 see 5037
1457 ETHYL ACETATE (GC)
1458 METHYL ACETATE (GC)
1459 METHYL ACRYLATE (GC)
1500 HYDROCARBONS, BP 36-126°C (GC)
benzene
cyclohexane
cyclohexene
n-heptane
n-hexane
methylcyclohexane
n-octane
n-pentane
toluene

1501 HYDROCARBONS, AROMATIC (GC)
benzene
p-tert-butyl toluene
cumene
ethylbenzene
α-methylstyrene
naphthlene
styrene
toluene
vinyl toluene
xylene
1550 NAPHTHAS (GC)
Coal tar naphtha
Kerosene
Mineral spirits
Petroleum ether
Petroleum naphtha
Rubber solvent
Stoddard solvent
1551 TURPENTINE (GC)
1552 TERPENES
limonene
α-pinene
β-pinene
3-carene
1600 CARBON DISULFIDE (GC)
1601 1,1-DICHLORO-1-NITROETHANE (GC)
1602 DIOXANE (GC)
1603 ACETIC ACID (GC)
1604 ACRYLONITRILE (GC)
1605 XX Ethers I
1606 ACETONITRILE (GC)
1607 XX Ethylene oxide - see 1614
1608 GLYCIDOL (GC)
1609 TETRAHYDROFURAN (GC)
1610 ETHYL ETHER (GC)
1611 METHYLAL (GC)
1612 PROPYLENE OXIDE (GC)
1613 PYRIDINE (GC)
1614 ETHYLENE OXIDE (GC)
1615 METHYL tert-BUTYL ETHER (MTBE)(GC)
1616 n-BUTYL GLYCIDYL ETHER (GC)
1617 PHENYL ETHER (GC)
1618 ISOPROPYL ETHER (GC)
1619 PHENYL GLYCIDYL ETHER (GC)
1620 ISOPROPYL GLYCIDYL ETHER (GC)

2000 METHANOL (GC)
2001 XX Cresol - see 2546
2002 AMINES, AROMATIC (GC)
aniline
N,N-dimethyl aniline
N,N-dimethyl-*p*-toluidine
o-toluidine
2,4-xylidine
2003 1,1,2,2-TETRABROMOETHANE(GC)
2004 DIMETHYLACETAMIDE and
DIMETHYLFORMAMIDE (GC)
2005 NITROBENZENES (GC)
4-chloronitrobenzene
nitrobenzene
nitrotoluene
2007 AMINOETHANOL COMPOUNDS I (GC)
2-aminoethanol
2-dibutylaminoethanol
2-diethylaminoethanol
2008 CHLOROACETIC ACID (IC)
2009 XX - see 2540
2010 AMINES, ALIPHATIC (GC)
diethylamine
dimethylamine
2011 FORMIC ACID (IC)
2012 n-BUTYLAMINE (GC)
2013 PHENYL ETHER & DIPHENYL (GC)
2014 *p*-CHLOROPHENOL (HPLC)
2015 CHLOROACETALDEHYDE
2500 METHYL ETHYL KETONE (GC)
2501 ACROLEIN (GC)
2502 XX Formaldehyde
2503 XX Mevinphos - see 5600
2504 TETRAETHYL PYROPHOSPHATE (TEPP)(GC)
2505 FURFURYL ALCOHOL (GC)
2506 ACETONE CYANOHYDRIN (GC)
2507 NITROGLYCERIN and ETHYLENE GLYCOL
DINITRATE (GC)
2508 ISOPHORONE (GC)
2509 XX Hydrazine
2510 1-OCTANETHIOL (GC)
2511 XX - see 2545
2512 XX Hexachlorobutadiene
2513 ETHYLENE CHLOROHYDRIN (GC)
2514 ANISIDINE (HPLC)
2515 DIAZOMETHANE (GC)
2516 DICHLOROFLUOROMETHANE (GC)

2517 PENTACHLOROETHANE (GC)
2518 HEXACHLORO-1,3-CYCLOPENTADIENE (GC)
2519 ETHYL CHLORIDE (GC)
2520 METHYL BROMIDE
2521 METHYL CYCLOHEXANONE (GC)
2522 NITROSAMINES (GC)
N-nitrosodimethylamine
N-nitrodiethylamine
N-nitrosodipropylamine
N-nitrosodibutylamine
N-nitrosomorpholine
N-nitrosopiperidine
N-nitrosopyrrolidine
2523 1,3-CYCLOPENTADIENE (GC)
2524 DIMETHYL SULFATE (GC)
2526 NITROETHANE (GC)
2527 NITROMETHANE (GC)
2528 2-NITROPROPANE (GC)
2529 FURFURAL (GC)
2530 DIPHENYL (GC)
2531 XX Glutaraldehyde (GC)
2532 GLUTARALDEHYDE (HPLC)
2533 TETRAETHYL LEAD, as Pb (GC)
2534 TETRAMETHYL LEAD, as Pb (GC)
2535 TOLUENE-2,4-DIISOCYANATE (HPLC)
2536 VALERALDEHYDE (GC)
2537 METHYL METHACRYLATE (GC)
2538 ACETALDEHYDE (GC)
2539 ALDEHYDES, SCREENING (GC)
2540 ETHYLENEDIAMINE, DIETHYLENETRIAMINE, and TRIETHYLENETETRAMINE (HPLC)
2541 FORMALDEHYDE by GC
2542 MERCAPTANS, METHYL, ETHYL, n-BUTYL (GC)
2543 HEXACHLOROBUTADIENE (GC/ECD)
2544 NICOTINE (GC/NPD)
2545 ALLYL GLYCIDIL ETHER (GC)
2546 CRESOLS and PHENOL (GC)
2549 VOLATILE ORGANIC CPDS (SCREENING) (GC/MS)

3500 FORMALDEHYDE (chromotropic acid)(VIS)
3501 XX Formaldehyde (Girard T)
3502 XX Phenol - see 2546
3503 HYDRAZINE (VIS)
3504 XX Hydrazine (color)
3505 TETRAMETHYL THIOUREA (VIS)
3506 ACETIC ANHYDRIDE (VIS)
3507 ACETALDEHYDE (HPLC)
3508 METHYL ETHYL KETONE PEROXIDE (VIS)
3509 AMINOETHANOL COMPOUNDS II (IC)
monoethanolamine (MEA)
diethanolamine (DEA)
triethanolamine (TEA)
3510 MONOMETHYLHYDRAZINE (VIS)
3511 n-METHYLANILINE (GC)
3512 MALEIC ANHYDRIDE (HPLC)
3513 TETRANITROMETHANE (GC/NPD)
3514 ETHYLENIMINE (HPLC)
3515 1,1-DIMETHYLHYDRAZINE (VIS)
3516 CROTONALDEHYDE (POL)
3518 PHENYLHYDRAZINE (VIS)
3700 BENZENE (portable GC)
3701 TRICHLOROETHYLENE (portable GC)
3702 ETHYLENE OXIDE (portable GC)
3703 XX Methylene chloride (portable GC)

4000 TOLUENE, passive (GC)

5000 CARBON BLACK (Grav)
5001 2,4-D AND 2,4,5-T (HPLC)

5002 WARFARIN (HPLC)
5003 PARAQUAT (HPLC)
5004 HYDROQUINONE (HPLC)

5005 THIRAM (HPLC)
5006 CARBARYL (SEVIN) (VIS)
5007 ROTENONE (HPLC)
5008 PYRETHRUM (HPLC)
5009 BENZOYL PEROXIDE (HPLC)
5010 BROMOXYNIL and BROMOXYNIL OCTANOATE (HPLC)
5011 ETHYLENE THIOUREA (VIS)
5012 EPN (GC)
5013 DYES, BENZIDINE, *o*-ANISIDINE, and *o*-TOLIDINE (HPLC)
5014 CHLORINATED TERPHENYL (GC)
5015 XX Xanthanates
5016 STRYCHNINE (HPLC)
5017 DIBUTYL PHOSPHATE (GC)

5018 2,4,7-TRINITROFLUOREN-9-ONE (HPLC)

5019 AZELAIC ACID (GC)
5020 DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE (GC)
5021 *o*-TERPHENYL (GC)
5022 ARSENIC, ORGANO- (IC/GFAAS)
p-aminophenyl arsonic acid
dimethyl arsenic acid
methylarsonic acid
5023 XX Coal Tar Pitch Volatiles
5024 XX Tetryl
5025 CHLORINATED DIPHENYL ETHER (GC)
5026 OIL MIST, MINERAL (IR)
5027 RIBAVARIN (HPLC)
5028 XX Picric acid
5029 4,4'-METHYLENEDIANILINE (MDA)(HPLC)
5030 CYANURIC ACID (HPLC)
5031 ASPARTAME (HPLC)
5032 PENTAMIDINE ISETHIONATE (HPLC)

5033 *p*-NITROANILINE (HPLC)
5034 TRIBUTYL PHOSPHATE (GC)
5035 SUPER ABSORBENT POLYMER (ICP)
5036 TRIMELLITIC ANHYDRIDE (GC)
5037 TRIORTHOCRESYL PHOSPHATE (GC)
5038 TRIPHENYL PHOSPHATE (GC)
5039 CHLORINATED CAMPHENE (GC)
5040 ELEMENTAL CARBON (DIESEL EXHAUST) (EGA)
5041 CAPSAICIN & DIHYDROCAPSAICIN (HPLC/FL)
5500 XX Ethylene glycol - see 5523
5501 XX 4-dimethylaminoazobenzene
5502 ALDRIN & LINDANE (GC)
5503 POLYCHLOROBIPHENYLS (GC)
5504 ORGANOTIN COMPOUNDS, as Sn (HPLC/GFAAS)
bibutyltin bis(isooctyl mercaptoacetate)
tetrabutyltin
tributyltin chloride
tricyclohexyltin hydroxide
5505 XX Isocyanates
5506 POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)
acenaphthene
acephthalene
anthracene
benz[a]anthracene
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[ghi]perylene
benzo[a]pyrene
benzo[e]pyrene
chrysene
dibenz[a,h]anthracene
fluoranthene
fluorene
indo[1,2,3-cd]pyrene
naphthalene
phenanthrene
pyrene
5507 XX Glutaraldehyde - see 2532
5508 KEPONE (GC/ECD)
5509 BENZIDINE and 3,3'-DICHLOROBENZIDINE (HPLC)
5510 CHLORDANE (GC)
5511 XX Ronnel - see 5600
5512 PENTACHLOROPHENOL (HPLC)
5513 XX Hexachloronaphthalene
5514 DEMETON (GC)
5515 POLYNUCLEAR AROMATIC HYDROCARBONS (GC)
acenaphthene
acephthalene
anthracene
benz[a]anthracene
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[ghi]perylene
benzo[a]pyrene
benzo[e]pyrene
chrysene
dibenz[a,h]anthracene
fluoranthene
fluorene
indo[1,2,3-cd]pyrene
naphthalene
phenanthrene
pyrene
5516 TOLUENEDIAMINES (HPLC)
5517 POLYCHLOROBENZENES (GC)
pentachlorobenzene
1,2,4,5-tetrachlorobenzene
1,2,4-trichlorobenzene
5518 NAPHTHYLAMINES (GC)
5519 ENDRIN (GC)
5520 XX Dinitrobenzene & dinitrotoluene
5521 ISOCYANATES, MONOMERIC (HPLC)
5522 ISOCYANATES (HPLC/FL)
5523 GLYCOLS (GC)
ethylene glycol
1,3-butylene glycol
triethylene glycol
propylene glycol
diethylene glycol
tetraethylene glycol
5600 ORGANOPHOSPHOROUS PESTICIDES (GC/FPD)
Azinphos methyl
Chlorpyrifos
Diazinon
Dicrotophos
Disulfoton
Ethion
Ethoprop
Fenamiphos
Fonofos
Malathion
Methamidophos
Methyl parathion
Mevinphos (E)
Mevinphos (E&Z)
Monocrotophos (E)
Monocrotophos (Z)
Parathion
Phorate
Ronnel
Sulprophos
Terbufos
5700 FORMALDEHYDE ON DUST/FIBERS (HPLC)

6000 XX Mercury - see 6009
6001 ARSINE (GFAAS)
6002 PHOSPHINE (UV/VIS)
6003 XX Tellurium fluoride
6004 SUFUR DIOXIDE/SULFATE (IC)
6005 IODINE (IC)
6006 DIBORANE (PES)
6007 NICKEL CARBONYL (GFAAS)
6008 STIBINE (VIS)
6009 MERCURY (Hopcalite)(cold vapor AAS)
6010 HYDROGEN CYANIDE (VIS)
6011 CHLORINE and BROMINE (IC)
6012 SULFURYL FLUORIDE (GC)
6013 HYDROGEN SULFIDE (IC)
6014 NITRIC OXIDE/NITROGEN DIOXIDE (VIS)
6015 AMMONIA (VIS)
6016 AMMONIA by IC

6400 XX Hydrogen sulfide - see 6013
6401 XX Phosphorus pentachloride
6402 PHOSPHORUS TRICHLORIDE (VIS)
6600 NITROUS OXIDE (portable IR)
6601 OXYGEN (EC sensor)
6602 SULFUR HEXAFLUORIDE (portable GC)
6603 CARBON DIOXIDE (portable GC)
6604 CARBON MONOXIDE (EC sensor)
6700 XX Nitrogen dioxide (pass)
6701 XX Ammonia (pass)

7013 ALUMINUM (FAAS)
7020 CALCIUM (FAAS)
7024 CHROMIUM (FAAS)
7027 COBALT (FAAS)
7029 COPPER (FUME/DUST) (FAAS)
7030 ZINC (ICP)
7048 CADMIUM (FAAS)
7056 BARIUM, soluble (FAAS)
7074 TUNGSTEN, sol/insol (FAAS)
7082 LEAD (FAAS)
7101 XX Vanadium, sol/insol (ICP)
7102 BERYLLIUM (GFAAS)
7103 XX Rhodium - see 7300
7104 XX Platinum - see 7300
7105 LEAD (GFAAS)
7300 ELEMENTS (ICP)
7400 ASBESTOS and other FIBERS by PCM
7401 ALKALINE DUST (titration)
7402 ASBESTOS by TEM
7403 see 9002
7500 SILICA (XRD)
7501 SILICA, AMORPHOUS (XRD)
7502 ZINC OXIDE (XRD)
7503 XX Talc
7504 VANADIUM OXIDES (XRD)
7505 LEAD SULFIDE (XRD)
7506 BORON CARBIDE (XRD)

7600 CHROMIUM HEXAVALENT (VIS)
7601 SILICA (VIS)
7602 SILICA (IR)
7603 SILICA IN COAL MINE DUST, (IR)
7604 CHROMIUM HEXAVALENT (IC)
7700 LEAD by Chemical Spot Test
7900 ARSENIC (HYDRIDE AAS)
7901 ARSENIC TRIOXIDE (GFAAS)
7902 FLUORIDES by ISE
7903 ACIDS,INORGANIC (IC)
- Hydrobromic acid
- Hydrochloric acid
- Hydrofluoric acid
- Nitric acid
- Phosphoric acid
- Sulfuric acid

7904 CYANIDES (ISE)
7905 PHOSPHORUS (GC)
7906 FLUORIDES by IC

8000 XX Alad in blood
8001 PENTACHLOROPHENOL in blood
8002 METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood
8003 LEAD in blood and urine
8004 POLYCHLORINATED BIPHENYLS in serum
8005 ELEMENTS in blood or tissue (ICP)
- antimony
- cadmium
- chromium
- cobalt
- copper
- iron
- lanthanum
- lead
- manganese
- molybdenum
- nickel
- platinum
- silver
- strontium
- tin
- titanium
- zinc

8300 HIPPURIC ACID in urine (VIS)
8301 HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC)
8302 MBOCA in urine
8303 PENTACHLOROPHENOL in urine
8304 XX Benzidine in urine (TLC)
8305 PHENOL & *p*-CRESOL in urine
8306 BENZIDINE in urine (GC)
8307 XX Arsenic in urine
8308 FLUORIDE in urine
8309 XX Mercury in urine
8310 METALS in urine (ICP)

Aluminum
Lead
Silver
Barium
Manganese
Strontium
Cadmium
Molybdenum
Tin
Chromium
Nickel
Titanium
Copper
Platinum
Zinc
Iron

9000 ASBESTOS, CHRYSOTILE by XRD
9002 ASBESTOS (bulk) by PLM
9100 LEAD in surface wipe samples
9101 CHROMIUM (VI) in settled dust (Test Kit)

V. B. INDEX OF SECOND EDITION METHOD NUMBERS

(The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols. 1 through 7).
CRDT = Criteria Document
SDS = Sampling Data Sheet from NIOSH Publication 77-159
NRNR = Not revised and not recommended for use
NRIU = Not revised because of infrequent usage by NIOSH; the 2nd Ed. method recommended for use at present.

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	102	1	Lead in blood (Dithizone)	LEAD [7082]; LEAD [7105]; LEAD IN BLOOD OR URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	106	1	Silica (colorimetric)	SILICA, CRYSTALLINE [7601]
	107	1	Antimony in urine	NRIU
	108	1	Nitrogen oxides	NITRIC OXIDE and NITROGEN DIOXIDE [6014]
	109	1	Silica (XRD)	SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)	SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide	NRNR; see CARBON MONOXIDE [6604]
	113	1	Carbon monoxide in blood	NRIU
	114	1	Fluoride in urine	FLUORIDE IN URINE [8308]
	115	1	Hydrogen chloride	ACIDS, INORGANIC [7903]
	116	1	Cyanide	CYANIDES [7904]
	117	1	Hydrogen fluoride	ACIDS, INORGANIC [7903]
	118	1	Acrolein	ACROLEIN [2501]
	121	1	Beryllium	BERYLLIUM [7102]; ELEMENTS by ICP [7300]
	124	1	Selenium in urine	NRIU
	125	1	Formaldehyde	FORMALDEHYDE [2541, 3500, 3501]
	126	1	Hydrogen sulfide	see HYDROGEN SULFIDE [6013]
	127	1	Acetone	KETONES I [1300]
	127	1	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; BENZENE [3700]; HYDROCARBONS, AROMATIC [1501]
	127	1	2-Butanone	METHYL ETHYL KETONE [2500]
	127	1	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	*p*-Dioxane	DIOXANE [1602]
	127	1	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methylene chloride	METHYLENE CHLORIDE [1005]
	127	1	Styrene	HYDROCARBONS, AROMATIC [1501]
	127	1	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1300]
	127	1	Toluene	HYDROCARBONS, BP 35-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
	127	1	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1300]
	127	1	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
	127	1	Xylene	HYDROCARBONS, AROMATIC [1501]

	2nd Ed.			4th Ed.
	Method Number	Vol. Number	Substance	Method [Number]
P&CAM	139	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	139	1	Arsenic in urine	NRIU
	140	1	Arsenic in urine	NRIU
	141	1	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]
	142	1	MDI	NRNR; see ISOCYANATES [5521, 5522]
	145	1	Mercury in urine	NRIU
	146	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	152	1	Chromium	CHROMIUM [7024]; ELEMENTS by ICP [7300]
	153	1	Ozone	NRIU
	154	1	Ozone	NRIU
	158	1	Parathion	ORGANOPHOSPHORUS PESTICIDES [5600]
	159	1	Oil mist	OIL MIST, MINERAL [5026]
	160	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	163	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	165	1	Mercury in urine	NRIU
	167	1	Mercury in blood	NRIU
	168	1	Aniline	AMINES, AROMATIC [2002]
	168	1	*o*-Toluidine	AMINES, AROMATIC [2002]
	168	1	2,4-Xylidine	AMINES, AROMATIC [2002]
	168	1	Dimethylaniline	AMINES, AROMATIC [2002]
	169	1	Chromic acid	CHROMIUM, HEXAVALENT [7600, 7604]
	173	1,5	Aluminum	ALUMINUM [7013]; ELEMENTS by ICP [7300]
	173	1	Antimony	NRIU
	173	1,5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	173	1,5	Barium	NRIU
	173	1,5	Beryllium	BERYLLIUM [7102]; ELEMENTS by ICP [7300]
	173	1,5	Bismuth	NRIU
	173	1,5	Cadmium	CADMIUM [7048]; ELEMENTS by ICP [7300]
	173	1,5	Calcium	CALCIUM [7020]; ELEMENTS by ICP [7300]
	173	1,5	Chromium	CHROMIUM [7024]; ELEMENTS by ICP [7300]
	173	1,5	Cobalt	COBALT [7027]; ELEMENTS by ICP [7300]
	173	1,5	Copper	COPPER [7029]; ELEMENTS by ICP [7300]
	173	1,5	Indium	NRIU
	173	1,5	Iron	ELEMENTS by ICP [7300]
	173	1,5	Lead	LEAD [7082, 7105]; ELEMENTS by ICP [7300]
	173	1,5	Lithium	ELEMENTS by ICP [7300]
	173	1,5	Magnesium	ELEMENTS by ICP [7300]
	173	1,5	Manganese	ELEMENTS by ICP [7300]
	173	1,5	Molybdenum	ELEMENTS by ICP [7300]
	173	1,5	Nickel	ELEMENTS by ICP [7300]
	173	1,5	Palladium	NRIU
	173	1,5	Potassium	NRIU
	173	1,5	Rubidium	NRIU

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	173	1,5	Silicon	NRIU
	173	1,5	Silver	ELEMENTS by ICP [7300]
	173	1,5	Sodium	ELEMENTS by ICP [7300]
	173	1,5	Strontium	ELEMENTS by ICP [7300]
	173	1,5	Tellurium	ELEMENTS by ICP [7300]
	173	1,5	Thallium	ELEMENTS by ICP [7300]
	173	1,5	Vanadium	ELEMENTS by ICP [7300]
	173	1,5	Zinc	ZINC [7030]; ELEMENTS by ICP [7300]
	175	5	Mercury	NRIU; see MERCURY [6009]
	176	1	Tin	ELEMENTS by ICP [7300]
	177	1	Gallium	NRIU
	178	1	Vinyl chloride	VINYL CHLORIDE [1007]
	179	1	Carbon disulfide	CARBON DISULFIDE [1600]
	180	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	181	1	Selenium	ELEMENTS by ICP [7300]
	182	1	Chromium	CHROMIUM [7024]; CHROMIUM HEXAVALENT [7600, 7604]; ELEMENTS by ICP [7300]
	183	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	184	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	186	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	187	1	Sulfuric acid	ACIDS, INORGANIC [7903]
	188	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS by ICP [7300]
	189	1	Antimony	NRIU
	190	1	Indium	NRIU
	191	1	Cadmium	CADMIUM [7048]; ELEMENTS by ICP [7300]
	191	1	Lead	LEAD [7082, 7105]; ELEMENTS by ICP [7300]
	192	1	Arsenic in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	193	1	Antimony in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	194	1	Indium in blood	NRIU
	195	1	Lead in blood	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	196	1	Arsenic in urine	NRIU
	197	1	Antimony in urine	NRIU
	198	1	Gallium in urine	NRIU
	199	1	Indium in urine	NRIU
	200	1	Lead in urine	LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	201	1	Methyl chloride	METHYL CHLORIDE [1001]
	202	1	Acrylonitrile	NRIU; see ACRYLONITRILE [1604]
	203	1	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
	204	1	Sulfur dioxide	NRIU; see SULFUR DIOXIDE [6004]

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P&CAM	205	1	Ammonia	NRIU; see AMMONIA [6015, 6016]
	206	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	208	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005] METALS IN URINE [8310]
	209	1	Chlorine	NRNR; see CHLORINE AND BROMINE [6011]
	211	1	Acrolein	ACROLEIN [2501]
	212	1	Fluorides	FLUORIDES [7902, 7906]; ACIDS, INORGANIC [7903]
	213	1	*bis*-(Chloromethyl)ether	NRIU
	214	1	Lead in air or blood	LEAD [7082, 7105]; ELEMENTS BY ICP [7300]; LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	215	1	Phosphate in urine	NRIU
	216	1	Phosphoric acid	ACIDS, INORGANIC [7903]
	217	1	Benzene solubles	NRNR; see OSHA METHOD 58, COAL TAR PITCH VOLATILES
	219	1	Phosgene	NRIU
	220	1	Chloromethyl methyl ether	NRIU
	221	1	Aliphatic amines	AMINES, ALIPHATIC [2010]
	222	1	Zinc oxide	ZINC OXIDE [7502]
	223	1	Cadmium in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	224	1	Cadmium in urine	METALS IN URINE [8310]
	225	1	Kepone	KEPONE [5508]
	226	1	2,6-Di-*t*-butyl-*p*-cresol	NRIU
	227	1	Polymethylsiloxane	NRIU
	228	1	Thiram	THIRAM [5005]
	230	1	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	231	1	Nitrogen oxides	NRIU; see NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
	232	1	Formic acid	NRIU; see FORMIC ACID [2011]
	234	1	Dyes, benzidine, o-tolidine	DYES [5013]
	235	1	Formaldehyde	NRIU; see FORMALDEHYDE [2541, 3500]
	236	1	MOCA	NRIU
	237	1	Tissue preparation	ELEMENTS IN BLOOD OR TISSUE [8005]
	239	1	Asbestos	ASBESTOS AND OTHER FIBERS BY PCM [7400]; ASBESTOS FIBERS BY TEM [7402]
	241	1	Sodium hydroxide	ALKALINE DUSTS [7401]
	242	1	Phosphorus	PHOSPHORUS [7905]
	243	1	Benzidine	BENZIDINE AND 3,3'-DICHLOROBENZIDINE [5509]
	244	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	245	1	Asbestos (chrysotile, bulk)	ASBESTOS,CHRYSOTILE BY XRD [9000]; ASBESTOS (bulk) BY PLM [9002]
	246	1	3,3'-Dichlorobenzidine	BENZIDINE and 3,3'-DICHLOROBENZIDINE [5509]
	247	1	Methanol	METHANOL [2000]

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P&CAM	248	1	1,1-Dimethyl hydrazine	NRNR; see 1,1-DIMETHYLHYDRAZINE [3515]
	248	1	Hydrazine	HYDRAZINE [3503]
	248	1	Methyl hydrazine	NRNR; see MONOMETHYLHYDRAZINE [3510]
	248	1	Phenyl hydrazine	NRNR; see PHENYLHYDRAZINE [3518]
	250	4	Zirconium oxide	NRIU
	251	1	Benzo(a)pyrene	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	252	1	Dimethylnitrosamine	NITROSAMINES [2522]
	253	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	255	1	Thiophene	NRIU
	256	1	Azelaic acid	AZELAIC ACID [5019]
	257	1	Phosphorus	PHOSPHORUS [7905]
	259	1,5	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
	260	4	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
	261	4	Antimony	NRIU
	262	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]; METALS IN URINE [8310]
	263	4	Hexamethylenetetramine	NRIU
	264	4	Naphthylamines	NAPHTHYLAMINES [5518]
	265	4	Arsine	ARSINE [6001]
	266	4	Vinylidene chloride	VINYLIDENE CHLORIDE [1015]
	267	5	Sulfuric acid	NRNR; see ACIDS, INORGANIC [7903]
	268	5	Sulfur dioxide, sulfates, sulfites	SULFUR DIOXIDE [6004]
	269	4	4-Aminobiphenyl	NRIU
	270	4	Aminoethanol compounds	AMINOETHANOL COMPOUNDS I [2007]; AMINOETHANOL COMPOUNDS II [3509]
	271	4	Tungsten	TUNGSTEN [7074]; ELEMENTS BY ICP [7300]
	272	4	2-Nitropropane	2-NITROPROPANE [2528]
	273	4	4-Nitrobiphenyl	NRIU
	276	4	Ethylenediamine	DIETHYLENETRIAMINE, ETHYLENEDIAMINE, & TRIETHYLENETETRAMINE [2540]
	277	4	Methylamine	NRIU
	278	4	Vinyl acetate	VINYL ACETATE [1453]
	279	4	Beryllium in tissue	ELEMENTS IN BLOOD OR TISSUE [8005]
	280	4	*N,N*-Dimethyl-*p*-toluidine	AMINES, AROMATIC [2002]
	281	4	Ethylene thiourea	ETHYLENE THIOUREA [5011]
	282	4	Tetramethyl thiourea	TETRAMETHYL THIOUREA [3505]
	283	4	Oil mist	OIL MIST, MINERAL [5026]
	284	4	4-Dimethylaminoazobenzene	NRIU
	285	5	Crotonaldehyde	CROTONALDEHYDE [3516]
	286	5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
	288	5	Beryllium	BERYLLIUM [7102]; ELEMENTS BY ICP [7300]
	290	5	Vanadium	ELEMENTS BY ICP [7300]
	291	5	α-Chloroacetophenone	NRIU

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P&CAM 294	5	Cyclopentadiene	1,3-CYCLOPENTADIENE [2523]
295	5	Dichlorovos	NRIU
296	6	Hydrogen sulfide	NRIU, see HYDROGEN SULFIDE [6013]
297	5	Dibutyl phosphate	DIBUTYL PHOSPHATE [5017]
298	5,7	Nickel	ELEMENTS BY ICP [7300]
299	5	Dimethylnitrosamine	NITROSAMINES [2522]
300	5	Ethylenimine (aziridine)	ETHYLENIMINE [3514]
301	5	Dimethyl sulfate	NRIU
302	5	Maleic anhydride	MALEIC ANHYDRIDE [3512]
303	5	Styrene oxide	NRIU
304	5	OCBM	NRIU
305	5	Phosphorus trichloride	PHOSPHORUS TRICHLORIDE [6402]
307	5	Hexachlorobutadiene	HEXACHLOROBUTADIENE [2543]
308	5	Hexachlorocyclopentadiene	HEXACHLORO-1,3-CYCLOPENTADIENE [2518]
309	5	Chrysotile asbestos (bulk)	ASBESTOS, CHRYSOTILE BY XRD [9000]
310	5	Hydrogen chloride	ACIDS, INORGANIC [7903]
313	6	Warfarin	WARFARIN [5002]
314	5	Trichloroisocyanuric acid	NRIU
315	5	Benzidine in urine	BENZIDINE IN URINE [8306]
316	6	Silica, amorphous	SILICA, AMORPHOUS [7501]
317	6	Diethylcarbamoyl chloride	NRIU
318	6	Formaldehyde	FORMALDEHYDE [2541, 3500, 5700]
319	6	Chromium (VI)	CHROMIUM, HEXAVALENT [7600, 7604]
320	6	Arsenic, organo-	ARSENIC, ORGANO- [5022]
321	6	1,2-Dichloroproane	1,2-DICHLOROPROPANE [1013]
322	6	Trimellitic anhydride	TRIMELLITIC ANHYDRIDE [5036]
323	6	Titanium diboride	NRIU
324	6	Boron carbide	BORON CARBIDE [7506]
325	6	Benzidine, o-anisidine, and *o*-Tolidine dyes	DYES [5013]
326	6	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]; ISOCYANATES [5521, 5522]
327	6	Hippuric acid in urine	HIPPURIC ACID IN URINE [8300]
328	6	ALAD in blood	NRNR; see LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
329	6	PCB in blood	POLYCHLORINATED BIPHENYLS IN SERUM [8004]
330	6	Phenol and Cresol in urine	PHENOL and p-CRESOL IN URINE [8305]
331	6	Methyl ethyl ketone peroxide	METHYL ETHYL KETONE PEROXIDE [3508]
332	6	Chloroacetic acid	CHLOROACETIC ACID [2008]
333	6	Bisphenol A	NRIU
335	6	Pentachloroethane	PENTACHLOROETHANE [2517]
336	6	Tetraethyl pyrophosphate	TETRAETHYL PYROPHOSPHATE-TEPP [2504]
337	7	*p*-Chlorophenol	β-CHLOROPHENOL [2014]
338	7	Ethylene glycol	NRNR; see GLYCOLS [5523]
339	7	Inorganic acids	ACIDS, INORGANIC [7903]

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Method Number	Vol. Number	Substance	Method [Number]
P&CAM 340	7	Acetone cyanohydrin	ACETONE CYANOHYDRIN [2506]
341	7	Diborane	DIBORANE [6006]
342	7	MOCA in urine	MBOCA IN URINE [8302]
343	7	Polychlorobenzenes	POLYCHLOROBENZENES [5517]
344	7	Nickel carbonyl	NICKEL CARBONYL [6007]
345	7	Welding and brazing fume	NRIU; see ELEMENTS BY ICP [7300]
346	7	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
347	7	MDI	NRNR; see ISOCYANATES [5521, 5522]
348	7	2,4,7-Trinitro-9-fluorenone	2,4,7-TRINITROFLUOREN-9-ONE [5018]
349	7	Vinyl bromide	VINYL BROMIDE [1009]
350	7	Lead sulfide	LEAD SULFIDE [7505]
351	7	Elements by ICP	ELEMENTS BY ICP [7300]
354	7	Formaldehyde	FORMALDEHYDE [2541, 3500, 5700]
355	--	Talc, respirable	NRIU
357	--	*n*-Octanethiol	1-OCTANETHIOL [2510]
358	--	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
359	--	Benzidine in urine	BENZIDINE IN URINE [8306]
360	--	Hippuric Acid in urine	HIPPURIC ACID IN URINE [8300]; HIPPURIC and METHYL HIPPURIC ACIDS IN URINE [8301]
361	--	2-Butanone, ethanol, and toluene in blood	METHYL ETHYL KETONE, ETHANOL, AND TOLUENE IN BLOOD [8002]
362	--	Pentachlorophenol in blood	PENTACHLOROPHENOL IN BLOOD [8001]
363	--	Polychlorinated terphenyls	CHLORINATED TERPHENYL [5014]
364	--	Vanadium oxides	VANADIUM OXIDES [7504]
365	--	2-Butanone	METHYL ETHYL KETONE [2500]
368	--	Tin, organo-	ORGANOTIN COMPOUNDS [5504]
374	--	Acrolein	ACROLEIN [2501]
S1	2	Acetone	KETONES I [1300]
S2	2	Antimony	NRIU
S3	2	2-Butanone	METHYL ETHYL KETONE [2500]
S4	2	Hydrogen sulfide	NRIU; see HYDROGEN SULFIDE [6013]
S5	2	Manganese	ELEMENTS BY ICP [7300]
S7	5	*p*-Nitroaniline	*p*-NITROANILINE [5033]
S8	2	Ozone	NRIU
S10	2	Camphor	KETONES II [1301]
S11	5	Chloroacetaldehyde	CHLOROACETALDEHYDE [2015]
S12	2	Mesityl oxide	KETONES II [1301]
S13	2	5-Methyl-3-heptanone	KETONES II [1301]
S15	2	Methyl (*n*-amyl) ketone	KETONES II [1301]
S16	2	Ethyl butyl ketone	KETONES II [1301]
S17	5	Furfural	FURFURAL [2529]
S18	2	Hexone (MIBK)	KETONES I [1300]
S19	2	Cyclohexanone	KETONES I [1300]
S20	2	2-Pentanone	KETONES I [1300]

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S22	2	*p-tert*-Butyltoluene	HYDROCARBONS, AROMATIC [1501]
S23	2	Cumene	HYDROCARBONS, AROMATIC [1501]
S24	4	Diphenyl	DIPHENYL [2530]
S25	2	Vinyl toluene	HYDROCARBONS, AROMATIC [1501]
S26	2	α-Methyl styrene	HYDROCARBONS, AROMATIC [1501]
S27	2	Terphenyl	*o*-TERPHENYL [1521]
S28	2	Cyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S29	2	Ethylbenzene	HYDROCARBONS, AROMATIC [1501]
S30	2	Styrene	HYDROCARBONS, AROMATIC [1501]
S31	2	*sec*-Amyl acetate	ESTERS I [1450]
S32	2	*tert*-Butyl acetate	ESTERS I [1450]
S33	2	Dibutyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
S35	2	Ethyl acrylate	ESTERS I [1450]
S36	2	Ethyl formate	ETHYL FORMATE [1452]
S37	2	Methyl isoamyl acetate	ESTERS I [1450]
S38	2	Methyl acrylate	METHYL ACRYLATE [1459]
S39	2	Methyl cellosolve acetate	METHYL CELLOSOLVE ACETATE [1451]
S40	2	Di-2-ethylhexyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
S41	2	2-Ethoxyethyl acetate	ESTERS I [1450]
S42	2	Methyl acetate	METHYL ACETATE [1458]
S43	6	Methyl methacrylate	METHYL METHACRYLATE [2537]
S44	2	Isobutyl acetate	ESTERS I [1450]
S45	2	Isoamyl acetate	ESTERS I [1450]
S46	2	*sec*-Butyl acetate	ESTERS I [1450]
S47	2	*n*-Butyl acetate	ESTERS I [1450]
S48	2	*n*-Propyl acetate	ESTERS I [1450]
S49	2	Ethyl acetate	ETHYL ACETATE [1457]
S50	2	Isopropyl acetate	ISOPROPYL ACETATE [1454]
S51	2	*n*-Amyl acetate	ESTERS I [1450]
S52	2	Allyl alcohol	ALCOHOLS III [1402]
S53	2	*sec*-Butyl alcohol	ALCOHOLS II [1401]
S54	2	Cyclohexanol	ALCOHOLS III [1402]
S55	2	Diacetone alcohol	ALCOHOLS III [1402]
S56	2	Ethanol	ALCOHOLS I [1400]
S57	2	Hydroquinone	HYDROQUINONE [5004]
S58	2	Isoamyl alcohol	ALCOHOLS III [1402]
S59	2	Methanol	METHANOL [2000]
S60	2	Methyl isobutyl carbinol	ALCOHOLS III [1402]
S62	2	*n*-Propyl alcohol	ALCOHOLS II [1401]
S63	2	*tert*-Butyl alcohol	ALCOHOLS I [1400]
S64	2	Isobutyl alcohol	ALCOHOLS II [1400]
S65	2	Isopropyl alcohol	ALCOHOLS I [1400]
S66	2	*n*-Butyl alcohol	ALCOHOLS II [1401]
S67	2	Chlorinated camphene	CHLORINATED CAMPHENE [5039]

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S69	2	Dipropylene glycol methyl ether	NRIU
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	PHENYL ETHER [1617]
S73	2	Phenyl ether-biphenyl mixture	PHENYL ETHER-DIPHENYL MIXTURE [2013]
S74	2	Phenyl glycidyl ether	PHENYL GLYCIDYL ETHER [1619]
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	ISOPROPYL GLYCIDYL ETHER [1620]
S78	2	Tetrahydrofuran	TETRAHYDROFURAN [1609]
S79	2	2-Methoxyethanol	ALCOHOLS IV [1403]
S80	2	Ethyl ether	ETHYL ETHER [1610]
S81	2	*n*-Butyl glycidyl ether	*n*-BUTYL GLYCIDYL ETHER [1616]
S82	2	Cyclohexene	HYDROCARBONS, BP 36-126 °C [1500]
S84	5	Methyl acetylene (propyne)	NRIU
S85	6	Methyl acetylene/propadiene	NRIU
S86	2	Naphtha, coal tar	NAPHTHAS [1550]
S87	2	Propane	NRIU
S88	2	Turpentine	TURPENTINE [1551]
S89	2	Heptane	HYDROCARBONS, BP 36-126 °C [1500]
S90	2	Hexane	HYDROCARBONS, BP 36-126 °C [1500]
S91	2	Butadiene	1,3-BUTADIENE [1024]
S92	2	Ketene	NRIU
S93	2	LPG	NRIU
S94	2	Methylcyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S95	2	Propylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S96	2	Pentachloronaphthalene	NRIU
S97	2	Octachloronaphthalene	NRIU
S98	2	Methyl iodide	METHYL IODIDE [1014]
S99	4	Methyl chloride	METHYL CHLORIDE [1001]
S100	2	Hexachloronaphthalene	NRIU
S101	2	Hexachloroethane	HYDROCARBONS, HALOGENATED [1003]
S102	2	Fluorotrichloromethane	FLUOROTRICHLOROMETHANE [1006]
S103	2	Ethylene chlorohydrin	ETHYLENE CHLOROHYDRIN [2513]
S104	2	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
S105	4	Ethyl chloride	ETHYL CHLORIDE [2519]
S106	2	Ethyl bromide	ETHYL BROMIDE [1011]
S107	2	Dibromodifluoromethane	DIFLUORODIBROMOMETHANE [1012]
S108	2	Dichlorotetrafluoroethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]
S109	2	Dichlorofluoromethane	DICHLOROFLUOROMETHANE [2516]
S110	2	1,2-Dichloroethylene	HALOGENATED HYDROCARBONS [1003]
S111	2	Dichlorodifluoromethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLORO-TETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]

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S112	2	Chloroprene	CHLOROPRENE [1002]
S113	2	Chlorobromomethane	HYDROCARBONS, HALOGENATED [1003]
S114	2	Bromoform	HYDROCARBONS, HALOGENATED [1003]
S115	2	Benzyl chloride	HYDROCARBONS, HALOGENATED [1003]
S116	2	Allyl chloride	ALLYL CHLORIDE [1000]
S117	2	Acetylene tetrabromide	1,1,2,2-TETRABROMOETHANE [2003]
S118	2	Epichlorohydrin	EPICHLOROHYDRIN [1010]
S119	2	Chlorinated diphenyl oxide	CHLORINATED DIPHENYL ETHER [5025]
S120	4	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S121	2	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S122	2	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S123	2	1,1-Dichloroethane	HYDROCARBONS, HALOGENATED [1003]
S124	2	1,1,2,2-Tetrachloroethane	1,1,2,2-TETRACHLOROETHANE [1019]
S125	2	Trifluorobromomethane	TRIFLUOROBROMOMETHANE [1017]
S126	2	1,2,3-Trichloropropane	HYDROCARBONS, HALOGENATED [1003]
S128	2	Trichloronaphthalene	NRIU
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE [1020]
S130	2	Tetrachloronaphthalene	NRIU
S131	2	1,1,1,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S132	2	1,1,2,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S133	2	Chlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S134	2	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1003]
S135	3	*o*-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S137	3	Diazomethane	DIAZOMETHANE [2515]
S138	4	*n*-Butylamine	*n*-BUTYLAMINE [2012]; AMINES, ALIPHATIC [2010]
S139	3	Diethylamine	AMINES, ALIPHATIC [2010]
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS I [2007]; AMINOETHANOL COMPOUNDS II [3509]
S141	4	Diisopropylamine	NRIU; see AMINES, ALIPHATIC [2010]
S142	3	Dimethylamine	AMINES, ALIPHATIC [2010]
S143	3	1,1-Dimethyl hydrazine	1,1-DIMETHYLHYDRAZINE [3515]
S144	3	Ethylamine	NRIU
S146	3	*N*-Ethyl morpholine	NRIU
S147	3	Isopropylamine	NRIU
S148	6	Methylamine	NRIU
S149	3	Methyl hydrazine	MONOMETHYLHYDRAZINE [3510]
S150	3	Morpholine	NRIU
S152	3	Triethylamine	NRIU
S153	3	Monomethylaniline	MONOMETHYLANILINE [3511]
S155	3	Tetramethylsuccinonitrile	NRIU

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S156	3	Acrylonitrile	ACRYLONITRILE [1604]
S158	4	2-Aminopyridine	NRIU
S160	3	Phenyl hydrazine	PHENYLHYDRAZINE [3518]
S161	3	Pyridine	PYRIDINE [1613]
S162	3	2,4-Xylidine	AMINES, AROMATIC [2002]
S163	5	Anisidine (*o* and *p*-)	ANISIDINE [2514]
S164	3	Dimethylaniline	AMINES, AROMATIC [2002]
S165	3	Acetonitrile	ACETONITRILE [1606]
S166	5	Dinitro-o-cresol	NRIU
S167	3	Cresol	CRESOLS AND PHENOL [2546]
S168	3	*o*-Toluidine	AMINES, AROMATIC [2002]
S169	4	Acetic acid	ACETIC ACID [1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE [3506]
S173	5	Formic acid	FORMIC ACID [2011]
S174	3	Sulfuric acid	ACIDS, INORGANIC [7903]
S175	3	Hydrogen bromide	ACIDS, INORGANIC [7903]
S176	3	Hydrogen fluoride	FLUORIDES [7902, 7906]; ACIDS, INORGANIC [7903]
S178	3	2-Hexanone	KETONES I [1300]
S179	3	Phthalic anhydride	NRIU
S181	4	Quinone	NRIU
S182	5	Silver	ELEMENTS BY ICP [7300]
S183	3	Tin	ELEMENTS BY ICP [7300]
S185	3	Zirconium	ELEMENTS BY ICP [7300]
S186	3	Copper	COPPER [7029]; ELEMENTS BY ICP [7300]
S187	3	Tellurium hexafluoride	NRIU
S188	3	Rhodium, fume and dust	NRIU
S189	3	Rhodium, soluble	NRIU
S190	3,7	Selenium	ELEMENTS BY ICP [7300]
S191	3,7	Platinum	ELEMENTS BY ICP [7300]
S193	3	Molybdenum	ELEMENTS BY ICP [7300]
S194	5	Hafnium	NRIU
S198	3	Barium	BARIUM [7056]
S199	4	Mercury	NRIU; see MERCURY [6009]
S200	3	Yttrium	ELEMENTS BY ICP [7300]
S201	5	Tantalum	ELEMENTS BY ICP [7300]
S203	4	Cobalt	COBALT [7027]; ELEMENTS BY ICP [7300]
S204	3,7	Tellurium	ELEMENTS BY ICP [7300]
S205	3	Calcium	CALCIUM [7020]; ELEMENTS BY ICP [7300]
S206	3	Nickel	ELEMENTS BY ICP [7300]
S208	3	Tributyl phosphate	TRIBUTYL PHOSPHATE [5034]
S209	3	Triorthocresyl phosphate	TRIORTHOCRESYL PHOSPHATE [5037]
S210	3	Triphenyl phosphate	TRIPHENYL PHOSPHATE [5038]
S211	5	1-Chloro-1-nitropropane	NRIU
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S215	4	Dinitrotoluene	NRIU
S216	3	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
S217	3	Nitrobenzene	NITROBENZENES [2005]
S218	3	*p*-Nitrochlorobenzene	NITROBENZENES [2005]
S219	4,6	Nitroethane	NITROETHANE [2526]
S220	6	Nitromethane	NITROMETHANE [2527]
S223	3	Nitrotoluene	NITROBENZENES [2005]
S224	3	Tetranitromethane	NRIU
S225	3	Tetryl	NRIU
S227	3	*n*-Propyl nitrate	NRIU
S228	4	Picric acid	NRIU
S229	3	Arsine	ARSINE [6001]
S237	3	Hydrazine	HYDRAZINE [3503]
S243	4	Stibine	STIBINE [6008]
S244	5	Sulfur hexafluoride	NRIU
S245	6	Sulfuryl fluoride	SULFURYL FLUORIDE [6012]
S246	3	Hydrogen chloride	ACIDS, INORGANIC [7903]
S248	3	Carbon disulfide	CARBON DISULFIDE [1600]
S249	3	Carbon dioxide	CARBON DIOXIDE [6603]
S250	3	Cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S253	4	Benzoyl peroxide	BENZOYL PEROXIDE [5009]
S254	3	Dimethylacetamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S255	3	Dimethylformamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S256	5	Thiram	THIRAM [5005]
S257	5	Phosphorus pentachloride	NRIU
S262	3	Carbon black	CARBON BLACK [5000]
S264	3	Ethyl silicate	NRIU
S272	3	Oil mist	OIL MIST, MINERAL [5026]
S273	3	Carbaryl (Sevin)	CARBARYL [5006]
S274	3	DDT	NRIU
S275	3	Aldrin	ALDRIN and LINDANE [5502]
S276	5	ANTU	NRIU
S278	6	Chlordane	CHLORDANE [5510]
S279	5	2,4-D	2,4-D and 2,4,5-T [5001]
S280	6	Demeton	DEMETON [5514]
S281	3	*p*-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S283	3	Dieldrin	NRIU
S284	6	Endrin	ENDRIN [5519]
S285	3	EPN	EPN [5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE [1607, 3702]
S287	5	Heptachlor	NRIU
S288	4	Hydrogen cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S290	3	Lindane	ALDRIN and LINDANE [5502]
S291	5	Methyl formate	NRIU

2nd Ed.			4th Ed.
Method Number	Vol. Number	Substance	Method [Number]
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]
S293	3	Nicotine	NRIU
S294	5	Paraquat	PARAQUAT [5003]
S295	3	Parathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S296	6	Mevinphos (Phosdrin)	ORGANOPHOSPHORUS PESTICIDES [5600]
S297	4	Pentachlorophenol	PENTACHLOROPHENOL [5512]
S298	6	Pyrethrum	PYRETHRUM [5008]
S299	6	Ronnel	ORGANOPHOSPHORUS PESTICIDES [5600]
S300	5	Rotenone	ROTENONE [5007]
S301	5	Sodium fluoroacetate	NRIU
S302	5	Strychnine	STRYCHNINE [5016]
S303	5	2,4,5-T	2,4-D and 2,4,5-T [5001]
S306	3	Thallium	ELEMENTS BY ICP [7300]
S308	4	Sulfur dioxide	SULFUR DIOXIDE [6004]
S309	3	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
S310	3	Aniline	AMINES, AROMATIC [2002]
S311	3	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; BENZENE [3700]
S312	3	Cadmium	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S313	3	Cadmium fume	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S314	3	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
S315	3	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
S316	4	Zinc oxide	ZINC OXIDE [7502]
S317	3	Chromium, hexavalent	CHROMIUM, HEXAVALENT [7600, 7604]
S318	3	Xylene	HYDROCARBONS, AROMATIC [1501]
S319	4	Nitric acid	ACIDS, INORGANIC [7903]
S320	4	Nitrogen dioxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
S321	4	Nitric oxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
S323	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S327	4	Formaldehyde (Girard T)	NRNR; see FORMALDEHYDE [2542, 3500, 5700]
S328	3	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
S329	3	Methylene chloride	METHYLENE CHLORIDE [1005]
S330	3	Phenol	CRESOLS AND PHENOL [2546]
S332	5	Phosphine	PHOSPHINE [6002]
S333	3	Phosphoric acid	ACIDS, INORGANIC [7903]
S334	3	Phosphorus	PHOSPHORUS [7905]
S335	3	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]
S336	3	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
S339	3	Beryllium	BERYLLIUM [7102]; ELEMENTS BY ICP [7300]
S340	4	Carbon monoxide	NRNR; see CARBON MONOXIDE [6604]
S341	3,7	Lead	LEAD [7082]; ELEMENTS BY ICP [7300]
S342	6	Mercury, organo	NRIU
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]

2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	4th Ed. Method [Number]
S345	5	Acetaldehyde	ACETALDEHYDE [3507]
S346	4	Allyl glycidyl ether	ALLYL GLYCIDYL ETHER [2545]
S347	5	Ammonia	see AMMONIA BY VIS [6015, 6016]
S348	5	Ammonium sulfamate	NRIU
S349	3	Boron oxide	PARTICULATES NOT OTHERWISE REGULATED, TOTAL [0500]
S350	4	*n*-Butyl mercaptan	*n*-BUTYL MERCAPTAN [2525]; MERCAPTANS, METHYL, ETHYL, and *n*-BUTYL [2542]
S351	3	Chloroform	HYDROCARBONS, HALOGENATED [1003]
S352	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S354	4	Copper fume	COPPER [7029]; ELEMENTS BY ICP [7300]
S356	5	Crag herbicide I	NRIU
S357	3	*sym*-Dichloroethyl ether	DICHLOROETHYL ETHER [1004]
S358	3	Diisobutyl ketone	KETONES I [1300]
S360	3	Dioxane	DIOXANE [1602]
S361	5	2-Ethoxyethanol	ALCOHOLS IV [1403]
S365	4	Furfuryl alcohol	FURFURYL ALCOHOL [2505]
S366	4	Iron oxide fume	ELEMENTS BY ICP [7300]
S367	3	Isophorone	ISOPHORONE [2508]
S368	3	Isopropyl ether	ISOPROPYL ETHER [1618]
S369	3	Magnesium oxide fume	ELEMENTS BY ICP [7300]
S370	3	Malathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S371	4	Methoxychlor	NRIU
S372	3	Methyl bromide	NRNR
S374	4	Methylcyclohexanol	METHYL CYCOHEXANOL [1404]
S375	4	Methylcyclohexanone	METHYL CYCLOHEXANONE [2521]
S376	3	Molybdenum	ELEMENTS BY ICP [7300]
S378	3	Octane	HYDROCARBONS, BP 36-126 °C [1500]
S379	3	Pentane	HYDROCARBONS, BP 36-126 °C [1500]
S380	3	Naphtha, petroleum	NAPHTHAS [1550]
S381	4	Sodium hydroxide	ALKALINE DUSTS [7401]
S382	3	Stoddard solvent	NAPHTHAS [1550]
S383	4	Tetraethyl lead	TETRAETHYL LEAD [2533]
S384	4	Tetramethyl lead	TETRAMETHYL LEAD [2534]
S385	3	Titanium dioxide	NRIU
S388	4	Vanadium	ELEMENTS BY ICP [7300]
S391	3	Vanadium	ELEMENTS BY ICP [7300]
CRDT	--	Fibrous glass	ASBESTOS AND OTHER FIBERS [7400]
CRDT	--	Nitrous oxide	NITROUS OXIDE [6600]
CRDT	--	Organotins	ORGANOTIN COMPOUNDS [5504]
SDS29	--	Nuisance dust, respirable	PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE [0600]

V. C. INDEX OF NAMES AND SYNONYMS

Example: The references to method title and number are listed in the following manner:

ACETIC ACID, 1603	(Method Title)
Ethanoic acid, see ACETIC ACID, 1603	(Synonym)
Glacial acetic acid, see ACETIC ACID, 1603	(Synonym)
Methane carboxylic acid, see ACETIC ACID, 1603	(Synonym)
CAS #64-19-7, see ACETIC ACID, 1603	(Chemical Abstracts Registry Number)

CAS # 50-00-0, see FORMALDEHYDE (2-HMP), 2541; (chromotropic acid), 3500; ALDEHYDES, SCREENING, 2539
CAS # 50-32-8, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 53-70-3, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 55-18-5, see NITROSAMINES (N-NITROSODIETHYLAMINE), 2522
CAS # 55-63-0, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
CAS # 56-23-5, see HYDROCARBONS, HALOGENATED, 1003
CAS # 56-38-2, see ORGANOPHOSPHORUS PESTICIDES, 5600
CAS # 56-55-3, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 56-81-5, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500; RESPIRABLE, 0600
CAS # 57-14-7, see 1,1-DIMETHYL HYDRAZINE, 3515
CAS # 57-24-9, see STRYCHNINE, 5016
CAS # 57-74-9, see CHLORDANE, 5510
CAS # 58-89-9, see ALDRIN and LINDANE, 5502
CAS # 59-89-2, see NITROSAMINES, 2522
CAS # 60-29-7, see ETHYL ETHER, 1610
CAS # 60-34-4, see MONOMETHYL HYDRAZINE, 3510
CAS # 62-53-3, see AMINES, AROMATIC, 2002
CAS # 62-75-9, see NITROSAMINES, 2522
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CAS # 67-72-1, see HYDROCARBONS, HALOGENATED, 1003
CAS # 68-12-2, see DIMETHYLFORMAMIDE, 2004
CAS # 71-23-8, see ALCOHOLS II, 1401
CAS # 71-36-3, see ALCOHOLS II, 1401; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS # 71-43-2, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126 °C, 1500; BENZENE by portable GC, 3700; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
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CAS # 74-83-9, see METHYL BROMIDE, 2520
CAS # 74-87-3, see METHYL CHLORIDE, 1001
CAS # 74-88-4, see METHYL IODIDE, 1014
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