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THIRD SUPPLEMENT

To

NIOSH Manual of Analytical Methods (NMAM®)
Fourth Edition

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Editor

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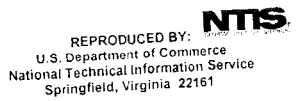

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TRANSMITTAL NOTICE

This is the Third Supplement to the NIOSH Manual of Analytical Methods (NMAM®), 4th Edition, which was printed August 15, 1994. This supplement, dated March 15, 2003, includes -- new methods, - revised methods, and seven new chapters, as well as an updated Method Finder, Contents, and Indexes.

INSTRUCTIONS FOR INSERTING 3rd SUPPLEMENT INTO YOUR MANUAL

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

Method Finder - Remove old Method Finder, pp. MF-1 to MF-27, and replace with new pages MF-1 to MF-34.
NOTE: Methods by number are listed at the end of the Method Finder.

Chapters (Blue pages) - Add new blue pages starting after Chapter K, pp. 143 through 280.

Indexes (Yellow pages - end of 3rd volume) - Remove yellow pages, pp. A-11 through A-62, and replace with new yellow pages, pp. A-11 through A-65.

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

Method	Method No.	Type
ACETOIN	2558	New
ALCOHOLS IV	1403	Revision
ALCOHOLS COMBINED	1405	New
ALIPHATIC ALDEHYDES	2018	New
ANILINE and o-TOLUIDINE in urine	8317	New
1- and 2-BROMOPROPANE	1025	New
BUTOXYACETIC ACID IN URINE	8316	New
CAPTAN AND THIOPHANATE-METHYL in Handrinse	9202	New
CAPTAN and THIOPHANATE-METHYL on Dermal Patch	9205	New
CELLULOSE INSULATION	7404	New
p-CHLOROBENZOTRIFLUORIDE	1026	New
CHROMIUM, HEXAVALENT by Ion Chromatography	7605	New
CHROMIUM, HEXAVALENT, by Field-Portable Spectrophotometry	7703	New
DECABROMODIPHENYL OXIDE	2559	New
DIACETYL	2557	New
DIESEL PARTICULATE MATTER (as Elemental Carbon)	5040	Revision
2-(DIMETHYLAMINO)ETHANOL and 1-DIMETHYLAMINO-2-PROPANOL	2561	New
ELEMENTS by ICP (Nitric/Perchloric Acid Ashing)	7300	Revision
ELEMENTS by ICP (Aqua Regia Ashing)	7301	New
ELEMENTS by ICP (Hot Block/HCl/HNO3 Digestion)	7303	New
ELEMENTS on wipes	9102	New
ESTERS 1	1450	Revision

Method	Method No.	Type
ESTROGENIC COMPOUNDS	5044	New
ETHYL ETHER	1610	Revision
FORMALDEHYDE	2016	Revision
GLYCOL ETHERS	2554	New
HIPPURIC and METHYL HIPPURIC ACIDS in urine	8301	Revision
HYDROCARBONS, AROMATIC	1501	Revision
HYDROCARBONS, BP 36-126	1500	Revision
HYDROCARBONS, HALOGENATED	1003	Revision
HYDROGEN CYANIDE	6017	New
ISOCYANATES, TOTAL (MAP)	5525	New
ISOPHORONE	2556	New
ISOPROPYL ACETATE	1460	New
ISOPROPYL ETHER	1618	Revision
KETONES I	2555	New
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LEAD by Portable Ultrasonic Extraction / ASV	7701	Revision
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MANEB (Dermal Patch)	3600	New
MANEB (Hand Wash)	3601	New
METALWORKING FLUIDS (MWF)	5524	New
METHYL ACRYLATE	2552	New
METHYL AND ETHYL METHACRYLATE	2537	Revision
METHYLTIN CHLORIDES	5526	New
1-NITROPYRENE IN DIESEL PARTICULATES	2560	New
ORGANIC AND INORGANIC GASES BY EXTRACTIVE FTIR	3800	New
QUARTZ in coal mine dust, by IR	7603	Revision
SILICA, CRYSTALLINE, by XRD	7500	Revision
SILICA, AMORPHOUS	7501	Revision
SILICA, CRYSTALLINE, by VIS	7601	Revision
SILICA, CRYSTALLINE, by IR	7602	Revision
1,1,2,2-TETRACHLOROETHANE	2562	New
TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM CHLORIDE	5046	New
THIOPHANATE-METHYL	5606	New
TRIAZINE HERBICIDES and THEIR METABOLITES in URINE	8315	New
TRIPHENYL TIN CHLORIDE	5527	New

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- Chromium
- Cobalt
- Copper
- Iron
- Lanthanum
- Lead
- Manganese
- Molybdenum
- Nickel
- Platinum
- Silver
- Strontium
- Tin
- Titanium
- Zinc

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- Cadmium
- Copper
- Manganese
- Phosphorus
- Silver
- Thallium
- Zinc
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- Cobalt
- Iron
- Molybdenum
- Lead
- Strontium
- Vanadium
- Zirconium
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- Chromium
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- Nickel
- Selenium
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- Yttrium

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

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Aluminum | Antimony | Arsenic | Barium
Beryllium | Bismuth | Boron | Cadmium
Calcium | Chromium | Cobalt | Copper
Gallium | Gold | Indium | Iron
Lead | Manganese | Magnesium | Molybdenum
Neodymium | Nickel | Palladium | Phosphorus
Platinum | Potassium | Selenium | Sodium
Strontium | Tellurium | Thallium | Tin
Titanium | Vanadium | Yttrium | Zinc
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Aluminum | Chromium | Manganese | Sodium
Antimony | Cobalt | Molybdenum | Strontium
Arsenic | Copper | Neodymium | Tellurium
Barium | Gallium | Nickel | Thallium
Beryllium | Gold | Palladium | Tin
Bismuth | Indium | Phosphorus | Titanium
Boron | Iron | Platinum | Vanadium
Cadmium | Lead | Potassium | Yttrium
Calcium | Magnesium | Selenium | Zinc
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Cyclohexene | n-Hexane | n-Pentane
n-Decane | Methylcyclohexane | n-Undecane
n-Dodecane | n-Nonane
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Benzene | α-Methylstyrene | o,m,p-Xylene
p-tert-Butyltoluene | β-Methylstyrene
Cumene | Styrene
Ethylbenzene | Toluene
HYDROCARBONS, HALOGENATED 1003
Benzyl chloride | *o*-Dichlorobenzene | Hexachloroethane
Bromoform | *p*-Dichlorobenzene | 1,1,1-Trichloroethane
Carbon tetrachloride | 1,1-Dichloroethane | 1,1,2-Trichloroethane
Chloroform | 1,2-Dichloroethylene | 1,2,3-Trichloropropane
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Toluene 2,6-diisocyanate (2,6-TDI)
Toluene 2,4-diisocyanate (2,4-TDI)
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Isophorone diisocyanate (IPDI)
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ISOVALERALDEHYDE 2018

KEPONE 5508
KETONES I (desorption in CS_2) 1300
Acetone | Diisobutyl ketone | Methyl isobutyl ketone
Cyclohexanone | 2-Hexanone | 2-Pentanone
KETONES I 2555
Acetone | Methyl isobutyl ketone | Diisobutyl ketone
Methyl ethyl ketone | 2-Hexanone | Cyclohexanone
2-Pentanone
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Ethyl butyl ketone | Methyl-(n-amyl)-ketone
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m-Xylene | 2-Butanone | Formaldehyde
p-Xylene | Methanol | Ethylene oxide
Styrene | Methylene chloride | Tetrahydrofuran
Toluene | Vinylidene fluoride | Nitrous oxide
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Disulfoton | Ethion | Ethoprop | Fenamiphos
Fonofos | Malathion | Methamidophos | Methyl parathion
Mevinphos (E) | Mevinphos (E&Z) | Monocrotophos (E) | Monocrotophos (Z)
Parathion | Phorate | Ronnel | Sulprophos
Terbufos
ORGANOTIN COMPOUNDS 5504
Dibutyltin *bis*(isooctyl mercaptoacetate) | Tetrabutyltin
Tributyltin chloride | Tricyclohexyltin hydroxide
OXYGEN (field-readable) 6601

PARAQUAT 5003
PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600
PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500
PENTACHLOROETHANE 2517
PENTACHLOROPHENOL 5512
PENTACHLOROPHENOL in blood 8001
PENTACHLOROPHENOL in urine 8303
PENTAMIDINE ISETHIONATE 5032
2-PENTANONE 2555
PERCHLOROETHYLENE (Portable GC) in Exhaled Breath and Air 3704
PHENOL and *p*-CRESOL in urine 8305
PHENYL ETHER 1617
PHENYL ETHER-DIPHENYL MIX 2013
PHENYL GLYCIDYL ETHER 1619
PHENYLHYDRAZINE 3518
PHOSPHINE 6002
PHOSPHORUS 7905
PHOSPHORUS TRICHLORIDE 6402
POLYCHLOROBENZENES 5517
1,2,4-Trichlorobenzene | 1,2,4,5-Tetrachlorobenzene | Pentachlorobenzene
POLYCHLOROBIPHENYLS 5503
POLYCHLOROBIPHENYLS in serum 8004
POLYCYCLIC AROMATIC HYDROCARBONS, TOTAL (PACs) 5800
POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC) 5506
Acenaphthene | Benzo[ghi]perylene | Fluorene
Acenaphthylene | Benzo[a]pyrene | Indeno[1,2,3-cd]pyrene
Anthracene | Benzo[e]pyrene | Naphthalene
Benz[a]anthracene | Chrysene | Phenanthrene
Benzo[b]fluoranthene | Dibenz[a,h]anthracene | Pyrene
Benzo[k]fluoranthene | Fluoranthene
POLYNUCLEAR AROMATIC HYDROCARBONS (GC) 5515
Acenaphthene | Benzo[ghi]perylene | Fluorene
Acenaphthylene | Benzo[a]pyrene | Indeno[1,2,3-cd]pyrene
Anthracene | Benzo[e]pyrene | Naphthalene
Benz[a]anthracene | Chrysene | Phenanthrene
Benzo[b]fluoranthene | Dibenz[a,h]anthracene | Pyrene
Benzo[k]fluoranthene | Fluoranthene
PROPIONALDEHYDE 2018
PROPYLENE DICHLORIDE 1013
PROPYLENE OXIDE 1612
PYRETHRUM 5008
PYRIDINE 1613

RESORCINOL 5701
RIBAVIRIN 5027
ROTENONE 5007

SILICA, AMORPHOUS 7501
SILICA in coal mine dust by IR 7603
SILICA, CRYSTALLINE, Respirable, by XRD 7500
SILICA, CRYSTALLINE by VIS 7601
SILICA, CRYSTALLINE by IR 7602
STIBINE 6008
STRYCHNINE 5016
SULFUR DIOXIDE 6004
SULFUR HEXAFLUORIDE by portable GC 6602
SULFURYL FLUORIDE 6012
SUPER ABSORBENT POLYMER 5035

TERPENES 1552
Limonene, d-, l- α-pinene β-pinene 3-carene
o-TERPHENYL 5021
1,1,2,2-TETRABROMOETHANE 2003
1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and
1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE 1016
1,1,2,2-TETRACHLOROETHANE 1019
1,1,2,2-TETRACHLOROETHANE 2562
TETRACHLOROETHYLENE 1003
TETRAETHYL LEAD 2533
TETRAETHYL PYROPHOSPHATE (TEPP) 2504
TETRAHYDROFURAN 1609
TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE 5046
TETRAMETHYL LEAD 2534
TETRAMETHYL THIOUREA 3505
TETRANITROMETHANE 3513
THIOPHENATE-METHYL in air 5606
THIOPHENATE-METHYL, hand rinse 9202
THIOPHENATE-METHYL on dermal patch 9205
THIRAM 5005
TOLUENE (diffusive sampler) 4000
2,4- & 2,6-TOLUENEDIAMINE (TDA) 5516
TOLUENE-2,4-DIISOCYANATE (TDI) 2535
p-TOLUENESULFONIC ACID 5043
o-TOLUIDINE 8317
TRIAZINE HERBICIDES and their METABOLITES 8315
Atrazine Cyanazine
Simazine Desethylatrazine
Propazine Desisopropylatrazine
TRIBUTYL PHOSPHATE 5034
TRICHLOROETHYLENE 1003
TRICHLOROETHYLENE 1022
TRICHLOROETHYLENE (portable GC) 3701
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE 1020
TRIFLUOROBROMOMETHANE 1017
TRIMELLITIC ANHYDRIDE 5036
2,4,7-TRINITROFLUOREN-9-ONE 5018
TRIORTHOCRESYL PHOSPHATE 5037

TRIPHENYL PHOSPHATE 5038
TRIPHENYL TIN CHLORIDE 5527
TUNGSTEN (soluble and insoluble) 7074
TURPENTINE 1551

VALERALDEHYDE 2018
VALERALDEHYDE 2536
VANADIUM OXIDES 7504
VINYL ACETATE 1453
VINYL BROMIDE 1009
VINYL CHLORIDE 1007
VINYLIDENE CHLORIDE 1015
VOLATILE ORGANIC COMPOUNDS (SCREENING) 2549

WARFARIN 5002

ZINC 7030
ZINC OXIDE 7502

III. APPENDIXES

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METHOD FINDER (Key on page MF-34]

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Acenaphthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Acenaphthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Acenaphthylene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Acenaphthylene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Acetaldehyde	2018	ALIPHATIC ALDEHYDES	0.1 - 1.5	1 - 15	ACN	HPLC/UV	SG-DNPH
Acetaldehyde	2538	ACETALDEHYDE	0.01 - 0.05	1 - 12	tol	GC-FID	XAD-2/HMP
Acetaldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Acetaldehyde	3507	ACETALDEHYDE	0.1 - 0.5	6 - 60	reag	HPLC-UV	BuB
Acetic acid	1603	ACETIC ACID	0.01 - 0.1	20 - 300	formic a	GC-FID	CCT
Acetic anhydride	3506	ACETIC ANHYDRIDE	0.2 - 1.0	25 - 100	reag	VIS	BuB
Acetoin	2558	ACETOIN	0.01 - 0.2	1 - 10	Acet-Meth	GC-FID	A-CMS
Acetone	1300	KETONES I	0.01 - 0.2	0.5 - 3	CS_2	GC-FID	CCT
Acetone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Acetone	3800	ORGANIC AND INORGANIC GASES BY EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. Dep.	NA	FTIR	Dir. Read
Acetone	2555	KETONES I	0.01 - 0.2	0.5 - 3.0	CS_2	GC-FID	A-CMS
Acetone cyanohydrin	2506	ACETONE CYANOHYDRIN	0.2	0.3 - 12	Et Ac	GC-NPD	Por QS
Acetonitrile	1606	ACETONITRILE	0.01 - 0.2	1 - 25	MeCl/MeOH	GC-FID	CCT
Acetylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.2 - 5	CS_2	GC-FID	CCT
Acetylene tetrabromide	2003	1,1,2,2-TETRABROMOETHANE	0.2 - 1.0	50 - 100	THF	GC-FID	SG
Acetylene tetrachloride	1019	1,1,2,2-TETRACHLOROETHANE	0.01 - 0.2	3.0 - 30	CS_2	GC-FID	PCT
Acids, inorganic	7903	ACIDS, INORGANIC	0.2 - 0.5	3.0 - 100	HCO_3^-/CO_3^{2-}	IC	SG(washed)
ACN	1606	ACETONITRILE	0.01 - 0.2	1 - 25	MeCl/MeOH	GC-FID	CCT lg
Acrolein	2501	ACROLEIN	0.01 - 0.1	1.5 - 48	tol	GC-NPD	XAD-2/HMP
Acrolein	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD 2/HMP
Acrylonitrile	1604	ACRYLONITRILE	0.01 - 0.2	3.5 - 20	acet/CS_2	GC-FID	CCT
Aerobic bacteria	0801	AEROBIC BACTERIA by GC-FAME	28.3	50 - 300	hex/MTBE	GC-FID	impactor
Alachlor	5603	ALACHLOR in AIR	1	70 - 1750	methanol	ELISA	SPE disk
Alachlor	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Alachlor	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Alachlor	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Aldehydes, screening	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2
Aldicarb	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC-UV	OVS-2
Aldrin	5502	ALDRIN & LINDANE	0.2 - 1.0	18 - 240	isooct	GC-ECN	GFF & BuB
Alkaline dusts	7401	ALKALINE DUSTS	1 - 4	70 - 1000	HCl	Titration	PTFE
Allyl alcohol	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	GC-FID	CCT
Allyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT
Allyl chloride	1000	ALLYL CHLORIDE	0.01 - 1.0	16 - 100	bz	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Allyl glycidyl ether	2545	ALLYL GLYCIDYL ETHER	0.01 - 0.2	1.5 - 8	diethyl ether	GC-FID	Tenax
Allyl trichloride	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	2 - 60	CS_2	GC-FID	CCT
Alumina	0500	PARTICULATES N.O.R.	1 - 2	7 - 133	-	Grav	PVC, tared
Aluminum	7300	ELEMENTS by ICP	1 - 4	5 - 100	$HNO_3/HClO_4$	ICP-AES	MCEF
Aluminum	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Aluminum	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 100	HCl/HNO_3	ICP-AES	MCEF
Aluminum	7013	ALUMINUM & CPDS, as Al	1 - 3	10 - 400	HNO_3	FAAS	MCEF
Amines, aliphatic	2010	AMINES, ALIPHATIC	0.01 - 1.0	3 - 30	H_2SO_4/aq MeOH	GC-FID	SG
Amines, aromatic	2002	AMINES, AROMATIC	0.2 - 1.0	30 - 150	Ethanol	GC-FID	SG
Aminobenzene	2002	AMINES, AROMATIC	0.2 - 1.0	30 - 150	Ethanol	GC-FID	SG
Aminobenzene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	Ethanol	GC-FID	GFF + SG
2-Aminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01 - 0.2	4 - 24	$MeOH/H_2O$	GC-FID	SG
2-Aminoethanol	3509	AMINOETHANOL COMPOUNDS II	0.5 - 1.0	5 - 300	HSA	IC	IMP
2-aminotoluene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF + SG
p-Aminophenylarsonic acid	5022	ARSENIC, ORGANO-	1 - 3	50 - 1000	buffer	IC-HYAAS	PTFE
2-Aminotoluene	2002	AMINES, AROMATIC	0.02 - 1.0	10 - 150	Ethanol	GC-FID	SG
Ammonia	6015	AMMONIA by VIS	0.1 - 0.2	0.1 - 90	H_2O	VIS-Auto	SG + H_2SO_4
Ammonia	6016	AMMONIA by IC	0.1 - 0.5	0.1 - 96	H_2O	IC	SG + H_2SO_4
n- and sec-Amyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
n-Amyl acetate	1450	ESTERS I	0.01 - 2	1 - 10	CS_2	GC-FID	CCT
Amyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
iso-Amylacetate	1450	ESTERS I	0.01 - 2	1 - 10	CS_2	GC-FID	CCT
Aniline	2002	AMINES, AROMATIC	0.02 - 0.2	5 - 30	Ethanol	GC-FID	SG
Aniline	2017	ANILINE, O-TOLUIDINE, & NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF+SG
Aniline	8317	ANALINE and o-TOLUIDINE in urine	NA	NA	Alk	HPLC/ECD	NA
Anisidine	2514	ANISIDINE	0.5 - 1.0	24 - 320	MeOH	HPLC-UV	XAD-2
Anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Antimony	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Antimony	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	50 - 2000	HCl/HNO_3	ICP-AES	MCEF
p-Arsanilic acid	5022	ARSENIC, organo-	1 - 3	50 - 1000	buffer	IC-HYAAS	PTFE
Arsenic	7900	ARSENIC & compounds, as As	1 - 3	30 - 1000	$HNO_3/H_2SO_4/HClO_4$	HYAAS	MCEF
Arsenic	7300	ELEMENTS by ICP	1 - 4	5 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Arsenic	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Arsenic	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Arsenic	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 2000	HCl/HNO_3	ICP-AES	MCEF
Arsenic trioxide	7901	ARSENIC TRIOXIDE, as As	1 - 3	30 - 1000	HNO_3/H_2O_2	GFAAS	MCEF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Arsine	6001	ARSINE	0.01 - 0.2	0.1 - 10	HNO_3	GFAAS	CCT
Asbestos	7400	ASBESTOS FIBERS by PCM	0.5 - 16	400 - var	NA	PCM	MCEF open
Asbestos	7402	ASBESTOS FIBERS by TEM	0.5 - 16	400 - var	NA	TEM	MCEF open
Asbestos	9000	ASBESTOS, CHRYSOTILE by XRD	NA	NA	NA	XRD	bulk
Asbestos	9002	ASBESTOS (bulk) by PLM	NA	NA	NA	PLM	bulk
Aspartame	5031	ASPARTAME	1 - 3	70 - 1200	eluent	HPLC - UV	PTFE
Asphalt fume	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 - 4	28 - 400	benzene	GRAVIMETRIC	Tared PTFE
Atrazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Atrazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GC-MSD	Urine
Atrazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Atrazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/ diazomethane	GC-ECD	PUF pad
Azelaic acid	5019	AZELAIC ACID	1 - 3	200 - 1000	Ethanol	GC - FID	PVC
Azinphos methyl	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1.0	12 - 240	tol/acet	GC - FPD	OVS 2
Bacteria	0801	AEROBIC BACTERIA by GC-FAME	28.3	50 - 300	hex/MTBE	GC-FID	impactor
B[a]P	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC - FL/UV	PTFE & XAD - 2
B[a]P	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC - FID	PTFE & XAD - 2
Barium	7056	BARIUM, SOLUBLE COMPOUNDS	1 - 4	50 - 2000	H_2O	FAAS	MCEF
Barium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Barium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Barium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	50 - 2000	HCl/HNO_3	ICP-AES	MCEF
Benomyl	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
Benzaldehyde	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC - MS	TD
Benz[a]anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC - FL/UV	PTFE & XAD - 2
Benz(a)anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC FID	PTFE & XAD 2
Benzene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC - MS	TD
Benzene	3700	BENZENE by portable GC	> 0.02	80% vol	NA	GC	air bag
Benzene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	5 - 30	CS_2	GC - FID	CCT
Benzene	1500	HYDROCARBONS, BP 36 - 216°C	0.01 - 0.2	2 - 30	CS_2	GC - FID	CCT
Benzene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. Dep.	NA	FTIR	Dir. Read
Benzene solubles	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 - 4	28	benzene	Grav	Tared PTFE
1,3-benzenediol	5701	RESORCINOL	0.2 - 1	5 - 160	methanol	GC-FID	OVS-7
Benzidine Dyes	5013	DYES	1 - 3	150 - 500	H_2O	HPLC - UV	PTFE
Benzidine	5509	BENZIDINE and 3,3'-DICHLORO-BENZIDINE	0.2	20 - 100	triethyl amine /MeOH	HPLC - UV	GFF
Benzo[a]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC - FL/UV	PTFE & XAD - 2
Benzo(a)pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC - FID	PTFE & XAD - 2

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Benzo[a]fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Benzo(b)fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD 2
Benzo[e]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Benzo(e)pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-ID	PTFE & XAD 2
Benzo[k]fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Benzo(k)fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-ID	PTFE & XAD 2
Benzo[ghi]perylene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC FL/UV	PTFE & XAD-2
Benzo(ghi)perylene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-ID	PTFE & XAD 2
Benzosulfonazole	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0 - 2.0	480 - 960	hexane	GC-SCD	PTFE + XD-2
Benzothiazole	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0 - 2.0	480 - 960	hexane	GC-SCD	PTFE + XD-2
Benzoyl peroxide	5009	BENZOYL PEROXIDE	1 - 3	40 - 400	diethyl ether	HPLC-UV	MCEF
Benzyl chloride	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	6 - 50	CS_2	GC-FID	CCT
Beryllium	7300	ELEMENTS by ICP	1 - 4	1250-2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Beryllium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Beryllium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Beryllium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	1250-2000	HCl/HNO_3	ICP-AES	MCEF
Beryllium & compounds	7102	BERYLLIUM and cpds, as Be	1 - 4	25 - 2000	HNO_3/H_2SO_4	GFAAS	MCEF
Bioaerosol	0800	BIOAEROSOL SAMPLING (Indoor Air)	28.3	varies	NA	varies	Impactor
Biphenyl	2530	DIPHENYL	0.01 - 0.5	15 - 30	CCl_4	GC-FID	Tenax GC
Bismuth	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Bitumen fume	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 - 4	28 - 400	benzene	Grav	Tared PTFE
Boron	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Boron carbide	7506	BORON CARBIDE	1.7 or 2.2	100 - 1000	ash	XRD	CYC & PVC
Boron oxide	0500	PARTICULATES N.O.R.	1.5 - 2.0	25 - 133	NA	Grav	PVC
Bromoform	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	4 - 70	CS_2	GC-FID	CCT
Bromine	6011	CHLORINE and BROMINE	0.3 - 1.0	8 - 360	$Na_2S_2O_3$	IC	Ag F
1-Bromopropane 2-Bromopropane	1025	1- and 2-BROMOPROPANE	0.01 - 0.2	0.1 - 12	CS_2	GC-FID	CCT
Bromoform	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	4 - 70	CS_2	GC-FID	CCT
Bromotrifluoromethane	1017	TRIFLUOROBROMOMETHANE	0.01 - 0.05	0.3 - 1.0	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
Bromoxynil	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	2 - 400	CH_3CN	HPLC-UV	PTFE
Bromoxynil octanoate	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	90 - 400	CH_3CN	HPLC-UV	PTFE
1,3-Butadiene	1024	1,3-BUTADIENE	0.01 - 0.5	5 - 25	CH_2Cl_2	GC-FID	CCT
2-Butanone	2500	METHYL ETHYL KETONE	0.01 - 0.2	1 - 12	CS_2	GC-FID	Carbon beads
2 Butanone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
2-Butanone	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. Dep.	NA	FTIR	Dir. Read

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Butoxyacetic acid	8316	BUTOXYACETIC ACID in urine	NA	NA	NA	GC-ECD	NA
2-Butoxyethyanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
2-Butoxyethanol	1403	ALCOHOLS IV	0.01 - 0.05	2 - 10	CH_2Cl_2/MeOH	GC-FID	CCT
n-, *sec*-, & *t*-Butyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Butyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
iso-Butyl acetate	1450	ESTERS I	0.01 - 2	1 - 10	CS_2	GC-FID	CCT
1-Butyl acetate	1450	ESTERS I	0.01 - 2	1 - 10	CS_2	GC-FID	CCT
Butyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
tert-Butyl alcohol	1400	ALCOHOLS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
n- & *sec*-Butyl alcohol	1401	ALCOHOLS II	0.01 - 0.2	2 - 10	CS_2	GC-FID	CCT
n-Butyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT
sec-Butyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT
n-Butylamine	2012	*n*-BUTYLAMINE	0.01 - 1.0	2 - 100	MeOH	GC-FID	SG + H_2SO_4
Butyl cellosolve	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Butyl cellosolve	1403	ALCOHOLS IV	0.01 - 0.05	1 - 10	CH_2Cl_2/MeOH	GC-FID	CCT
1,3-Butylene glygol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Butyl glycidyl ether	1616	BUTYL GLYCIDYL ETHER	0.01 - 0.2	15 - 30	CS_2	GC-FID	CCT
n-Butyl mercaptan	2525	*n*-BUTYL MERCAPTAN	0.01 - 0.05	1 - 4	acet	GC-FPD	Chrom 104
n-Butyl mercaptan	2542	MERCAPTANS	0.1 - 0.2	10 - 150	HCl/DCE	GC-FPD	GFF/HgAc
p-*tert*-Butyltoluene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 29	CS_2	GC-FID	CCT
Butyraldehyde	2539	ALDEHYDES, SCREENING	0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Cadmium	7300	ELEMENTS by ICP	1 - 4	13 - 2000	HNO_3/$HClO_4$	ICP-AES	MCEF
Cadmium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Cadmium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Cadmium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	13 - 2000	HCl/HNO_3	ICP-AES	MCEF
Cadmium & compounds	7048	CADMIUM and cpds, as Cd	1 - 3	25 - 1500	HNO_3/HCl	FAAS	MCEF
Calcium	7300	ELEMENTS by ICP	1 - 4	5 - 200	HNO_3/$HClO_4$	ICP-AES	MCEF
Calcium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Calcium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 200	HCl/HNO_3	ICP-AES	MCEF
Calcium & compounds	7020	CALCIUM and cpds as Ca	1 - 3	20 - 400	HNO_3/$HClO_4$	FAAS	MCEF
Camphor	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC-FID	CCT
Camphor	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
Capsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	5 - 1000	CH_3CN	HPLC-FL	GFF
Captan	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC- UV	OVS-2
Captan	9205	CAPTAN and THIOPHENATE-METHYL on DERMAL PATCH	NA	NA	IPA/ACN	HPLC-UV	Patch
Captan	9202	CAPTAN and THIOPHENATE-METHYL in Handrinse	NA	NA	NA	HPLC-UV	Hand wash
Carbaryl	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC- UV	OVS-2
Carbaryl (Sevin)	5006	CARBARYL	1 - 3	20 - 400	reagent	VIS	GFF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Carbendazim	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
Carbitol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Carbofuran	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC-UV	OVS-2
Carbon black	5000	CARBON BLACK	1 - 2	30 - 570	NA	Grav	PVC
Carbon, elemental	5040	ELEMENTAL CARBON (DIESEL PART.)	2 - 4	142-19000	thermal	EGA/TOA	QFF
Carbon dioxide	6603	CARBON DIOXIDE	0.02 - 0.1	80% vol	NA	GC TCD	air bag
Carbon disulfide	1600	CARBON DISULFIDE	0.01 -0.2	2 - 25	toluene	GC-FPD	CCT & dry tube
Carbon monoxide	6604	CARBON MONOXIDE	NA	NA	NA	Sensor	Port Instr
Carbon tetrachloride	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	3 - 150	CS_2	GC-FID	CCT
δ-3-Carene	1552	TERPENES	0.01 - 0.02	2 - 30	CS_2	GC-FID	CCT
Cellulose	7404	CELLULOSE INSULATION	1	NA	NA	SEM	ACF
Chlordane	5510	CHLORDANE	0.5 - 1.0	10 - 200	tol	GC-ECD	MCEF & Chrom 102
Chlorinated camphene	5039	CHLORINATED CAMPHENE	0.2 - 1	2 - 30	pet ether	GC-ECD	MCEF
Chlorinated diphenyl oxide	5025	CHLORINATED DIPHENYL OXIDE	0.5 - 1.5	8 - 200	isooctane	GC-ECN	MCEF
Chlorinated terphenyl	5014	CHLORINATED TERPHENYL	1 - 3	100 - 1500	isooctane	GC-ECD	GFF
Chlorine	6011	CHLORINE and BROMINE	0.3 - 1.0	2 - 90	$Na_2S_2O_3$	IC	Ag F
Chloroacetaldehyde	2015	CHLOROACETALDEHYDE	0.05 - 0.2	3 - 16	MeOH	GC-ECD	SG
Chloroacetic acid	2008	CHLOROACETIC ACID	0.05 - 0.2	1 - 100	H_2O	IC	SG
Chlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1.5 - 40	CS_2	GC-FID	CCT
p-Chlorobenzotrifluoride	1026	*p*-CHLOROBENZOTRIFLUORIDE	0.01 - 0.2	0.1 - 10	CS_2/MeOH	GC-FID	CCT
Chlorobromomethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.5 - 60	CS_2	GC-FID	CCT
Chlorobromomethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.5 - 8	CS_2	GC-FID	CCT
Chlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC-FID	2CCT (lg + sm)
Chlorodiphenyl (42 & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05 - 0.2	1 - 50	hexane	GC-ECD	GFF & Florisil
2-Chloroethanol	2513	ETHYLENE CHLOROHYDRIN	0.01 - 0.2	2 - 35	IPA/CS_2	GC-FID	PCT
Chloroform	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 50	CS_2	GC-FID	CCT
4-Chloronitrobenzene	2005	NITROAROMATIC COMPOUNDS	0.01 - 1.0	1 - 150	MeOH	GC-FID	SG
p-Chlorophenol	2014	*p-CHLOROPHENOL*	0.05 - 0.2	1.5 - 40	CH_3CN	HPLC-UV	SG
Chloroprene	1002	β-CHLOROPRENE	0.01 - 0.1	1.5 - 8	CS_2	GC-FID	CCT
Chlorpropham	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC, UV	OVS-2
Chlorpyrifos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1.0	12 - 240	tol/acet	GC-FPD	OVS-2
Chromic acid	7600	CHROMIUM, HEXAVALENT	1 - 4	8 - 400	reagent	VIS	PVC
Chromic acid	7604	CHROMIUM, HEXAVALENT	1 - 4	100 - 1000	NaOH/Na_2CO_3	IC	PVC
Chromium	7024	CHROMIUM and cpds, as Cr	1 - 3	10 - 1000	HCl/HNO_3	FAAS	MCEF
Chromium	7300	ELEMENTS by ICP	1 - 4	5 - 1000	HNO_3/$HClO_4$	ICP-AES	MCEF
Chromium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Chromium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Chromium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Chromium, hexavalent	7600	CHROMIUM, HEXAVALENT	1 - 4	8 - 400	reagent	VIS	PVC
Chromium, hexavalent	7604	CHROMIUM, HEXAVALENT	1 - 4	100 - 1000	NaOH/Na_2CO_3	IC	PVC

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Chromium, hexavalent	7605	CHROMIUM HEXAVALENT by ION CHROMATOGRAPHY	0.1 - 4	1 - 400	$NaOH-Na_2CO_3$	IC	PVC
Chromium, hexavalent	7703	CHROMIUM, HEXAVALENT by Field-Portable Spectrophotometry	1 - 4	10 - 1200	$(NH_4)_2SO_4/NH_4OH$	VIS	PVC, MCE, PTFE
Chromium, hexavalent	9101	CHROMIUM, HEXAVALENT in settled dust	NA	NA	NA	Spot	Test strip
Chrysene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD 2
Chrysene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Coal tar naphtha	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Coal tar pitch volatiles	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 - 4	28 - 400	benzene	Grav	tared PTFE
Cobalt	7300	ELEMENTS by ICP	1 - 4	25 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Cobalt	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Cobalt	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	25 - 2000	HCl/HNO_3	ICP-AES	MCEF
Cobalt	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Cobalt & compounds	7027	COBALT and cpds, as Co	1 - 3	30 - 1500	aq reg/HNO_3	FAAS	MCEF
Copper	7300	ELEMENTS by ICP	1 - 4	5 - 1000	$HNO_3/HClO_4$	ICP-AES	MCEF
Copper	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Copper	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Copper	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Copper (dust & fume)	7029	COPPER (dust & fumes)	1 - 3	50 - 1500	HNO_3/HCl	FAAS	MCEF
Cresol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Cresol, all isomers	2546	CRESOLS and PHENOL	0.01 - 0.1	1 - 24	MeOH	GC-FID	XAD-7
Crotonaldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Crotonaldehyde	3516	CROTONALDEHYDE	0.1 - 0.2	1 - 49	buffer	DPP	BuB
Cryofluorane	1018	DICHLORODIFLUOROMETHANE, 1,2 DICHLOROTETRAFLUORO-ETHANE, & CHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC-FID	2 CCT
Cumene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
Cyanides	7904	CYANIDES, aerosol and gas	0.5 - 1.0	10 - 180	KOH	ISE	MCEF & BuB
Cyanides	6010	HYDROGEN CYANIDE	0.05 - 0.2	0.6 - 90	H_2O	VIS	soda lime
Cyanuric acid	5030	CYANURIC ACID	1 - 3	10 - 1000	reagents	HPLC-UV	PVC
Cyanazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Cyanazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GS-MSD	Urine
Cyanazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Cyanazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Cyclohexane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	2.5 - 5	CS_2	GC-FID	CCT
Cyclohexanol	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	CG-FID	CCT
Cyclohexanol	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Cyclohexanone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Cyclohexanone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Cyclohexanone	1300	KETONES I	0.01 - 0.2	1 - 10	CS_2	CG-FID	CCT
Cyclohexene	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	5 - 7	CS_2	CG-FID	CCT
1,3-Cyclopentadiene	2523	1,3-CYCLOPENTADIENE	0.01 - 0.05	1 - 5	Et Ac	GC-FID	Chrom104/ maleic anhy
2,4-D	5001	2,4-D and 2,4,5-T	1 - 3	15 - 200	MeOH	HPLC-UV	GFF
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC-ECD	OVS-2
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
2,4-D acid; 2,4-D,2-ethylhexyl ester; 2,4-D,2-butoxyethyl ester	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Decabromodiphenyl Oxide	2559	DECABROMODIPHENYL OXIDE	2.0	48 - 960	Tol	GC/NCD	GFF
n-Decane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Decane	1500	HYDROCARBONS, BP 36°-216°C	NA	NA	CS_2	GC-FID	CCT
Demeton	5514	DEMETON	0.2 - 1.0	30 - 500	toluene	GC-FPD	MCEF &XAD-2
Desethylatrazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GC-MSD	Urine
Desisopropylatrazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GC-MSD	Urine
Diacetone alcohol	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	GC-FID	CCT
Diacetone alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	1 - 10	IPA-CS_2	GC-FID	CCT
Diacetyl	2557	DIACETYL	0.01 - 0.2	1 - 10	Acet-Meth	GC-FID	A-CMS
o-Dianisidine	5013	DYES	1 - 3	150 - 500	H_2O	HPLC-UV	PTFE
Diatomaceous earth	7501	SILICA, AMORPHOUS	1 - 3	50 - 400	ash	XRD	PVC/CYC
Diazinon	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	toluene/acetone	GC-FPD	OVS-2
Diazomethane	2515	DIAZOMETHANE	0.2	6 - 30	CS_2	GC-FID	XAD-2(coated)
Dibenz[a,h]anthracene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Dibenz(a,h) anthracene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD 2
Diborane	6006	DIBORANE	0.5 - 1.0	60 - 260	H_2O_2	PES	PTFE & CCT w/oxidizer
Dibromodifluoromethane	1012	DIFLUORODIBROMOMETHANE	0.01 - 0.2	2.5 - 10	IPA	GC-FID	2 CCT
2-Dibutylaminoethanol	2007	AMINOETHANOL COMPOUNDS	0.01 - 0.2	4 - 24	MeOH/H_2O	GC-FID	SG
Dibutyl phosphate	5017	DIBUTYL PHOSPHATE	1 - 3	50 - 250	CH_3CN	GC-FPD	PTFE
Dibutyl phthalate	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	1 - 3	6 - 200	CS_2	GC-FID	MCEF
Dibutyltin bis(isooctyl mercaptoacetate)	5504	ORGANOTIN COMPOUNDS	1 - 1.5	50 - 500	Acetic a/CH_3CN	HPLC/GFAAS	GFF + XAD-2
o-, *p*-Dichlorobenzene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	varies	TD/GC-MS	TD
o-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
p-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 8	CS_2	GC-FID	CCT
p-Dichlorobenzene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
3,3'-Dichlorobenzidine	5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE	0.2	20 - 100	TEA/MeOH	HPLC-UV	GFF
Dichlorodifluoromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
1,1-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.5 - 15	CS_2	GC FID	CCT
1,2-Dichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.5 - 50	CS_2	GC-FID	CCT
Dichloroethyl ether	1004	DICHLOROETHYL ETHER	0.01 - 1.0	2 - 15	CS_2	GC-FID	CCT
1,2-Dichloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.2 - 5	CS_2	GC-FID	CCT
Dichlorofluoromethane	2516	DICHLOROFLUOROMETHANE	0.01 - 0.05	0.25 - 3	CS_2	GC-FID	2 CCT (lg)
Dichloromethane	1005	METHYLENE CHLORIDE	0.01 - 0.2	0.5 - 2.5	CS_2	GC-FID	2 CCT
Dichloromethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC MS	TD
1,1-Dichloro-1-nitroethane	1601	1,1-DICHLORO-1-NITROETHANE	0.01 - 1.0	1.5 - 15	CS_2	GC-FID	PCT
1,2-Dichloropropane	1013	PROPYLENE DICHLORIDE	0.01 - 0.2	0.1 - 3.5	Acet/cyclohexane	GC-ECN	PCT
1,2-Dichlorotetra-fluoroethane	1018	DICHLORODIFLUOROMETHANE, 1,2 DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC FID	2 CCT (lg + sm)
Dicrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Diesel exhaust	5040	ELEMENTAL CARBON (DIESEL PART.)	1 - 4	142 -19000	thermal	EGA/TOA	QFF
Diethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5 - 1.0	5 - 300	HSA	IC	IMP
Diethylamine	2010	AMINES, ALIPHATIC	0.01 - 1.0	3 - 30	H_2SO_4/MeOH	GC-FID	SG
2-Diethylaminoethanol	2007	AMINOETHANOL COMPOUNDS I	0.01 - 0.2	4 - 24	MeOH/H_2O	GC-FID	SG
Diethylene glycol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Diethylene glycol ether	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Diethylenetriamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01 - 0.1	1 - 20	DMF	HPLC-UV	XAD-2 w/10% NITC
Di-(2-ethylhexyl) phthalate	5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE	1 - 3	10 - 200	CS_2	GC-FID	MCEF
Difluorodibromomethane	1012	DIFLUORODIBROMOMETHANE	0.01 - 0.2	2.5 - 10	IPA	GC-FID	2 CCT
Difluorodichloromethane	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE & CHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC-FID	2 CCT
Dihydrocapsaicin	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	7 - 1000	CH_3CN	HPLC-FL	GFF
Diisobutyl ketone	1300	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Diisobutyl ketone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Dimethylacetamide	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	0.01 - 1.0	15 - 80	MeOH	GC-FID	SG
Dimethylamine	2010	AMINES, ALIPHATIC	0.01 - 1.0	3 - 30	H_2SO_4/MeOH	GC-FID	SG
2-(Dimethylamino)ethanol 1-Dimethylamino-2-propanol	2561	2-(DIMETHYLAMINO)ETHANOL 1-DIMETHYLAMINO-2-PROPANOL	0.02 - 0.1	10 - 24	MeOH	GC-FID	XAD
N,N-Dimethylaniline	2002	AMINES, AROMATIC	0.02 - 1.0	3 - 30	Ethanol	GC-FID	SG
Dimethylarsinic acid	5022	ARSENIC, ORGANO-	1 - 3	50 - 1000	buffer	IC-HYAAS	PTFE

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Dimethylformamide	2004	DIMETHYLACETAMIDE & DIMETHYLFORMAMIDE	0.01 - 1.0	15 - 80	MeOH	GC-FID	SG
1,1-Dimethylhydrazine	3515	1,1-DIMETHYLHYDRAZINE	0.2 - 1.0	2 - 100	reagent	VIS	BuB (0.1 *M* HCl)
N,N-Dimethyl-*p*-toluidine	2002	AMINES, AROMATIC	0.02 - 1.0	20 - 100	Ethanol	GC FID	SG
Dimethyl sulfate	2524	DIMETHYL SULFATE	0.01 - 0.2	0.25 - 12	diEt ether	GC ECN	Por P
Dioxane	1602	DIOXANE	0.01 - 0.2	0.5 - 15	CS_2	GC-FID	CCT
Diphenyl	2530	DIPHENYL	0.01 - 0.5	15 - 30	CCl_4	GC-FID	Tenax GC
Dipropylene glycol monomethyl ether	2554	GLYCOL ETHERS	0.1 - 0.2	3 - 25	$MeCl_2$/Meth	GC-FID	A-747
Disulfoton	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS 2
Diuron	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC, UV	OVS-2
n-Dodecane	1500	HYDROCARBONS, BP 36°-216°C	NA	NA	CS_2	GC-FID	CCT
Dyes- benzidine-, o-tolidine-, o-dianisidine-	5013	DYES, BENZIDINE-, o-TOLIDINE-, o-DIANISIDINE	1 - 3	150 - 500	H_2O	HPLC UV	PTFE
Elemental carbon	5040	ELEMENTAL CARBON (DIESEL PART.)	2 - 4	142 -19000	thermal	EGA-TOA	QFF
Elements	7300	ELEMENTS by ICP	1 - 4	Varies	$HNO_3/HClO_4$	ICP AES	MCEF
Elements	7301	ELEMENTS by ICP (Aqua Region Ashing)	1 - 4	Varies	Aq Reg	ICP-AES	MCEF PVCF
Elements	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Endrin	5519	ENDRIN	0.5 - 1.0	12 - 400	tol	GC-ECD	MCEF & Chrom 102
Epichlorohydrin	1010	EPICHLOROHYDRIN	0.01 - 0.2	2 - 30	CS_2	GC-FID	CCT
EPN	5012	EPN	1 - 2	15 - 700	isooctane	GC-FPD	GFF
1,2-Epoxypropane	1612	PROPYLENE OXIDE	0.01 - 0.2	0.5 - 5	CS_2	GC-FID	CCT
β-Estradiol	5044	ESTROGENIC COMPOUNDS	1	150 - 1000	Meth	HPLC-UV	PTFE
Estrone	5044	ESTROGENIC COMPOUNDS	1	150 - 1000	Meth	HPLC-UV	PTFE
β-Estrodiol-3-Benzoate	5044	ESTROGENIC COMPOUNDS	1	150 - 1000	Meth	HPLC-UV	PTFE
Ethanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Ethanol	1400	ALCOHOLS I	0.01 - 0.05	0.1 - 1	2-butanol/CS_2	GC FID	CCT
Ethanolamine	2007	AMINOETHANOL COMPOUNDS I	0.01 - 0.2	4 - 24	5600	GC FID	SG
Ethion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC FPD	OVS-2
Ethoprop	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC FPD	OVS-2
2-Ethoxyethanol	1403	ALCOHOLS IV	0.01 - 0.05	1 - 6	MeOH	GC-FID	CCT
2-Ethoxyethyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Ethyl acetate	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Ethyl acetate	1457	ETHYL ACETATE	0.01 - 0.2	0.1 - 10	CS_2	GC-FID	CCT
Ethyl acrylate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Ethyl amyl ketone	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC-FID	CCT
Ethylbenzene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 24	CS_2	GC-FID	CCT
Ethyl bromide	1011	ETHYL BROMIDE	0.01 - 0.2	0.5 - 4	IPA	GC-FID	CCT
Ethyl butyl ketone	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC-FID	CCT
Ethyl chloride	2519	ETHYL CHLORIDE	0.02 - 0.05	0.3 - 3	CS_2	GC-FID	2 CCT (lg)
Ethylene chlorohydrin	2513	ETHYLENE CHLOROHYDRIN	0.01 - 0.2	2 - 35	IPA/CS_2	GC FID	PCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Ethylenediamine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01 - 0.1	1 - 20	DMF	HPLC - UV	XAD 2 w/10% NITC
Ethylene dibromide	1008	ETHYLENE DIBROMIDE	0.02 - 0.2	0.1 - 25	bz/MeOH	GC - ECD	CCT
Ethylene dichloride	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 50	CS_2	GC - FID	CCT
Ethylene glycol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC FID	OVS 7
Ethylene glycol dinitrate	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2 - 1.0	3 - 100	Ethanol	GC ECD	Tenax GC
Ethylene oxide	1614	ETHYLENE OXIDE	0.05 - 0.15	1 - 24	DMF	GC - ECD	PCT w/HBr
Ethylene oxide	3702	ETHYLENE OXIDE by portable GC	> 0.02	80% vol	NA	GC PID	air bag
Ethylene oxide	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. dep.	NA	FTIR	Dir. Read
Ethylene thiourea	5011	ETHYLENE THIOUREA	1 - 3	200 - 800	H_2O	VIS	PVC or MCEF
Ethylenimine	3514	ETHYLENIMINE	0.2	1 - 48	$CHCl_3$	HPLC - UV	BuB
Ethyl ether	1610	ETHYL ETHER	0.01 - 0.2	0.25 - 3	CS_2	GC-FID	CCT
Ethyl ether	1610	ETHYL ETHER	0.01 - 0.2	0.25 - 3	Et Ac	GC - FID	CCT
Ethyl formate	1452	ETHYL FORMATE	0.01 - 0.2	0.3 - 10	CS_2	GC - FID	CCT
Ethyl mercaptan	2542	MERCAPTANS	0.1 - 0.2	10 - 150	HCl/DCE	GC - FPD	GFF/HgAc
Ethyl methacrytate	2537	METHYL and ETHYL METHACRYLATE	0.01 - 0.05	1 - 8	CS_2	GC-FID	XAD
Fenamiphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC - FPD	OVS - 2
Fibrous glass	7400	ASBESTOS & other FIBERS by PCM	0.5 - 16	400 - varies		PCM	MCEF
Fluoranthene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC FL/UV	PTFE & XAD 2
Fluoranthene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC - FID	PTFE & XAD 2
Fluorene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC - FL/UV	PTFE & XAD 2
Fluorene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC - FID	PTFE & XAD 2
Fluorides	7902	FLUORIDES, aerosol & gas	1 - 2	12 - 800	NaOH	ISE	MCEF & pad w/ Na_2CO_3
Fluorides	7906	FLUORIDES by IC	1 - 2	s 1 - 800 i 120 - 800	NaOH	IC	MCEF & pad w/ Na_2CO_3
Fluorotrichloromethane	1006	FLUOROTRICHLOROMETHANE	0.01 - 0.05	0.3 - 7	CS_2	GC - FID	CCT (lg)
Fonofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1.0	12 - 240	tol/acet	GC - FPD	OVS - 2
Formaldehyde	2016	FORMALDEHYDE	0.1 - 1.5	1 - 15	acetonitrile	HPLC-UV	SG/DNPH
Formaldehyde	2541	FORMALDEHYDE	0.01 - 0.1	1 - 36	tol	GC - FID	XAD - 2/HMP
Formaldehyde	3500	FORMALDEHYDE	0.2 - 1.0	1 - 100	$NaHSO_3$	VIS	PTFE & 2 IMP
Formaldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC - FID/MS	XAD - 2/HMP
Formaldehyde	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. dep.	NA	FTIR	Dir. Read
Formaldehyde	5700	FORMALDEHYDE on dust	2	240 - 1050	H_2O/DNPH/CH_3CN	HPLC UV	IOM/PVC
Formetanate.HCl	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var-480	reagent	HPLC, UV	OVS-2
Formic acid	2011	FORMIC ACID	0.05 - 0.2	1 - 24	H_2O	IC	PTFE & SG (washed)
Furfural	2529	FURFURAL	0.01 - 0.05	1 - 12	tol	GC - FID	XAD - 2/HMP
Furfural	2539	ALDEHYDES, SCREENING	0.05	5 - 5	tol	GC FID/MS	XAD - 2/HMP

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Furfuryl alcohol	2505	FURFURYL ALCOHOL	0.01 - 0.05	3 - 25	acet	GC-FID	Por Q
Gallium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Glutaraldehyde	2532	GLUTARALDEHYDE	0.01 - 0.08	4 - 39	CH_3CN	HPLC-UV	SG/DNPH
Glycerin mist	0500	PARTICULATES N.O.R.	1 - 2	7 - 133	NA	Grav	PVC
Glycidol	1608	GLYCIDOL	0.01 - 1.0	5 - 100	THF	GC-FID	CCT
Glycols	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Gold	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Heptanal	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
n-Heptane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Heptane	1500	HYDROCARBONS BP 36-216°C	0.01 - 0.2	NA	CS_2	GC-FID	CCT
2-Heptanone	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
3-Heptanone	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
Herbicides	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Herbicides	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Herbicides	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Hexachlorobutadiene	2543	HEXACHLOROBUTADIENE	0.05 - 0.2	1 - 100	hexane	GC-ECD	XAD-2
Hexachloro-1,3-cyclo pentadiene	2518	HEXACHLORO-1,3-CYCLOPENTA DIENE	0.01 - 0.2	0.25 - 90	hexane	GC-ECD	2 Por T
Hexachloroethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	3 - 70	CS_2	GC-FID	CCT
Hexamethylene-diisocyanate	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine/DMSO	HPLC-FL	IMP
1,6-Hexamethylene-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	reagents	HPLC-ECHD	IMP
1,6-Hexamethylene diisocyanate (HDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC/UV	GFF, IMP
Hexanal	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Hexanal	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Hexane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Hexane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	4 - 4	CS_2	GC FID	CCT
n-Hexane	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 2.0	Instr. dep.	NA	FTIR	Dir. Read
2-Hexanone	1300	KETONES I	0.01 - 1.0	1 - 10	CS_2	GC-FID	CCT
2-Hexanone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Hippuric acid	8301	HIPPURIC and METHYL HIPPURIC ACID in urine	NA	NA	Etac	HPLC-UV	NA
Hydrazine	3503	HYDRAZINE	0.2 - 1.0	7 - 100	reagents	VIS	BuB
Hydrogen bromide	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG
Hydrogen chloride	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG
Hydrogen cyanide	6010	HYDROGEN CYANIDE	0.05 - 0.2	2 - 90	H_2O	VIS	soda lime
Hydrogen cyanide	6017	HYDROGEN CYANIDE	0.05 - 2	2 - 90	H_2O	IC-DC Amp	SL

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Hydrogen cyanide	7904	CYANIDES, AEROSOL & GAS	0.5 - 1.0	7 - 100	KOH	ISE	MCEF
Hydrogen flouride	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG
Hydrogen flouride	7902	FLUORIDES, AEROSOL & GAS	1 - 2	12 - 800	NaOH	ISE	MCEF & pad w/Na_2CO_3
Hydrogen flouride	7906	FLUORIDES by IC	1 - 2	1 - 800	NaOH	IC	MCEF & pad w/Na_2CO_3
Hydrogen sulfide	6013	HYDROGEN SULFIDE (withdrawn)	0.1 - 1.5	1.2 - 40	NH_4OH/H_2O_2	IC	PTFE & CCT (lg)
Hydroquinone	5004	HYDROQUINONE	1 - 4	30 - 180	acetic acid	HPLC-UV	MCEF
Indeno[1,2,3-cd]pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Indeno [1,2,3-cd] pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Iodine	6005	IODINE	0.5 - 1.0	15 - 225	Na_2CO_3	IC	CCT w/alkali
Indium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Iron	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Iron	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 100	HCl/HNO_3	ICP-AES	MCEF
Iron	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Iron	7300	ELEMENTS by ICP	1 - 4	5 - 100	$HNO_3/HClO_4$	ICP-AES	MCEF
Isoamyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Isoamyl alcohol	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	GC-FID	CCT
Isoamyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	1 - 10	IPA-CS_2	GC-FID	CCT
Isobutyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Isobutyl alcohol	1401	ALCOHOLS II	0.01 - 0.2	2 - 10	IPA/CS_2	GC-FID	CCT
Isobutyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT
Isobutyraldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Isocyanates	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	reagents	HPLC-ECHD	IMP
Isocyanates	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
Isophorone	2508	ISOPHORONE	0.01 - 1.0	2 - 25	CS_2	GC-FID	PCT
Isophorone	2556	ISOPHORONE	0.01 - 1	2 - 25	DEE	GC-FID	XAD
Isophorone diisocyanate (IPDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC/UV	GFF, IMP
Isopropyl acetate	1454	ISOPROPYL ACETATE	0.02 - 0.2	0.1 - 9	CS_2	GC-FID	CCT
Isopropyl acetate	1460	ISOPROPYL ACETATE	0.02 - 0.2	0.1 - 9	CS_2-Meth	GC-FID	CCT
Isopropyl alcohol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Isopropyl alcohol	1400	ALCOHOLS I	0.01 - 0.2	0.2 - 3	2-butanone/CS_2	GC-FID	CCT
Isopropyl ether	1618	ISOPROPYL ETHER	0.01 - 0.05	0.1 - 3	CS_2	GC-FID	CCT
Isopropyl glycidyl ether	1620	ISOPROPYL GLYCIDYL ETHER	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
Isovaleraldehyde	2018	ALIPHATIC ALDEHYDES	0.1 - 1.5	1 - 15	ACN	HPLC/UV	SG-DNPH
Isovaleraldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Kepone	5508	KEPONE	0.5 - 1.0	50 - 600	bz/MeOH	GC-ECD	MCEF & IMP
Kerosene	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Lanthanum	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Lanthanum	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Lead	7082	LEAD by FAAS	1 - 4	200 - 1500	HNO_3/H_2O_2	FAAS	MCEF
Lead	7702	LEAD BY FIELD PORTABLE XRF	1 - 4	570 - 1900	NA	XRF (port)	MCEF
Lead	7105	LEAD by GFAAS	1 - 4	1 - 1500	HNO_3/H_2O_2	GFAAS	MCEF
Lead	7701	LEAD BY ULTRASOUND/ASV	1 - 4	20 - 1500	HNO_3	Port ASV	MCEF
Lead	7300	ELEMENTS by ICP	1 - 4	1250 -2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Lead	7700	LEAD in Air by Chemical Spot Test	2	10 - 240	-	Spot	MCEF
Lead	9100	LEAD in Surface Wipe Samples	NA	NA	$HNO_3/HClO_4$	AAS; ICP	Wipes
Lead	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	50 - 2000	HCl/HNO_3	ICP-AES	MCEF
Lead	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Lead	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Lead	9105	LEAD in DUST WIPES by Chemical Spot Test	NA	NA	NA	Spot	Wipe
Lead sulfide	7505	LEAD SULFIDE	1.7 or 2.2	600 - 1000	THF	XRD	CYC & PVC
Limonene	1552	TERPENES	0.01 - 0.2	2 - 30	CS_2	GC-FID	CCT
Limonene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Lindane	5502	ALDRIN and LINDANE	0.2 - 1.0	18 - 240	isooctane	GC-ECN	GFF & BuB
Lithium	7300	ELEMENTS by ICP	1 - 4	100 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Lithium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	100 - 2000	HCl/HNO_3	ICP-AES	MCEF
Lithium hydroxide	7401	ALKALINE DUSTS	1 - 4	70 - 1000	HCl	Titration	PTFE
Magnesium	7300	ELEMENTS by ICP	1 - 4	5 - 67	$HNO_3/HClO_4$	ICP-AES	MCEF
Magnesium	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 67	HCl/HNO_3	ICP-AES	MCEF
Magnesium	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Malathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 60	toVacet	GC-FPD	OVS-2
Maleic Anhydride	3512	MALEIC ANHYDRIDE	0.2 - 1.5	40 - 500	H_2O	HPLC-UV	BuB
Maneb	3601	MANEB	NA	NA	NA	HPLC-UV	Hand wash
Maneb	3600	MANEB	NA	NA	Cys/EDTA	HPLC-UV	Patch
Manganese	7300	ELEMENTS by ICP	1 - 4	5 - 200	$HNO_3/HClO_4$	ICP-AES	MCEF
Manganese	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Manganese	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	5 - 200	HCl/HNO_3	ICP-AES	MCEF
Manganese	7303	ELEMENTS by ICP (HOT BLOCK/HCl/HNO_3 DIGESTION)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
MBK	1300	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
MDI (4,4'-methylene-bisphenyl isocyanate)	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	reagents	HPLC-ECHD	IMP
MDI (4,4'-methylene-bisphenyl isocyanate)	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine	HPLC-FL/ECHD	IMP
Mercury	6009	MERCURY	0.15 - 0.25	2 - 100	HNO_3/HCl	AAS-cold vap	Hopcalite

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Mercaptans	2542	MERCAPTANS	0.1 - 0.2	10 - 150	HCl/DCE	GC-FPD	GFF/HgAc
Mesityl oxide	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC FID	CCT
Mesityl oxide	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
Metals in air	7300	ELEMENTS by ICP	1 - 4	var - 2000	HNO_3/$HClO_4$	ICP AES	MCEF
Metalworking Fluids	5524	METALWORKING FLUIDS (MWF) ALL CATEGORIES	1.6 - 2.0	1000 - ND	DCM/MeOH/Tol MeOH	Grav	PTFE/CYC
Methanal	2016	FORMALDEHYDE	0.1 - 1.5	1 - 15	acetonitrile	HPLC-UV	SG/DNPH
Methamidophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Methanol	2000	METHANOL	0.02 - 0.2	1 - 5	H_2O/IPA	GC-FID	SG
Methanol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Methanol	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
Methiocarb	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
Methomyl	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
Metolachlor	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Metolachlor	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Metolachlor	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
2 Methoxyethyl acetate	1451	METHYL CELLOSOLVE ACETATE	0.01 - 0.2	0.2 - 20	CS_2	GC-FID	CCT
2-Methoxyethanol	1403	ALCOHOLS IV	0.01 - 0.05	6 - 50	MeOH/CH_2Cl_2	GC FID	CCT
Methyl acetate	1458	METHYL ACETATE	0.01 - 0.2	0.2 - 10	CS_2	GC FID	CCT
Methyl acrylate	1459	METHYL ACRYLATE	0.01 - 0.2	1 - 5	CS_2	GC FID	CCT
Methyl acrylate	2552	METHYL ACRYLATE	0.01 - 0.2	1 - 5	CS_2	GC-FID	A-CMS
Methyl alcohol	2000	METHANOL	0.02 - 0.2	1 - 5	H_2O/IPA	GC-FID	SG
Methylal	1611	METHYLAL	0.01 - 0.2	1 - 3	hexane	GC FID	CCT
4-Methylbenzenesulfonic acid	5043	*p*-TOLUENESULFONIC ACID	1 - 3	10 - 1000	IPA/H_2O	HPLC-UV	GFF
N-Methyl-y-butyrolactone	1302	*N*-METHYL-2-PYRROLIDINONE	0.05 - 0.2	0.5 - 125	CH_2Cl_2/MeOH	GC-NPD or FID	CCT
Methyl (n amyl) ketone	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC FID	CCT
Methylarsonic acid	5022	ARSENIC, ORGANO	1 - 3	50 - 1000	buffer	IC-HYAAS	PTFE
Methyl bromide	2520	METHYL BROMIDE	0.01 - 0.1	1 - 5	CS_2	GC-AED	PCT(2)+drytube
Methyl cellosolve	1403	ALCOHOLS IV	0.01 - 0.05	6 - 50	MeOH/CH_2Cl_2	GC-FID	CCT
Methyl cellosolve acetate	1451	METHYL CELLOSOLVE ACETATE	0.01 - 0.2	0.2 - 20	CS_2	GC-FID	CCT
Methyl chloride	1001	METHYL CHLORIDE	0.01 - 0.1	0.4 - 3	CH_2Cl_2	GC FID	2 CCT (lg+sm)
Methyl chloroform	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.1 - 8	CS_2	GC FID	CCT
Methyl chloroform	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Methyl cyanide	1606	ACETONITRILE	0.01 - 0.2	3 - 25	MECI/MEOH	GC-FID	CCT
Methyl cyclohexane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	4 - 4	CS_2	GC-FID	CCT
Methylcyclohexanol	1404	METHYLCYCLOHEXANOL	0.01 - 0.2	1 - 15	CH_2Cl_2	GC-FID	CCT
Methylcyclohexanone	2521	METHYLCYCLOHEXANONE	0.01 - 0.05	1 - 6	acet	GC FID	Por Q
4,4'-Methylene-bis (cyclo hexyl isocyanate) (HMDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC/UV	GFF, IMP

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
4,4-Methylene-bis (phenyl isocyanate) (MDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC/UV	GFF, IMP
Methylene chloride	1005	METHYLENE CHLORIDE	0.01 - 0.2	0.5 - 2.5	CS_2	GC-FID	2 CCT
Methylene chloride	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Methylene chloride	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
4,4'-Methylenedianiline	5029	4,4'-METHYLENEDIANILINE	1 - 2	10 - 1000	KOH/MeOH	HPLC-UV	GFF/H_2SO_4
4,4-Methylene diphenyl diisocyanate	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine	HPLC-FL/ECHD	IMP
Methyl ethyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Methyl ethyl ketone	2500	METHYL ETHYL KETONE	0.01 - 0.2	0.25 - 12	CS_2	GC-FID	Carbon beads
Methyl ethyl ketone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Methyl ethyl ketone peroxide	3508	METHYL ETHYL KETONE PEROXIDE	0.5 - 0.2	52 - 520	reagent	VIS	IMP
5-Methyl-3-heptanone	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC-FID	CCT
5-Methyl-3-heptanone	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
Methyl hippuric acid	8301	HIPPURIC and METHYL HIPPURIC ACID in urine	NA	NA	Etac	HPLC-UV	NA
Methyl iodide	1014	METHYL IODIDE	0.01 - 1.0	15 - 50	tol	GC-FID	CCT
Methyl isoamyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Methyl isobutyl carbinol	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	GC-FID	CCT
Methyl isobutyl carbinol	1405	ALCOHOLS COMBINED	0.01 - 0.2	1 - 10	IPA-CS_2	GC-FID	CCT
Methyl isobutyl ketone	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Methyl isobutyl ketone	1300	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Methyl isobutyl ketone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Methyl mercaptan	2542	MERCAPTANS	0.1 - 0.2	10 - 150	HCl/DCE	GC-FPD	GFF/HgAc
Methyl methacrylate	2537	METHYL and ETHYL METHACRYLATE	0.01 - 0.05	1 - 8	CS_2	GC-FID	XAD
Methyl parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Methyl phenol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
N-methyl-2-pyrrolidinone	1302	*N*-METHYL-2-PYRROLIDINONE	0.05 - 0.2	0.5 - 125	CH_2Cl_2/MeOH	GC-NPD or FID	CCT
α-Methyl styrene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
β-Methylstyrene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
Methyl *tert*-butyl ether	1615	METHYL *tert*-BUTYL ETHER	0.1 - 0.2	2 - 96	CS_2	GC-FID	2 CCT (lg)
Methyltin chloride	5526	METHYLTIN CHLORIDES	0.25 - 1	15 - 75	AAA	GC-FPD	OVS
Mevinphos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1.0	12 - 240	tol/acet	GC-FPD	OVS-2
Mineral spirits	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Molybdenum	7300	ELEMENTS by ICP	1 - 4	5 - 67	HNO_3/$HClO_4$	ICP-AES	MCEF
Molybdenum	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 67	HCl/HNO_3	ICP-AES	MCEF
Molybdenum	7303	ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Molybdenum	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Monocrotophos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Monomethylaniline	3511	MONOMETHYLANILINE	0.2 - 1.0	11 - 100	NaOH	GC-FID	BuB/H_2SO_4
Monomethylhydrazine	3510	MONOMETHYLHYDRAZINE	0.5 - 1.5	3 - 20	PMA/HCl	VIS	BuB/HCl
Mycobacterium	0900	MYCOBACTERIUM TUBERCULOSIS	>4	varies	PCR	reagent	PTFE
Naphtha (coal tar)	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Naphthalene	1501	HYDROCARBONS, AROMATIC	0.01 - 1.0	100 - 200	CS_2	GC-FID	CCT
Naphthalene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Naphthalene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
1,5-Naphthalene diisocyanate (NDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC-UV	GFF, IMP
Naphthylamines	5518	NAPHTHYLAMINES	0.2 - 0.8	30 - 100	acetic a /IPA	GC-FID	GFF & SG
Neodymium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Nickel	7300	ELEMENTS by ICP	1 - 4	25 - 1000	HNO_3/$HClO_4$	ICP-AES	MCEF
Nickel	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Nickel	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Nickel	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Nickel carbonyl	6007	NICKEL CARBONYL	0.05 - 0.2	7 - 80	HNO_3	GFAAS	CCT (low Ni)
Nicotine	2544	NICOTINE	1.0	60 - 400	EtAc	GC-NPD	XAD-2
Nicotine	2551	NICOTINE	0.1 - 1.0	0.5 - 600	ethyl acetate	GC-NPD	XAD-4
Nitric acid	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG (washed)
Nitric oxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025	1.5 - 6	reagent	VIS	MS w/TEA & oxidizer
p-Nitroaniline	5033	*p*-NITROANILINE	1 - 3	20	IPA	HPLC-UV	MCEF
Nitrobenzene	2005	NITROAROMATIC COMPOUNDS	0.01 - 1	10 - 150	MeOH	GC-FID	SG
Nitrobenzene	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF + SG
Nitrobenzol	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF + SG
p-Nitrochlorobenzene	2005	NITROAROMATIC COMPOUNDS	0.01 - 1	1 - 150	MeOH	GC-FID	SG
Nitroethane	2526	NITROETHANE	0.01 - 0.05	1.5 - 3	EtAc	GC-FID	2XAD-2
Nitrogen dioxide	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025 - 0.2	1.5 - 6	reagent	VIS	MS w/TEA
Nitrogen dioxide	6700	NITROGEN DIOXIDE	NA	NA	reagent	VIS	Diffusive
Nitrogen peroxide	6700	NITROGEN DIOXIDE	NA	NA	reagent	VIS	Diffusive
Nitroglycerin	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2 - 1.0	3 - 100	ethanol	GC-ECD	Tenax-GC
Nitromethane	2527	NITROMETHANE	0.01 - 0.05	1.2 - 3	EtAc	GC-FPD	Chrom 106
2-Nitropropane	2528	2-NITROPROPANE	0.01 - 0.05	0.1 - 2	EtAc	GC-FID	Chrom 106
1-Nitropyrene	2560	1-NITROPYRENE in DIESEL PARTICULATES	1.0 - 2.0	480 - 960	Tol	GC/NCD	GFF
Nitrosamines	2522	NITROSAMINES	0.2 - 2.0	15 - 1000	MeOH/CH_2Cl_2	GC-TEA	TD tube
o-,*m*-, *p*-Nitrotoluene	2005	NITROAROMATIC COMPOUNDS	0.01 - 0.2	1 - 30	MeOH	GC-FID	SG
Nitrous oxide	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Nitrous oxide	6600	NITROUS OXIDE	NA	80% vol	NA	IR	air bag
n-Nonane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	4 - 4	CS_2	GC-FID	CCT
NMP	1302	N-Methyl-2-Pyrrolidinone	0.05 - 0.2	0.5 - 125	CH_2Cl_2/MeOH	GC-FID/NPD	CCT
Nuisance dusts	0500	PARTICULATES N.O.R.	1 - 2	7 - 133	NA	GRAV	PVC
n-Octane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Octane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	4 - 4	CS_2	GC-FID	CCT
Octamethylcyclotetra-siloxane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
1-Octanethiol	2510	1-OCTANETHIOL	0.01 - 0.2	1 - 15	acet	GC-FPD	Tenax GC
Oil mist (mineral)	5026	OIL MIST, MINERAL	1 - 3	20 - 500	CCl_4	IR	PVC or MCE
Organonitrogen pesticides	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	varies-480	reagent	HPLC-UV	OVS-2
Organophosphorus Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Oxamyl	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC, UV	OVS-2
Oxygen	6601	OXYGEN	NA	1 - NA	NA	Sensor	portable
PAC	5800	POLY AROMATIC COMPOUNDS, TOTAL (PACs)	1 - 2	5 - 1000	hexane	FI-FL	PTFE + XAD-2
Palladium	7303	ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Paraquat	5003	PARAQUAT	1 - 4	40 - 1000	H_2O	HPLC-UV	PTFE
Parathion	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1.0	12 - 240	tol/acet	GC-FPD	OVS-2
Particulates N.O.R.	0500	PARTICULATES N.O.R., TOTAL	1 - 2	7 - 133	NA	GRAV	PVC
Particulates N.O.R.	0600	PARTICULATES, N.O.R, RESPIRABLE	1.7, 2.2, 2.5	20 - 400	NA	Grav.	CYC & PVC
Pentachlorobenzene	5517	POLYCHLOROBENZENES	0.01 - 0.2	3 - 12	hexane	GC-ECD	PTFE & XAD-2
Pentachloroethane	2517	PENTACHLOROETHANE	0.01 - 0.2	1 - 10	hexane	GC-ECD	Por R
Pentachlorophenol	5512	PENTACHLOROPHENOL	0.5 - 1.0	48 - 480	MeOH	HPLC-UV	MCEF & BuB
Pentamidine	5032	PENTAMIDINE ISETHIONATE	1 - 2	50 - 1500	reagents	HPLC/FL	PVC/opaque
n-Pentane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Pentane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	4 - 4	CS_2	GC-FID	CCT
2-Pentanone	1300	KETONES I	0.01 - 2.0	1 - 10	CS_2	GC-FID	CCT
2-Pentanone	2555	KETONES I	0.01 - 0.2	1 - 10	CS_2	GC-FID	A-CMS
Perchloroethylene	3704	PERCHLOROETHYLENE (port GC) in exhaled breath and air	0.02 - 5	<80% cap	NA	GC (port)-PID	air bag
Perchloroethylene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Pesticides	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Pesticides	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
Petroleum ether/naphtha	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Phenanthrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Phenanthrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Phenol	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Phenol	2546	CRESOLS and PHENOL	0.01 - 0.1	1 - 24	MeOH	GC FID	XAD-7
Phenyl ether	1617	PHENYL ETHER	0.01 - 0.2	1 - 50	CS_2	GC-FID	CCT
Phenyl ether-diphenyl mixture	2013	PHENYL ETHER DIPHENYL MIXTURE	0.01 - 0.2	1 - 40	bz	GC-FID	SG
Phenyl glycidyl ether	1619	PHENYL GLYCIDYL ETHER	0.01 - 1	80 - 150	CS_2	GC-FID	CCT
Phenylhydrazine	3518	PHENYLHYDRAZINE	0.2 - 1.0	25 - 120	PMA	VIS	BuB/HCl
Phorate	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Phosdrin (mevinphos)	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 480	tol/acet	GC-FPD	OVS-2
Phosphine	6002	PHOSPHINE	0.01 - 0.2	1 - 16	reagent	VIS	SG/$Hg(CN)_2$
Phosphoric acid	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG (washed)
Phosphorus	7300	ELEMENTS by ICP	1 - 4	50 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Phosphorus	7905	PHOSPHORUS	0.01 - 0.2	5 - 100	xylene	GC-FPD	Tenax GC
Phosphorus	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	25 - 2000	HCl/HNO_3	ICP-AES	MCEF
Phosphorus	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Phosphorus	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Phosphorus trichloride	6402	PHOSPHORUS TRICHLORIDE	0.05 - 0.2	11 - 100	reagents	VIS	BuB/H_2O
Pinene	1552	TERPENES	0.01 - 0.2	2 - 30	CS_2	GC-FID	CCT
Pinene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Platinum	7300	ELEMENTS by ICP	1 - 4	13 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
PAH	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	HPLC-FL/UV	PTFE & XAD-2
Polyacrylate	5035	SUPER ABSORBENT POLYMER	1 - 2	50 - 1500	$Cu(Ac)_2$	ICP or AAS	PVC
PACs	5800	POLYCYCLIC AROMATIC COMPOUNDS, TOTAL	1 - 2	5 - 1000	hexane	FI-FL	
Platinum	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Polychlorobiphenyl (42% & 54% Cl)	5503	POLYCHLOROBIPHENYLS	0.05 - 0.2	1 - 50	hexane	GC-ECD	GFF & Florisil
Potassium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Potassium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Potassium hydroxide	7401	ALKALINE DUSTS	1 - 4	70 - 1000	HCl	titration	PTFE
Progesterone	5044	ESTROGENIC COMPOUNDS	1	150 - 1000	Meth	HPLC-UV	PTFE
Propazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GC-MSD	Urine
Propham	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC, UV	OVS-2
Propionaldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2/HMP
Propionaldehyde	2018	ALIPHATIC ALDEHYDES	0.1 - 1.5	1 - 15	ACN	HPLC-UV	SG-DNPH
Propoxur	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC, UV	OVS-2
n-Propyl acetate	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
n-Propyl alcohol	1401	ALCOHOLS II	0.01 - 0.2	1 - 10	IPA/CS_2	GC-FID	CCT
n-Propyl alcohol	1405	ALCOHOLS COMBINED	0.01 - 0.2	1 - 10	IPA-CS_2	GC-FID	CCT
Propylene dichloride	1013	PROPYLENE DICHLORIDE	0.01 - 0.2	0.1 - 3.5	acet/cychex	GC-ECN	PCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Propylene glycol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Propylene glycol monomethyl ether	2554	GLYCOL ETHERS	0.1 - 0.2	3 - 25	$MeCl_2$/Meth	GC-FID	A-747
Propylene glycol monomethyl ether acetate	2554	GLYCOL ETHERS	0.1 - 0.2	3 - 25	$MeCl_2$/Meth	GC-FID	A-747
Propylene oxide	1612	PROPYLENE OXIDE	0.01 - 0.2	0.5 - 5	CS_2	GC FID	CCT
Pyrene	5506	POLYNUCLEAR AROMATIC HYDROCARBONS by HPLC	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
Pyrene	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
Pyrethrum	5008	PYRETHUM	1 - 4	20 - 400	CH_3CN	HPLC-UV	GFF
Pyridine	1613	PYRIDINE	0.01 - 1.0	18 - 150	CH_2Cl_2	GC-FID	CCT
Resorcinol	5701	RESORCINOL	0.2 - 1	5 - 160	MeOH	GC-FID	OVS-7
Ribavirin	5027	RIBAVIRIN	1 - 4	5 - 1000	H_2SO_4	HPLC-UV	GFF
Ronnel	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 60	tol/acet	GC-FPD	OVS-2
Rotenone	5007	ROTENONE	1 - 4	8 - 400	CH_3CN	HPLC-UV	PTFE
Rubber solvent	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Selenium	7300	ELEMENTS by ICP	1 - 4	5 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Selenium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	13 - 2000	HCl/HNO_3	ICP-AES	MCEF
Selenium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Selenium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Silica, amorphous	7501	SILICA, AMORPHOUS	1.7 or 2.2	50 - 400	ash	XRD	PVC (total) PVC&CYC
Silica, crystalline	7500	SILICA, CRYSTALLINE, by XRD	1.7, 2.2, 2.5	400 - 1000	ash or THF	XRD	CYC & PVC
Silica, crystalline	7601	SILICA, CRYSTALLINE	1.7, 2.2, 2.5	400 - 800	H_3PO_4/HF	VIS	CYC & MCE or PVC
Silica, crystalline	7602	SILICA, CRYSTALLINE (IR)	1.7, 2.2, 2.5	400 - 800	ash	IR	CYC & MCE or PVC
Silicon dioxide	7500	SILICA, CRYSTALLINE, by XRD.	1.7, 2.2, 2.5	400 - 1000	ash or THF	XRD	CYC & PVC
Silica in coal mine dust	7603	QUARTZ in coal mine dust	1.7, 2.2, 2.5	300 - 1000	ash	IR	CYC & PVC
Silver	7300	ELEMENTS by ICP	1 - 4	250 - 2000	HNO_3+	ICP-AES	MCEF
Silver	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	250 - 2000	HCl/HNO_3	ICP-AES	MCEF
Silver	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Simazine	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
Simazine	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
Simazine	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
Sodium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Sodium hexafluoro-aluminate	7902	FLUORIDES, aerosol & gas	1 - 2	12 - 800	NaOH	ISE	MCEF& pad w/Na_2CO_3

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Sodium hexafluoro-aluminate	7906	FLUORIDES by IC	1 - 2	120 - 800	NaOH	IC	MCEF& pad w/Na_2CO_3
Sodium hydroxide	7401	ALKALINE DUSTS	1 - 4	70 - 1000	HCl	Titration	PTFE
Stibine	6008	STIBINE	0.01 - 0.2	4 - 50	HCl	VIS	SG w/$HgCl_2$
Stoddard solvent	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
Strontium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	10 - 1000	HCl/HNO_3	ICP-AES	MCEF
Strontium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Strontium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Strychnine	5016	STRYCHNINE	1 - 3	70 - 1000	reagents	HPLC-UV	GFF
Styrene	1501	HYDROCARBONS, AROMATIC	0.01 - 1.0	1 - 14	CS_2	GC-FID	CCT
Styrene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. Dep.	NA	FTIR	Dir. Read
Sulfur dioxide	6004	SULFUR DIOXIDE	0.5 - 1.5	4 - 200	HCO_3^-/CO_3^{2-}	IC	MCEF& pad w/Na_2CO_3
Sulfur hexafluoride	6602	SULFUR HEXAFLUORIDE	0.01 - 0.05	80% vol	NA	GC-ECD	air bag
Sulfuric acid	7903	ACIDS, INORGANIC	0.2 - 0.5	3 - 100	HCO_3^-/CO_3^{2-}	IC	SG(washed)
Sulfuryl fluoride	6012	SULFURYL FLUORIDE	0.05 - 0.1	1.3 - 10	NaOH	IC	CCT (ig)
Sulprofos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FPD	OVS-2
Super absorbent polymer	5035	SUPER ABSORBENT POLYMER	1 - 3	50 - 1500	$Cu(Ac)_2$	ICP or AAS	PVC
Simazine	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	GC-MSD	Urine
2,4,5-T	5001	2,4-D and 2,4,5-T	1 - 3	15 - 200	MeOH	HPLC-UV	GFF
TB	0900	MYCOBACTERIUM TUBERCULOSIS, AIRBORNE	≥4	varies	reagent	PCR	PTFE
Tellurium	7300	ELEMENTS by ICP	1 - 4	25 - 2000	HNO_3	ICP-AES	MCEF
Tellurium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	25 - 2000	HCl/HNO_3	ICP-AES	MCEF
Tellurium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Tellurium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Terbufos	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC-FID	OVS-2
Terpenes	1552	TERPENES	0.01 - 2	2 - 30	CS_2	GC-FID	CCT
o-Terphenyl	5021	o-TERPHENYL	1 - 3	2 - 30	CS_2	GC-FID	PTFE
1,1,2,2-Tetrabromo ethane	2003	1,1,2,2-TETRABROMOETHANE	0.2 - 1.0	50 - 100	THF	GC-FID	SG
Tetrabutyltin	5504	ORGANOTIN COMPOUNDS	1 - 1.5	50 - 500	aqa	HPLC/GFAAS	GFF & XAD-2
1,2,4,5-Tetrachlorobenzene	5517	POLYCHLOROBENZENES	0.01 - 0.2	3 - 12	hexane	GC-ECD	PTFE & XAD-2
1,1,2,2-Tetrachloro-2,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	0.01 -0.035	0.5 - 2	CS_2	GC-FID	CCT
1,1,1,2-Tetrachloro-1,2-difluoroethane	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	0.01 -0.035	0.5 - 2	CS_2	GC-FID	CCT
1,1,2,2-Tetrachloroethane	1019	1,1,2,2-TETRACHLOROETHANE	0.01 - 0.2	3 - 30	CS_2	GC-FID	PCT
1,1,2,2-Tetrachloroethane	2562	1,1,2,2-TETRACHLOROETHANE	0.01 - 0.2	3 - 30	CS_2	GC-FID	A-CMS

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Tetrachloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 40	CS_2	GC-FID	CCT
Tetrachloroethylene	3704	PERCHLOROETHYLENE (port GC) in exhaled breath and air	0.1 - 1	<80% cap	NA	Port GC-PID	air bag
Tetraethylene glycol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Tetraethyl lead	2533	TETRAETHYL LEAD (as Pb)	0.01 - 1.0	30 - 200	pentane	GC-PID	XAD-2
Tetraethyl pyrophosphate	2504	TETRAETHYL PYROPHOSPHATE	0.01 - 0.2	20 - 48	toluene	GC FPD	2 Chrom 102
Tetrafluoroethylene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
Tetrahydrofuran	1609	TETRAHYDROFURAN	0.01 - 0.2	1 - 9	CS_2	GC FID	CCT
Tetrahydrofuran	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
Tetrakis(hydroxymethyl) phosphonium chloride	5046	TETRKIS(HYDROXYMETHYL) PHOSPHONIUM CHLORIDE	1 - 1.7	1 - 400	ACN	HPLC-UV	GFF
Tetramethyl lead	2534	TETRAMETHYL LEAD (as Pb)	0.01 - 0.2	15 - 100	pentane	GC-PID	XAD-2
Tetramethyl thiourea	3505	TETRAMETHYL THIOUREA	0.2 - 1.0	50 - 250	reagents	VIS	IMP/H_2O
Tetranitromethane	3513	TETRANITROMETHANE	0.5 - 1.0	20 - 250	-	GC FID	IMP/EtAc
Thallium	7300	ELEMENTS by ICP	1 - 4	25 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Thallium	7310	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	25 - 2000	HCl/HNO_3	ICP-AES	MCEF
Thallium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Thiobencarb	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC, UV	OVS-2
Thiophenate-methyl	9205	CAPTAN and THIOPHENATE-METHYL on DERMAL PATCH	NA	NA	IPA/ACN	HPLC-UV	Patch
Thiophenate-methyl	9202	CAPTAN and THIOPHENATE-METHYL in Hand Rinse	NA	NA	NA	HPLC-UV	Hand wash
Thiophenate-methyl	5606	THIOPHENATE-METHYL in AIR	0.1 - 1.0	20 - 480	IPA/ACN	HPLC-UV	QFF/SST
Thiram	5005	THIRAM	1 - 4	10 - 400	CH_3CN	HPLC-UV	PTFE
Tin	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Tin	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Tin, organic compds as Sn	5504	ORGANOTIN CPDS. (as Sn)	1 - 1.5	50 - 500	acetic a/CH_3CN	HPLC/GFAAS	GFF & XAD-2
Titanium	7300	ELEMENTS by ICP	1 - 4	5 - 100	$HNO_3/HClO_4$	ICP-AES	MCEF
Titanium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 100	HCl/HNO_3	ICP-AES	MCEF
Titanium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Toluene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Toluene	4000	TOLUENE(Diffusive sampler)	NA	15 min-8h	CS_2	GC-FID	Diffusive
Toluene	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	2 - 8	CS_2	GC-FID	CCT
Toluene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 8	CS_2	GC-FID	CCT
Toluene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
2,4 & 2,6-Toluenediamine	5516	2,4- & 2,6-TOLUENEDIAMINE	1.0	30 - 500	acetylate/MeOH	HPLC-UV	IMP
Toluene-2,4-diisocyanate	2535	TOLUENE-2,4-DIISOCYANATE	0.2 - 1.0	2 - 170	MeOH	HPLC-UV	GW coated
Toluene-2,4-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	acetylate/MeOH	HPLC-ECHD	IMP

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Toluene-2,4-diisocyanate	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
Toluene 2,4-dissocyanate (2,4-TDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC-UV	GFF, IMP
Toluene-2,6-diisocyanate	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
Toluene-2,6-diisocyanate	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	acetylate/MeOH	HPLC-ECHD	IMP
Toluene-2,6-diisocyanate (2,6-TDI)	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC-UV	GFF, IMP
p-Toluenesulfonic acid	5043	*P*-TOLUENESULFONIC ACID	1 - 3	10 - 1000	IPA/H_2O	HPLC-UV	GFF
o-Toluidine	2002	AMINES, AROMATIC	0.02 - 1.0	10 - 150	Ethanol	GC-FID	SG
o-Toluidine	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF + SG
o-Toluidine	5013	DYES	1 - 3	150 - 500	H_2O	HPLC-UV	PTFE
o-Toluidine	8317	ANALINE and o-TOLUIDINE in urine	NA	NA	ALK	HPLC-ECD	NA
o-Toluidine	8313	ANALINE and o-TOLUIDINE in urine	NA	NA	ALK	HPLC-ECD	NA
Tribromomethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	4 - 70	CS_2	GC-FID	CCT
Tributyl phosphate	5034	TRIBUTYL PHOSPHATE	1 - 3	2 - 100	diethyl ether	GC-FPD	MCEF
Tributyltin chloride	5504	ORGANOTIN COMPOUNDS	1 - 1.5	50 - 500	acetic a/CH_3CN	HPLC/GFAAS	GFF & XAD-2
1,2,4-Trichlorobenzene	5517	POLYCHLOROBENZENES	0.01 - 0.2	3 - 12	hexane	GC-ECD	PTFE & XAD-2
1,1,2-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	2 - 60	CS_2	GC-FID	CCT
1,1,1-Trichloroethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.1 - 8	CS_2	GC-FID	CCT
1,1,1-Trichloroethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Trichloroethylene	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.2 - 30	CS_2	GC-FID	CCT
Trichloroethylene	1022	TRICHLOROETHYLENE	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
Trichloroethylene	3701	TRICHLOROETHYLENE by port GC	> 0.02	80% vol	NA	GC-port	air bag
Trichloroethylene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
Trichlorofluoromethane	1006	FLUOROTRICHLOROMETHANE	0.01 - 0.05	0.3 - 7	CS_2	GC-FID	CCT(lg)
Trichloromethane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	1 - 50	CS_2	GC-FID	CCT
1,2,3-Trichloropropane	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	0.6 - 60	CS_2	GC-FID	CCT
Trichcylohexyltin hydroxide	5504	ORGANOTIN COMPOUNDS	1 - 1.5	50 - 500	acetic a/CH_3CN	HPLC-GFAAS	GFF & XAD-2
1,1,2-Trichloro-1,2,2-trifluoroethane	1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	0.01 - 0.05	0.1 - 3	CS_2	GC-FID	CCT
1,1,2-Trichloro-1,2,2-trifluoroethane	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Triethanolamine	3509	AMINOETHANOL COMPOUNDS II	0.5 - 1.0	5 - 300	HSA	IC	IMP
Triethylene glycol	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7
Triethylenetetramine	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01 - 0.1	1 - 20	DMF	HPLC-UV	XAD-2 W/10% NITC
Trifluorobromomethane	1017	TRIFLUOROBROMOMETHANE	0.01 - 0.05	0.1 - 1	CH_2Cl_2	GC-FID	2 CCT(lg+sm)
Trimellitic anhydride	5036	TRIMELLITIC ANHYDRIDE	1.5 - 2	400 - 1000	MeOH	GC-FID	PVC
2,4,7 Trinitrofluoren 9 one	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	1 - 3	100 - 500	toluene	HPLC-UV	PTFE
Triorthocresyl phosphate	5037	TRIORTHOCRESYL PHOSPHATE	1 - 3	2 - 100	diethyl ether	GC-FPD	MCEF
Triphenyl phosphate	5038	TRIPHENYL PHOSPHATE	1 - 3	10 - 400	diethyl ether	GC-FPD	MCEF
Triphenyltin chloride	5527	TRIPHENYL TIN CHLORIDE	1 - 4	100 - 2000	TWM	HPLC-ICP	PVC

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Tubercle bacilli	0900	MYCOBACTERIUM TUBERCULOSIS	≥4	varies	reagent	PCR	PTFE
Tungsten	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	50 - 1000	HCl/HNO_3	ICP-AES	MCEF
Tungsten, soluble/insoluble	7074	TUNGSTEN (soluble/insoluble)	1 - 4	200 - 1000	HF/HNO_3	FAAS	MCEF
Turpentine	1551	TURPENTINE	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
Turpentine	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
n-Undecane	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.05	2 - 2	CS_2	GC-FID	CCT
Valeraldehyde	2018	ALIPHATIC ALDEHYDES	0.1 - 1.5	1 - 15	ACN	HPLC-UV	SG-DNPH
Valeraldehyde	2536	VALERALDEHYDE	0.01 - 0.04	0.5 - 10	toluene	GC-FID	XAD-2/HMP
Valeraldehyde	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	toluene	GC-FID/MS	XAD-2/HMP
Vanadium	7300	ELEMENTS by ICP	1 - 4	5 - 2000	$HNO_3/HClO_4$	ICP-AES	MCEF
Vanadium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 2000	HCl/HNO_3	ICP-AES	MCEF
Vanadium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Vanadium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Vanadium oxides	7504	VANADIUM OXIDES	1.7 or 2.2	200 - 1000	THF	XRD	CYC & PVC
Vinyl acetate	1453	VINYL ACETATE	0.1 - 0.2	0.75 - 24	CH_2Cl_2/MeOH	GC-FID	MS(carbon)
Vinyl benzene	1501	HYDROCARBONS, AROMATIC	.01 - 1	1 - 14	CS_2	GC-FID	CCT
Vinyl bromide	1009	VINYL BROMIDE	0.01 - 0.2	2 - 10	Ethanol	GC-FID	CCT (lg)
Vinyl chloride	1007	VINYL CHLORIDE	0.05	0.7 - 5	CS_2	GC-FID	2 CCT
Vinylidene chloride	1015	VINYLIDENE CHLORIDE	0.01 - 0.2	2.5 - 7	CS_2	GC-FID	CCT
Vinylidene Fluoride	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
Vinyl toluene uene	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	1 - 24	CS_2	GC-FID	CCT
VM&P naphtha	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
VOCs	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Warfarin	5002	WARFARIN	1 - 4	200 - 1000	MeOH	HPLC-UV	PTFE
Wood alcohol	2000	METHANOL	0.02 - 0.2	1 - 5	H_2O/IPA	GC-FID	SG
Xylene	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
Xylene (*o,m,p*)	1501	HYDROCARBONS, AROMATIC	0.01 - 0.2	2 - 23	CS_2	GC-FID	CCT
p-Xylene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
m-Xylene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
o-Xylene	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
2,4-Xylidine	2002	AMINES, AROMATIC	0.02 - 0.2	3 - 20	Ethanol	GC-FID	SG
Yttrium	7300	ELEMENTS by ICP	1 - 4	5 - 1000	$HNO_3/HClO_4$	ICP-AES	MCEF
Yttrium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 1000	HCl/HNO_3	ICP-AES	MCEF
Yttrium	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Yttrium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
Zinc and compounds	7030	ZINC and compounds, as Zn	1 - 3	2 - 400	HNO_3	FAAS	MCEF
Zinc	7300	ELEMENTS by ICP	1 - 4	5 - 200	$HNO_3/HClO_4$	ICP-AES	MCEF
Zinc	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 200	HCl/HNO_3	ICP-AES	MCEF
Zinc	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
Yttrium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
Zinc oxide	7502	ZINC OXIDE	1 - 3	10 - 400	--	XRD	PVC
Zirconium	7300	ELEMENTS by ICP	1 - 4	5 - 200	$HNO_3/HClO_4$	ICP AES	MCEF
Zirconium	7301	ELEMENTS by ICP (Aqua Regia Ashing)	1 - 4	5 - 200	HCl/HNO_3	ICP-AES	MCEF
Zirconium	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
METHODS BY NUMBER							
	0500	PARTICULATES N.O.R.	1 - 2	7 - 133	NA	GRAV	PVC
	0600	PARTICULATES, N.O.R, RESP.	1.7, 2.2,2.5	20 - 400	NA	Grav.	CYC & PVC
	0800	BIOAEROSOL SAMPLING	28.3	varies	NA	varies	Impactor
	0801	AEROBIC BACTERIA - GC-FAME	28.3	50 - 300	hex/MTBE	GC-FID	Impactor
	0900	MYCOBACTERIUM TUBERCULOSIS	4	varies	reagent	PCR	PTFE
	1000	ALLYL CHLORIDE	0.01 - 1.0	16 - 100	bz	GC-FID	CCT
	1001	METHYL CHLORIDE	0.01 - 0.1	0.4 - 3	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
	1002	β-CHLOROPRENE	0.01 - 0.1	1.5 - 8	CS_2	GC-FID	CCT
	1003	HYDROCARBONS, HALOGENATED	0.01 - 0.2	3 - 70	CS_2	GC-FID	CCT
	1004	DICHLOROETHYL ETHER	0.01 - 1.0	2 - 15	CS_2	GC-FID	CCT
	1005	METHYLENE CHLORIDE	0.01 - 0.2	0.5 - 2.5	CS_2	GC-FID	2 CCT
	1006	FLUOROTRICHLOROMETHANE	0.01 - 0.05	0.3 - 7	CS_2	GC-FID	CCT (lg)
	1007	VINYL CHLORIDE	0.05	0.7 - 5	CS_2	GC-FID	2 CCT
	1008	ETHYLENE DIBROMIDE	0.02 - 0.2	0.1 - 25	bz/MeOH	GC-ECD	CCT
	1009	VINYL BROMIDE	0.01 - 0.2	2 - 10	Ethanol	GC-FID	CCT (lg)
	1010	EPICHLOROHYDRIN	0.01 - 0.2	2 - 30	CS_2	GC-FID	CCT
	1011	ETHYL BROMIDE	0.01 - 0.2	0.5 - 4	IPA	GC FID	CCT
	1012	DIFLUORODIBROMOMETHANE	0.01 - 0.2	2.5 - 10	IPA	GC-FID	2 CCT
	1013	PROPYLENE DICHLORIDE	0.01 - 0.2	0.1 - 3.5	acet/cyclohexane	GC-ECN	PCT
	1014	METHYL IODIDE	0.01 - 1.0	15 - 50	tol	GC-FID	CCT
	1015	VINYLIDENE CHLORIDE	0.01 - 0.2	2.5 - 7	CS_2	GC-FID	CCT
	1016	1,1,2,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	0.01 -0.035	0.5 - 2	CS_2	GC-FID	CCT
	1017	TRIFLUOROBROMOMETHANE	0.01 - 0.05	0.1 - 1	CH_2Cl_2	GC-FID	2 CCT(lg + sm)
	1018	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUORO-ETHANE& CHLORODIFLUOROMETHANE	0.01 - 0.05	1 - 4	CH_2Cl_2	GC-FID	2 CCT (lg + sm)
	1019	1,1,2,2-TETRACHLOROETHANE	0.01 - 0.2	3 - 30	CS_2	GC-FID	PCT
	1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE	0.01 - 0.05	0.1 - 3	CS_2	GC-FID	CCT
	1022	TRICHLOROETHYLENE	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	1024	1,3-BUTADIENE	0.01 - 0.5	5 - 25	CH_2Cl_2	GC-FID	CCT
	1025	1- and 2-BROMOPROPANE	0.01 - 0.2	0.1 - 12	CS_2	GC-FID	CCT
	1026	*P*-CHLOROBENZOTRIFLUORIDE	0.01 - 0.2	0.1 - 10	CS_2/MeOH	GC-FID	CCT
	1300	KETONES I	0.01 - 2.0	1 - 10	CS_2	GC-FID	CCT
	1301	KETONES II	0.01 - 0.2	1 - 25	MeOH/CS_2	GC-FID	CCT
	1302	*N*-METHYL-2-PYRROLIDINONE	0.05 - 0.2	0.5 - 125	CH_2Cl_2/MeOH	GC-FID/NPD	CCT
	1400	ALCOHOLS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
	1401	ALCOHOLS II	0.01 - 0.2	2 - 10	IPA/CS_2	GC-FID	CCT
	1402	ALCOHOLS III	0.01 - 0.2	1 - 10	IPA/CS_2	CG-FID	CCT
	1403	ALCOHOLS IV	0.01 - 0.05	6 - 50	MeOH/CH_2Cl_2	GC-FID	CCT
	1404	METHYLCYCLOHEXANOL	0.01 - 0.2	1 - 15	CH_2Cl_2	GC-FID	CCT
	1405	ALCOHOLS COMBINED	0.01 - 0.2	2 - 10	IPA-CS_2	GC-FID	CCT
	1450	ESTERS I	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
	1451	METHYL CELLOSOLVE ACETATE	0.01 - 0.2	0.2 - 20	CS_2	GC-FID	CCT
	1452	ETHYL FORMATE	0.01 - 0.2	0.3 - 10	CS_2	GC-FID	CCT
	1453	VINYL ACETATE	0.1 - 0.2	0.75 - 24	CH_2Cl_2/MeOH	GC-FID	MS(carbon)
	1454	ISOPROPYL ACETATE	0.02 - 0.2	0.1 - 9	CS_2	GC-FID	CCT
	1457	ETHYL ACETATE	0.01 - 0.2	0.1 - 10	CS_2	GC-FID	CCT
	1458	METHYL ACETATE	0.01 - 0.2	0.2 - 10	CS_2	GC-FID	CCT
	1459	METHYL ACRYLATE	0.01 - 0.2	1 - 5	CS_2	GC-FID	CCT
	1460	ISOPROPYL ACETATE	0.02 - 0.2	0.1 - 9	CS_2/Meth	GC-FID	CCT
	1500	HYDROCARBONS, BP 36-216°C	0.01 - 0.2	2 - 7	CS_2	GC-FID	CCT
	1501	HYDROCARBONS, AROMATIC	0.01 - 1.0	1 - 30	CS_2	GC-FID	CCT
	1550	NAPHTHAS	0.01 - 0.2	1.3 - 20	CS_2	GC-FID	CCT
	1551	TURPENTINE	0.01 - 0.2	1 - 10	CS_2	GC-FID	CCT
	1552	TERPENES	0.01 - 2	2 - 30	CS_2	GC-FID	CCT
	1600	CARBON DISULFIDE	0.01 - 0.2	2 - 25	tol	GC-FPD	CCT & dry tube
	1601	1,1-DICHLORO-1-NITROETHANE	0.01 - 1.0	1.5 - 15	CS_2	GC-FID	PCT
	1602	DIOXANE	0.01 - 0.2	0.5 - 15	CS_2	GC-FID	CCT
	1603	ACETIC ACID	0.01 - 0.1	20 - 300	formic a	GC-FID	CCT
	1604	ACRYLONITRILE	0.01 - 0.2	3.5 - 20	acet/CS_2	GC-FID	CCT
	1606	ACETONITRILE	0.01 - 0.2	1 - 25	CH_2Cl_2/MeOH	GC-FID	CCT
	1608	GLYCIDOL	0.01 - 1.0	5 - 100	THF	GC-FID	CCT
	1609	TETRAHYDROFURAN	0.01 - 0.2	1 - 9	CS_2	GC-FID	CCT
	1610	ETHYL ETHER	0.01 - 0.2	0.25 - 3	CS_2	GC-FID	CCT
	1611	METHYLAL	0.01 - 0.2	1 - 3	hexane	GC-FID	CCT
	1612	PROPYLENE OXIDE	0.01 - 0.2	0.5 - 5	CS_2	GC-FID	CCT
	1613	PYRIDINE	0.01 - 1.0	18 - 150	CH_2Cl_2	GC-FID	CCT
	1614	ETHYLENE OXIDE	0.05 - 0.15	1 - 24	DMF	GC-ECD	PCT w/HBr
	1615	METHYL *tert*-BUTYL ETHER	0.1 - 0.2	2 - 96	CS_2	GC-FID	2 CCT (lg)
	1616	BUTYL GLYCIDYL ETHER	0.01 - 0.2	15 - 30	CS_2	GC-FID	CCT
	1617	PHENYL ETHER	0.01 - 0.2	1 - 50	CS_2	GC-FID	CCT

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	1618	ISOPROPYL ETHER	0.01 - 0.05	0.1 - 3	CS_2	GC-FID	CCT
	1619	PHENYL GLYCIDYL ETHER	0.01 - 1	80 - 150	CS_2	GC-FID	CCT
	1620	ISOPROPYL GLYCIDYL ETHER	0.01 - 0.2	1 - 30	CS_2	GC-FID	CCT
	2000	METHANOL	0.02 - 0.2	1 - 5	H_2O/IPA	GC-FID	SG
	2002	AMINES, AROMATIC	0.2 - 1.0	30 - 150	Ethanol	GC-FID	SG
	2003	1,1,2,2-TETRABROMOETHANE	0.2 - 1.0	50 - 100	THF	GC-FID	SG
	2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE	0.01 - 1.0	15 - 80	MeOH	GC-FID	SG
	2005	NITROAROMATIC COMPOUNDS	0.01 - 1	1 - 150	MeOH	GC-FID	SG
	2007	AMINOETHANOL COMPOUNDS I	0.01 - 0.2	4 - 24	MeOH/H_2O	GC-FID	SG
	2008	CHLOROACETIC ACID	0.05 - 0.2	1 - 100	H_2O	IC	SG
	2010	AMINES, ALIPHATIC	0.01 - 1.0	3 - 30	H_2SO_4/aq MeOH	GC-FID	SG
	2011	FORMIC ACID	0.05 - 0.2	1 - 24	H_2O	IC	PTFE & SG (washed)
	2012	*n*-BUTYLAMINE	0.01 - 1.0	2 - 100	MeOH	GC-FID	SG + H_2SO_4
	2013	PHENYL ETHER-DIPHENYL MIXTURE	0.01 - 0.2	1 - 40	bz	GC-FID	SG
	2014	*p-CHLOROPHENOL*	0.05 - 0.2	1.5 - 40	CH_3CN	HPLC-UV	SG
	2015	CHLOROACETALDEHYDE	0.05 - 0.2	3 - 16	MeOH	GC-ECD	SG
	2016	FORMALDEHYDE	0.03 - 1.5	1 - 15	acetonitrile	HPLC-UV	SG/DNPH
	2017	ANILINE, o-TOLUIDINE, AND NITROBENZENE	0.2	5 - 50	ethanol	GC-FID	GFF + SG w/H_2SO_4
	2018	ALIPHATIC ALDEHYDES	0.1 - 1.5	1 - 15	ACN	HPLC-UV	SG-DNPH
	2500	METHYL ETHYL KETONE	0.01 - 0.2	0.25 - 12	CS_2	GC FID	Carbon beads
	2501	ACROLEIN	0.01 - 0.1	1.5 - 48	tol	GC-NPD	XAD-2/HMP
	2504	TETRAETHYL PYROPHOSPHATE	0.01 - 0.2	20 - 48	toluene	GC-FPD	2 Chrom 102
	2505	FURFURYL ALCOHOL	0.01 - 0.05	3 - 25	acet	GC-FID	Por Q
	2506	ACETONE CYANOHYDRIN	0.2	0.3 - 12	Et Ac	GC NPD	Por QS
	2507	NITROGLYCERIN & ETHYLENE GLYCOL DINITRATE	0.2 - 1.0	3 - 100	Ethanol	GC-ECD	Tenax-GC
	2508	ISOPHORONE	0.01 - 1.0	2 - 25	CS_2	GC-FID	PCT
	2510	1-OCTANETHIOL	0.01 - 0.2	1 - 15	acet	GC-FPD	Tenax GC
	2513	ETHYLENE CHLOROHYDRIN	0.01 - 0.2	2 - 35	IPA/CS_2	GC-FID	PCT
	2514	ANISIDINE	0.5 - 1.0	24 - 320	MeOH	HPLC-UV	XAD-2
	2515	DIAZOMETHANE	0.2	6 - 30	CS_2	GC-FID	XAD-2 (coated)
	2516	DICHLOROFLUOROMETHANE	0.01 - 0.05	0.25 - 3	CS_2	GC-FID	2 CCT (lg)
	2517	PENTACHLOROETHANE	0.01 - 0.2	1 - 10	hexane	GC-ECD	Por R
	2518	HEXACHLORO-1,3-CYCLOPENTA-DIENE	0.01 - 0.2	0.25 - 90	hexane	GC-ECD	2 Por T
	2519	ETHYL CHLORIDE	0.02 - 0.05	0.3 - 3	CS_2	GC-FID	2 CCT (lg)
	2520	METHYL BROMIDE	0.01 - 0.1	1 - 5	CS_2	GC-AED	PCT(2)+dry tube
	2521	METHYLCYCLOHEXANONE	0.01 - 0.05	1 - 6	acet	GC-FID	Por Q
	2522	NITROSAMINES	0.2 - 2.0	15 - 1000	MeOH/CH_2Cl_2	GC-TEA	Thermalosorb/N
	2523	1,3-CYCLOPENTADIENE	0.01 - 0.05	1 - 5	Et Ac	GC-FID	Chrom104/ maleic anh.

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	2524	DIMETHYL SULFATE	0.01 - 0.2	0.25 - 12	diEt ether	GC-ECN	Por P
	2525	*n*-BUTYL MERCAPTAN	0.01 - 0.05	1 - 4	acet	GC-FPD	Chrom 104
	2526	NITROETHANE	0.01 - 0.05	1.5 - 3	EtAc	GC-FID	2XAD-2
	2527	NITROMETHANE	0.01 - 0.05	1.2 - 3	EtAc	GC-FPD	Chrom 106
	2528	2-NITROPROPANE	0.01 - 0.05	0.1 - 2	EtAc	GC-FID	Chrom 106
	2529	FURFURAL	0.01 - 0.05	1 - 12	tol	GC-FID	XAD-2/HMP
	2530	DIPHENYL	0.01 - 0.5	15 - 30	CCl_4	GC-FID	Tenax GC
	2532	GLUTARALDEHYDE	0.01 - 0.08	4 - 39	CH_3CN	HPLC-UV	SG/DNPH
	2533	TETRAETHYL LEAD (as Pb)	0.01 - 1.0	30 - 200	pentane	GC-PID	XAD-2
	2534	TETRAMETHYL LEAD (as Pb)	0.01 - 0.2	15 - 100	pentane	GC-PID	XAD-2
	2535	TOLUENE-2,4-DIISOCYANATE	0.2 - 1.0	2 - 170	MeOH	HPLC-UV	GW coated
	2536	VALERALDEHYDE	0.01 - 0.04	0.5 - 10	toluene	GC-FID	XAD-2/HMP
	2537	METHYL and ETHYL METHACRYLATE	0.01 - 0.05	1 - 8	CS_2	GC-FID	XAD-2
	2538	ACETALDEHYDE	0.01 - 0.05	1 - 12	tol	GC-FID	XAD-2/HMP
	2539	ALDEHYDES, SCREENING	0.01 - 0.05	5 - 5	tol	GC-FID/MS	XAD-2
	2540	ETHYLENEDIAMINE, DIETHYLENETRIAMINE, & TRIETHYLENETETRAMINE	0.01 - 0.1	1 - 20	DMF	HPLC-UV	XAD-2 w/10% NITC
	2541	FORMALDEHYDE	0.01 - 0.1	1 - 36	tol	GC-FID	XAD-2/HMP
	2542	MERCAPTANS	0.1 - 0.2	10 - 150	HCl/DCE	GC-FPD	GFF/HgAc
	2543	HEXACHLOROBUTADIENE	0.05 - 0.2	1 - 100	hexane	GC-ECD	XAD-2
	2544	NICOTINE	1.0	60 - 400	EtAc	GC-NPD	XAD-2
	2545	ALLYL GLYCIDYL ETHER	0.01 - 0.2	1.5 - 8	diethyl ether	GC-FID	Tenax
	2549	VOLATILE ORGANIC CPDS (Screening)	0.01 - 0.05	1 - 6	thermal	TD/GC-MS	TD
	2550	BENZOTHIAZOLE IN ASPHALT FUME	1.0 - 2.0	480 - 960	hexane	GC-SCD	PTFE + XD-2
	2551	NICOTINE	0.1 - 1.0	0.5 - 600	ethyl acetate	GC-NPD	XAD-4
	2552	METHYL ACRYLATE	0.01 - 0.2	1 - 5	CS_2	GC-FID	A-CMS
	2553	KETONES II	0.01 - 0.2	1 - 25	IPA-CS_2	GC-FID	A-CMS
	2554	GLYCOL ETHERS	0.1 - 0.2	3 - 25	$MeCl_2$/Meth	GC-FID	A-747
	2555	KETONES I	0.01 - 0.2	0.5 - 3.0 1 - 10	CS_2	GC-FID	A-CMS
	2556	ISOPHORONE	0.01 - 1	2 - 25	DEE	GC-FID	XAD
	2557	DIACETYL	0.01 - 0.2	1 - 10	Acet-Meth	GC-FID	A-CMS
	2558	ACETOIN	0.01 - 0.2	1 - 10	Acet-Meth	GC-FID	A-CMS
	2559	DECABROMODIPHENYL OXIDE	2.0	48 - 960	DMSO	HPLC/UV	QFF
	2560	1-NITROPYRENE in DIESEL PARTICULATES	1.0 - 2.0	480 - 960	Tol	GC-NCD	GFF
	2561	2-(DIMETHYLAMINO)ETHANOL 1-DIMETHYLAMINO-2-PROPANOL	0.02 - 1	10 - 24	MeOH	GC-FID	XAD
	2562	1,1,2,2-TETRACHLOROETHANE	0.01 - 0.2	3 - 30	CS_2	GC-FID	A-CMS
	3500	FORMALDEHYDE	0.2 - 1.0	1 - 100	$NaHSO_3$	VIS	PTFE & 2 IMP
	3503	HYDRAZINE	0.2 - 1.0	7 - 100	reagents	VIS	BuB
	3505	TETRAMETHYL THIOUREA	0.2 - 1.0	50 - 250	reagents	VIS	IMP/H_2O
	3506	ACETIC ANHYDRIDE	0.2 - 1.0	25 - 100	reagent	VIS	BuB

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	3507	ACETALDEHYDE	0.1 - 0.5	6 - 60	reagent	HPLC-UV	BuB
	3508	METHYL ETHYL KETONE PEROXIDE	0.5 - 0.2	52 - 520	reagent	VIS	IMP
	3509	AMINOETHANOL COMPOUNDS II	0.5 - 1.0	5 - 300	HSA	IC	IMP
	3510	MONOMETHYLHYDRAZINE	0.5 - 1.5	3 - 20	PMA/HCl	VIS	BuB/HCl
	3511	MONOMETHYLANILINE	0.2 - 1.0	11 - 100	NaOH	GC-FID	BuB/H_2SO_4
	3512	MALEIC ANHYDRIDE	0.2 - 1.5	40 - 500	--	HPLC-UV	BuB/H_2O
	3513	TETRANITROMETHANE	0.5 - 1.0	20 - 250	--	GC-FID	IMP/EtAc
	3514	ETHYLENIMINE	0.2	1 - 48	$CHCl_3$	HPLC-UV	BuB
	3515	1,1-DIMETHYLHYDRAZINE	0.2 - 1.0	2 - 100	reagent	VIS	BuB (.1 M HCl)
	3516	CROTONALDEHYDE	0.1 - 0.2	1 - 49	buffer	DPP	BuB
	3518	PHENYLHYDRAZINE	0.2 - 1.0	25 - 120	PMA	VIS	BuB/HCl
	3600	MANEB	NA	NA	Cys/EDTA	HPLC-UV	Patch
	3601	MANEB	NA	NA	NA	HPLC-UV	Hand wash
	3700	BENZENE by portable GC	> 0.02	80% vol	NA	GC	air bag
	3701	TRICHLOROETHYLENE by port GC	> 0.02	80% vol	NA	GC-port	air bag
	3702	ETHYLENE OXIDE by portable GC	> 0.02	80% vol	NA	GC-PID	air bag
	3704	PERCHLOROETHYLENE (portable GC) in exhaled breath and air	0.1 - 1	80% VOL	NA	Port GC-PID	air bag
	3800	ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY	0.1 - 20	Instr. dep.	NA	FTIR	Dir. Read
	4000	TOLUENE (Diffusive sampler)	NA	15 min-8h	CS_2	GC-FID	Diffusive
	5000	CARBON BLACK	1 - 2	30 - 570	NA	Grav	PVC
	5001	2,4-D and 2,4,5-T	1 - 3	15 - 200	MeOH	HPLC-UV	GFF
	5002	WARFARIN	1 - 4	200 - 1000	MeOH	HPLC-UV	PTFE
	5003	PARAQUAT	1 - 4	40 - 1000	H_2O	HPLC-UV	PTFE
	5004	HYDROQUINONE	1 - 4	30 - 180	acetic acid	HPLC-UV	MCEF
	5005	THIRAM	1 - 4	10 - 400	CH_3CN	HPLC-UV	PTFE
	5006	CARBARYL	1 - 3	20 - 400	reagent	VIS	GFF
	5007	ROTENONE	1 - 4	8 - 400	CH_3CN	HPLC-UV	PTFE
	5008	PYRETHUM	1 - 4	20 - 400	CH_3CN	HPLC-UV	GFF
	5009	BENZOYL PEROXIDE	1 - 3	40 - 400	diethyl ether	HPLC-UV	MCEF
	5010	BROMOXYNIL and B'OCTANOATE	1 - 3	2 - 400	CH_3CN	HPLC-UV	PTFE
	5011	ETHYLENE THIOUREA	1 - 3	200 - 800	H_2O	VIS	PVC or MCEF
	5012	EPN	1 - 2	15 - 700	isooctane	GC-FPD	GFF
	5013	DYES	1 - 3	150 - 500	H_2O	HPLC-UV	PTFE
	5014	CHLORINATED TERPHENYL	1 - 3	100 - 1500	isooctane	GC-ECD	GFF
	5016	STRYCHNINE	1 - 3	70 - 1000	reagents	HPLC-UV	GFF
	5017	DIBUTYL PHOSPHATE	1 - 3	50 - 250	CH_3CN	GC-FPD	PTFE
	5018	2,4,7-TRINITRO-FLUOREN-9-ONE	1 - 3	100 - 500	toluene	HPLC-UV	PTFE
	5019	AZELAIC ACID	1 - 3	200 - 1000	Ethanol	GC-FID	PVC
	5020	DIBUTYL PHTHALATE & DI(2-ETHYLHEXYL) PHTHALATE	1 - 3	6 - 200	CS_2	GC-FID	MCEF
	5021	o-TERPHENYL	1 - 3	2 - 30	CS_2	GC-FID	PTFE
	5022	ARSENIC, organo-	1 - 3	50 - 1000	buffer	IC-HYAAS	PTFE

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	5025	CHLORINATED DIPHENYL OXIDE	0.5 - 1.5	8 - 200	Isooctane	GC-ECN	MCEF
	5026	OIL MIST, MINERAL	1 - 3	20 - 500	CCl_4	IR	PVC or MCE
	5027	RIBAVIRIN	1 - 4	5 - 1000	H_2SO_4	HPLC-UV	GFF
	5029	4,4'-METHYLENEDIANILINE	1 - 2	10 - 1000	KOH/MeOH	HPLC-UV	GFF/H_2SO_4
	5030	CYANURIC ACID	1 - 3	10 - 1000	reagents	HPLC-UV	PVC
	5031	ASPARTAME	1 - 3	70 - 1200	eluent	HPLC-UV	PTFE
	5032	PENTAMIDINE ISETHIONATE	1 - 2	50 - 1500	reagents	HPLC/FL	PVC/opaque
	5033	*p*-NITROANILINE	1 - 3	20	IPA	HPLC-UV	MCEF
	5034	TRIBUTYL PHOSPHATE	1 - 3	2 - 100	diethyl ether	GC-FPD	MCEF
	5035	SUPER ABSORBENT POLYMER	1 - 3	50 - 1500	$Cu(Ac)_2$	ICP or AAS	PVC
	5036	TRIMELLITIC ANHYDRIDE	1.5 - 2	400 - 1000	MeOH	GC-FID	PVC
	5037	TRIORTHOCRESYL PHOSPHATE	1 - 3	2 - 100	diethyl ether	GC-FPD	MCEF
	5038	TRIPHENYL PHOSPHATE	1 - 3	10 - 400	diethyl ether	GC-FPD	MCEF
	5039	CHLORINATED CAMPHENE	0.2 - 1	2 - 30	pet ether	GC-ECD	MCEF
	5040	ELEMENTAL CARBON (DIESEL PARTICULATE)	2 - 4	142 -19000	thermal	EGA/TOA	QFF
	5041	CAPSAICIN and DIHYDROCAPSAICIN	1 - 3	5 - 1000	CH_3CN	HPLC-FL	GFF
	5042	BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)	1 -4	28 - 400	benzene	Grav	tared PTFE
	5043	*p*-TOLUENESULFONIC ACID	1 - 3	10 - 1000	IPA/H_20	HPLC-UV	GFF
	5044	ESTROGENIC COMPOUNDS	1	150 - 1000	Meth	HPLC-UV	PTFE
	5046	TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE	1 - 1.7	1 - 400	ACN	HPLC-UV	GFF
	5502	ALDRIN & LINDANE	0.2 - 1.0	18 - 240	isooct	GC-ECN	GFF & BuB
	5503	POLYCHLOROBIPHENYLS	0.05 - 0.2	1 - 50	hexane	GC-ECD	GFF & Florisil
	5504	ORGANOTIN COMPOUNDS	1 - 1.5	50 - 500	acetic a/CH_3CN	HPLC-GFAAS	GFF & XAD-2
	5506	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	acetonitrile	HPLC-FL/UV	PTFE & XAD-2
	5508	KEPONE	0.5 - 1.0	50 - 600	bz/MeOH	GC-ECD	MCEF & IMP
	5509	BENZIDINE and 3,3'-DICHLORO-BENZIDINE	0.2	20 - 100	triethyl amine /MeOH	HPLC-UV	GFF
	5510	CHLORDANE	0.5 - 1.0	10 - 200	tol	GC-ECD	MCEF & Chrom 102
	5512	PENTACHLOROPHENOL	0.5 - 1.0	48 - 480	MeOH	HPLC-UV	MCEF & BuB
	5514	DEMETON	0.2 - 1.0	30 - 500	tol	GC-FPD	MCEF &XAD-2
	5515	POLYNUCLEAR AROMATIC HYDROCARBONS	2.0	200 - 1000	varies	GC-FID	PTFE & XAD-2
	5516	2,4- & 2,6-TOLUENEDIAMINE	1.0	30 - 500	acetylate/MeOH	HPLC-UV	IMP
	5517	POLYCHLOROBENZENES	0.01 - 0.2	3 - 12	hexane	GC-ECD	PTFE & XAD-2
	5518	NAPHTHYLAMINES	0.2 - 0.8	30 - 100	acetic a /IPA	GC FID	GFF & SG
	5519	ENDRIN	0.5 - 1.0	12 - 400	tol	GC-ECD	MCEF & Chrom 102
	5521	ISOCYANATES, MONOMERIC	1.0	5 - 500	reagents	HPLC-ECHD	IMP
	5522	ISOCYANATES	1 - 2	15 - 360	tryptamine/DMSO	HPLC-FL/ECHD	IMP
	5523	GLYCOLS	0.5 - 2	5 - 60	MeOH	GC-FID	OVS-7

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	5524	METALWORKING FLUIDS (MWF) ALL CATEGORIES	1.6 - 2.0	1000 - ND	DCM/MeOH/Tol MeOH	Grav	PTFE/CYC
	5525	ISOCYANATES, TOTAL (MAP)	1 - 2	1 - 500	MAP	HPLC-UV	GFF, IMP
	5526	METHYLTIN CHLORIDES	0.25 - 1	15 - 75	AAA	GC-FPD	OVS
	5527	TRIPHENYL TIN CHLORIDE	1 - 4	100 - 2000	TWM	HPLC-ICP	PVC
	5600	ORGANOPHOSPHORUS PESTICIDES	0.2 - 1	12 - 240	tol/acet	GC FPD	OVS-2
	5601	ORGANONITROGEN PESTICIDES	0.1 - 1	var - 480	reagent	HPLC-UV	OVS-2
	5602	CHLORINATED ORGANONITROGEN HERBICIDES (AIR SAMPLING)	0.2 - 1	12 - 480	reagent	GC/ECD	OVS-2
	5603	ALACHLOR in AIR	1	70 - 1750	MeOH	ELISA	SPE disk
	5606	THIOPHENATE-METHYL in AIR	0.1 - 1.0	20 - 480	IPA/ACN	HPLC-UV	QFF/SST
	5700	FORMALDEHYDE on dust	2	240 - 1050	H_2O/DNPH/CH_3CN	HPLC UV	IOM/PVC
	5701	RESORCINOL	0.2 - 1	5 - 160	MeOH	GC-FID	OVS-7
	5800	POLY AROMATIC COMPOUNDS (PACs)	1 - 2	5 - 1000	hexane	FI-FL	PTFE + XAD-2
	6001	ARSINE	0.01 - 0.2	0.1 - 10	HNO_3	GFAAS	CCT
	6002	PHOSPHINE	0.01 - 0.2	1 - 16	reagent	VIS	SG/$Hg(CN)_2$
	6004	SULFUR DIOXIDE	0.5 - 1.5	4 - 200	HCO_3^-/CO_3^{2-}	IC	MCEF& pad w/Na_2CO_3
	6005	IODINE	0.5 - 1.0	15 - 225	Na_2CO_3	IC	CCT w/alkali
	6006	DIBORANE	0.5 - 1.0	60 - 260	H_2O_2	PES	PTFE & CCT w/oxidizer
	6007	NICKEL CARBONYL	0.05 - 0.2	7 - 80	HNO_3	GFAAS	CCT (low Ni)
	6008	STIBINE	0.01 - 0.2	4 - 50	HCl	VIS	SG w/$HgCl_2$
	6009	MERCURY	0.15 - 0.25	2 - 100	HNO_3/HCl	AAS cold vap	Hopcalite
	6010	HYDROGEN CYANIDE	0.05 - 0.2	2 - 90	H_2O	VIS	soda lime
	6011	CHLORINE and BROMINE	0.3 - 1.0	2 - 90	$Na_2S_2O_3$	IC	Ag F
	6012	SULFURYL FLUORIDE	0.05 - 0.1	1.3 - 10	NaOH	IC	CCT (lg)
	6013	HYDROGEN SULFIDE (withdrawn)	0.1 - 1.5	1.2 - 40	NH_4OH/H_2O_2	IC	PTFE & CCT (lg)
	6014	NITRIC OXIDE & NITROGEN DIOXIDE	0.025	1.5 - 6	reagent	VIS	MS w/TEA & oxidizer
	6015	AMMONIA by VIS	0.1 - 0.2	0.1 - 90	H_2O	VIS-Auto	SG + H_2SO_4
	6016	AMMONIA by IC	0.1 - 0.5	0.1 - 96	H_2O	IC	SG + H_2SO_4
	6017	HYDROGEN CYANIDE	0.05 - 2	2 - 90	H_2O	IC-DC Amp	SL
	6402	PHOSPHORUS TRICHLORIDE	0.05 - 0.2	11 - 100	reagents	VIS	BuB/H_2O
	6600	NITROUS OXIDE	NA	80% vol	NA	IR	air bag
	6601	OXYGEN	NA	1 - NA	NA	Sensor	portable
	6602	SULFUR HEXAFLUORIDE	0.01 - 0.05	80% vol	NA	GC ECD	air bag
	6603	CARBON DIOXIDE	0.02 - 0.1	80% vol	NA	GC TCD	air bag
	6604	CARBON MONOXIDE	NA	NA	NA	Sensor	Port Instr
	6700	NITROGEN DIOXIDE (Diffusive)	NA	NA	reagent	VIS	Diffusive
	7013	ALUMINUM & CPDS, as Al	1 - 3	10 - 400	HNO_3	FAAS	MCEF
	7020	CALCIUM and cpds as Ca	1 - 3	20 - 400	$HNO_3/HClO_4$	FAAS	MCEF
	7024	CHROMIUM and cpds, as Cr	1 - 3	10 - 1000	HCl/HNO_3	FAAS	MCEF

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	7027	COBALT and cpds, as Co	1 - 3	30 - 1500	aq reg/HNO_3	FAAS	MCEF
	7029	COPPER (dust & fumes)	1 - 3	50 - 1500	HNO_3/HCl	FAAS	MCEF
	7030	ZINC and compounds, as Zn	1 - 3	2 - 400	HNO_3	FAAS	MCEF
	7048	CADMIUM and cpds, as Cd	1 - 3	25 - 1500	HNO_3/HCl	FAAS	MCEF
	7056	BARIUM, SOLUBLE COMPOUNDS	1 - 4	50 - 2000	H_2O	FAAS	MCEF
	7074	TUNGSTEN (soluble/insoluble)	1 - 4	200 - 1000	HF/HNO_3	FAAS	MCEF
	7082	LEAD by FAAS	1 - 4	200 - 1500	HNO_3/H_2O_2	FAAS	MCEF
	7102	BERYLLIUM and cpds, as Be	1 - 4	25 - 2000	HNO_3/H_2SO_4	GFAAS	MCEF
	7105	LEAD by GFAAS	1 - 4	1 - 1500	HNO_3/H_2O_2	GFAAS	MCEF
	7300	ELEMENTS by ICP	1 - 4	Varies	$HNO_3/HClO_4$	ICP-AES	MCEF
	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	Varies	Aq Reg	ICP-AES	MCEF PVCF
	7301	ELEMENTS by ICP (AQUA REGIA ASHING)	1 - 4	Varies	HCl/HNO_3	ICP-AES	MCEF
	7303	ELEMENTS by ICP (Hot Block/HCl/ HNO_3 Digestion)	1 - 4	See Table	HCl/HNO_3	ICP-AES	MCEF
	7400	ASBESTOS FIBERS by PCM	0.5 - 16	400 - var	NA	PCM	MCEF open
	7401	ALKALINE DUSTS	1 - 4	70 - 1000	HCl	Titration	PTFE
	7402	ASBESTOS FIBERS by TEM	0.5 - 16	400 - var	NA	TEM	MCEF open
	7404	CELLULOSE INSULATION	1	NA	NA	SEM	ACF
	7500	SILICA, CRYSTALLINE, by XRD.	1.7, 2.2,2.5	400 - 1000	ash or THF	XRD	CYC + PVC
	7501	SILICA, AMORPHOUS	1.7, 2.2,2.5	50 - 400	ash	XRD	PVC (total) PVC&CYC
	7502	ZINC OXIDE	1 - 3	10 - 400	NA	XRD	PVC
	7504	VANADIUM OXIDES	1.7, 2.2,2.5	200 - 1000	THF	XRD	CYC & PVC
	7505	LEAD SULFIDE	1.7, 2.2,2.5	600 - 1000	THF	XRD	CYC & PVC
	7506	BORON CARBIDE	1.7, 2.2,2.5	100 - 1000	ash	XRD	CYC & PVC
	7600	CHROMIUM, HEXAVALENT	1 - 4	8 - 400	reagent	VIS	PVC
	7601	SILICA, CRYSTALLINE	1.7, 2.2,2.5	400 - 800	H_3PO_4/HF	VIS	CYC & MCE or PVC
	7602	SILICA, CRYSTALLINE (IR)	1.7, 2.2,2.5	400 - 800	ash	IR	CYC & MCE or PVC
	7603	SILICA in coal mine dust	1.7, 2.2,2.5	300 - 1000	ash	IR	CYC & PVC
	7604	CHROMIUM, HEXAVALENT	1 - 4	100 - 1000	NaOH/Na_2CO_3	IC	PVC
	7605	CHROMIUM, HEXAVALENT by IONCHROMATOGRAPHY	0.1 - 4	1 - 400	NaOH-Na_2CO_3	IC	PVC
	7700	LEAD in Air by Chemical Spot Test	2	10 - 240	NA	Spot	MCEF
	7701	LEAD BY ULTRASOUND/ASV	1 - 4	20 - 1500	HNO_3	Port ASV	MCEF
	7702	LEAD by Field Portable XRF	1 - 4	570 - 1900	NA	XRF (port)	MCEF
	7703	CHROMIUM, HEXAVALENT by Field-Portable Spectrophotometry	1 - 4	10 - 1200	$(NH_4)_2SO_4$/ NH_4OH	VIS	PVC, MCE, PTFE
	7900	ARSENIC & compounds, as As	1 - 3	30 - 1000	$HNO_3/H_2SO_4/HClO_4$	HYAAS	MCEF
	7901	ARSENIC TRIOXIDE, as As	1 - 3	30 - 1000	HNO_3/H_2O_2	GFAAS	MCEF
	7902	FLUORIDES, aerosol & gas	1 - 2	12 - 800	NaOH	ISE	MCEF & pad w/ Na_2CO_3
	7903	ACIDS, INORGANIC	0.2 - 0.5	3.0 - 100	HCO_3^-/CO_3^{2-}	IC	SG(washed)

Chemical	Meth No.	Method Name	Flow Rate (L/min)	Vol. (L) min max	Extraction	Analytical Technique	Sampler
	7904	CYANIDES, aerosol and gas	0.5 - 1.0	10 - 180	KOH	ISE	MCEF & BuB
	7905	PHOSPHORUS	0.01 - 0.2	5 - 100	xylene	GC-FPD	Tenax GC
	7906	FLUORIDES by IC	1 - 2	s 1 - 800 i 120 - 800	NaOH	IC	MCEF & pad w/ Na_2CO_3
	8301	HIPPURIC and METHYL HIPPURIC ACID in URINE	NA	NA	Etac	HPLC-UV	NA
	8315	TRIAZINE HERBICIDES and their METABOLITES	NA	NA	NA	SC-MSD	Urine
	8316	BUTOXYACETIC ACID in URINE	NA	NA	NA	GC-ECD	NA
	8317	ANALINE and o-TOLUIDINE in urine	NA	NA	ALK	HPLC-ECD	NA
	9000	ASBESTOS, CHRYSOTILE by XRD	NA	NA	NA	XRD	bulk
	9002	ASBESTOS (bulk) by PLM	NA	NA	NA	PLM	bulk
	9100	LEAD in Surface Wipe Samples	NA	NA	HNO_3/H_2O_2	AAS; ICP	Wipes
	9101	CHROMIUM, HEXAVALENT in settled dust	NA	NA	NA	Spot	Test strip
	9102	ELEMENTS on WIPES	NA	NA	NA	ICP-AES	Wipe
	9105	LEAD in DUST WIPES by Chemical Spot Test	NA	NA	NA	Spot	Wipe
	9200	CHLORINATED ORGANONITROGEN HERBICIDES (HAND WASH)	NA	NA	NA	GC-ECD	polyethylene bag
	9201	CHLORINATED ORGANONITROGEN HERBICIDES (DERMAL PATCH))	NA	NA	IPA/diazomethane	GC-ECD	PUF pad
	9202	CAPTAN and THIOPHENATEMETHYL in Handrinse	NA	NA	NA	HPLC-UV	Hand wash
	9205	CAPTAN and THIOPHENATEMETHYL on Dermal Patch	NA	NA	IPA-ACN	HPLC-UV	Patch

METHOD FINDER KEY TO ABBREVIATIONS

Sampling Media/Devices

A-747	Anasorb 747
A-CMS	Anasorb CMS
Ag F	Silver membrane filter
BuB	Bubbler
CCT	Coconut shell charcoal tube
Chrom	Chromosorb
CYC	Cyclone
DNPH	Dinitrophenylhydrazine Hcl
Dry	Drying tube
GFF	Glass fiber filter
GW	Glass wool
HMP	2-(Hydroxymethyl)piperidine
IMP	Impinger
IOM	Inspirable dust sampler
MCEF	Mixed cellulose ester filter
MS	Molecular sieve
NITC	1-naphthylisothiocyanate
OVS-2	OSHA versatile sampler (quartz filter/XAD-2)
OVS-7	OSHA versatile sampler (glass fiber filter/XAD-7)
Pad	Cellulose backup pad
PCT	Petroleum charcoal tube
Por	Poropak
PTFE	Polytetrafluoroethylene (Teflon) filter
PUF	Polyurethane foam
PVC	Polyvinyl chloride filter
QFF	Quartz fiber filter
SG	Silica gel
SL	Soda lime
TD	Thermalalal desorption tube
TEA	Triethanolamine
XAD	Polymeric resin

Extraction Media

aaa	acetic acid/acetonitrile
a	acid
ac	acetate
ACN	acetonitrile
acet	acetone
al	alcohol
alk	alkali
aq	aqueous / water
aq reg	aqua regia
bz	benzene
cychex	cyclohexane
DCE	dichloroethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DNPH	dinitrophenyl hydrazine
Et	ethyl
Etac	ethyl acetate
hex	hexane
HSA	hexanesulfonic acid
IPA	isopropanol
isooct	isooctane
$MeCl_2$/Meth	methylene chloride/methanol
Me	methyl
Meth	methanol
MTBE	methyl-tert-butyl ether
pet	petroleum
PMA	phosphomolybdic acid
pyr	pyridine
reag	reagent
THF	tetrahydrofuran
tol	toluene
TWM	tropolone-water-methanol

Analytical Techniques

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

Other

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

L. MEASUREMENT OF FIBERS
by Paul A. Baron, Ph.D., NIOSH/DART

Adapted from Baron [1]

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1. INTRODUCTION

Fiber-related disease has provided much of the impetus for fiber research in recent years. Asbestos has been the fiber type most commonly associated with disease. The name "asbestos" is a commercial term applied to the fibrous forms of several minerals that have been used for similar purposes and includes chrysotile, amosite, crocidolite, and the fibrous forms of tremolite, anthophyllite, and actinolite. The three primary diseases associated with asbestos exposure are asbestosis, the result of inflammation and collagen formation in lung tissue; lung cancer; and mesothelioma, an otherwise rare form of cancer associated with the lining surrounding the lungs. A current theory describing the toxicity of fibers indicates that fiber dose, fiber dimension, and fiber durability in lung fluid are the three primary factors determining fiber toxicity [2].

The dose, or number of fibers deposited in the lungs, is clearly an important factor in determining the likelihood of disease. Both fiber diameter and length are important in the deposition of fibers in the lungs and how long they are likely to remain in the lungs. Figure 1 indicates some of the factors that determine fiber deposition and removal in the lungs. Fiber length is thought to be important because the macrophages that normally remove particles from the lungs cannot engulf fibers having lengths greater than the macrophage diameter.

Thus, longer fibers are more likely to remain in the lungs for an extended period of time. The macrophages die in the process of trying to engulf the fibers and release inflammatory cytokines and other chemicals into the lungs [3]. This and other cellular interactions with the fibers appear to trigger the collagen buildup in the lungs known as fibrosis or asbestosis and, over a longer period, produce cancer as well. Fiber diameter is also important because fiber aerodynamic behavior indicates that only small diameter fibers are likely to reach into and deposit in the airways of the lungs. The smaller the fiber diameter, the greater its likelihood of reaching the gas exchange regions. Finally, fibers that dissolve in lung fluid in a matter of weeks or months, such as certain glass fibers, appear to be somewhat less toxic than more insoluble fibers. The surface properties of fibers are also thought to have an effect on toxicity. Asbestos is one of the most widely studied toxic materials and there have been many symposia dedicated to and reviews of its behavior in humans and animals [4-8].

Several techniques were used for asbestos measurement up until the late 1960s [8]. Earlier than this, it was not widely recognized that the fibrous nature of asbestos was intimately related to its toxicity, so many techniques involved collection of airborne particles and counting all large particles at low magnification by optical microscopy. Thermal precipitators, impactors (konimeters), impingers, and electrostatic precipitators were all used to sample asbestos. Perhaps the primary technique in the United States (US) and the United Kingdom (UK) during this early period was the liquid impinger, in which particles of dust larger than about 1-µm aerodynamic diameter were sampled at 2.7 L/min and impacted into a liquid reservoir [8]. After sampling, an aliquot of the liquid was placed on a slide in a special cell, particles larger than 5-µm size were counted, and the results were reported in millions of particles per cubic foot. Dissatisfaction with this approach stemmed from lack of correlation between measured particle concentration and disease in the workplace. Various indices of exposure have been developed that attempt to relate a portion of the fiber size distribution to the toxic effects. The appropriate indices for each of the asbestos related diseases as a function of fiber length and diameter (Figure 2) were suggested by Lippmann [9].

2. FIBER DIMENSIONS

Fibers are particles that have one dimension significantly larger than the other two. Fibers are often characterized or selected according to their aspect ratio, i.e., the ratio of the large dimension to one of the small dimensions. If no other criteria are used, then materials that might not normally be considered fibrous may contain a fraction of particles that meet the criteria for fibers. The distribution of fiber dimensions in a sample can usually be characterized by assuming a cylindrical geometry (i.e., the two small dimensions are identical) and measuring the length and diameter of individual fibers. The distribution of airborne fiber sizes generated by grinding bulk material or by mechanically releasing particles into the air often results in a two-dimensional (bivariate) lognormal distribution. Such a distribution is characterized by five parameters: the geometric mean length, the geometric mean diameter, the length and diameter geometric standard deviations, and a correlation term that relates length to diameter [10]. In addition, several other parameters that are a function of length and diameter, such as aerodynamic diameter, can also be characterized by a lognormal distribution [11].

Often the discussion of fibers assumes that fibers are straight objects that can be well defined by several parameters as indicated above. However, many real-world particles are not so simple to describe. In fact, the detailed features of many fibers can aid in their identification [12]. Fibers are often curved, have splayed ends, or differ in other ways from a cylindrical shape. Asbestos mineral is composed of fibrils (about 0.03-µm diameter) that are packed together. This fibrillar structure is characteristic of asbestiform minerals. When the mineral is broken apart mechanically, the material separates primarily between fibrils and the resulting fibers are usually bundles of fibrils. The ends of the fibers can be broken apart, with smaller bundles or individual fibrils spread apart, yet still be part of the fiber. Fibers can be contaminated by attachment of other dust particles, creating a complex structure with aerodynamic behavior not matching that of cylindrical fibers. The complexity of fiber shapes affects all of the measurement and separation techniques described below and frequently makes it difficult to compare one method to another.

In addition to asbestos fibers, there are many types of fibrous materials being produced for commercial purposes. These include fibrous glass, mineral wool, refractory ceramic fibers, wood and other plant fibers, and synthetic organic fibers. Most of these fibers tend to have larger diameters than asbestos fibers. On the other hand, carbon nanotubes (<0.005-µm diameter) have recently been produced in small-scale commercial quantities and because of their high tensile strength, high conductivity, and other special properties, show great promise as a commercial material [13]. Measurement techniques must be tailored to the size distribution and physicochemical properties of the fibers.

This review primarily relates to measurement of fibers in air. There are a several techniques that address concentration of asbestos and other fibers in bulk material and measurement of mass concentration of fibers [14]. One of these bulk methods, polarizing light microscopy, will be discussed below.

3. PHASE CONTRASTING LIGHT MICROSCOPE COUNTING (PCM)

As asbestos-induced disease became widely studied in the 1960s, cellulose-based membrane filter sampling was applied to asbestos sampling in combination with high magnification phase contrast light microscopy (PCM) for counting fibers. This technique involved collection of fibers uniformly over the surface of a cellulose ester filter, placing the filter or a segment of the filter on a microscope slide and making it transparent, and observing the fibers in the sample with a high magnification (~450X) phase contrast light microscope. Over the years, many researchers have endeavored to improve and standardize the PCM method. One researcher, Walton, discussed many aspects of this technique in a review [15]. The high variability of the analysis results and the method's dependence on operator technique made method improvement and research difficult. The PCM method does not measure all fibers; typically only those >0.25-µm diameter are visible and counted and only those >5 µm length are counted by protocol. Therefore, the PCM method is only an index of exposure and uses the assumption that what is detected is correlated with the fibers actually causing disease (Figure 2). The PCM method does not allow identification of asbestos fibers. This is an important limitation when the method is used in settings where fiber concentrations with a significant non-asbestos fraction may occur. This should be remembered when considering some of the parameters discussed below. The aim of evaluating changes to the PCM technique may depend on whether consistency with other

laboratories within a country or throughout the world is more important than making measurements that are more closely related to health effects. A number of factors which influence analysis results have been investigated, including the following.

a. Microscope-related parameters

Microscope magnification. The exact level of microscope magnification depends on microscope design, but most current methods use 450X (±10%) total magnification. Pang and coworkers investigated 1250X magnification to improve fiber detectability, but this has not been adopted in any established methods [16]. Pang also investigated the effect of using lower magnification (400X) and found that counts were lower for chrysotile asbestos by 25%, but that amosite fiber counts were unaffected [17].

Phase contrast optics. This contrast enhancement technique allows detection of asbestos fibers down to about 0.25 µm diameter for chrysotile and about 0.15-µm for amphiboles. Other techniques such as dark field microscopy may offer improved detectability, but also increase the background from non-fibrous particles.

Test slide to check optics. A test slide was developed to allow a check of proper alignment and magnification in the microscope [18]. This ensures a reasonable level of uniformity in microscope setup and operation, including the operator's visual perception. Improper setup can reduce detectability of fibers. There have also been cases where the optics were "too good," and results were obtained that were higher than the reference count.

Counting area in microscope field. Some early measurements with the phase contrast microscope were made using a rectangular graticule for defining the counting area, while others were made using the entire microscope viewing area. It was found that larger viewing areas resulted in lower counts, so the Walton-Beckett graticule [19] was developed that nominally gave a 100-µm diameter counting area (the area is calibrated more precisely for each microscope) and has been incorporated in all current methods.

b. Sample preparation techniques

Filter type. Virtually all measurements are made using 0.8-µm pore size mixed cellulose ester (MCE) filters. Some measurements are made using 1.2-µm pore size filters when sampling low concentrations to allow higher flow rate through the filter. Smaller pore size filters are used to ensure that fibers are deposited as near the surface of the filters as possible. This results in fibers ending up in the same plane so that they can be readily viewed with a minimum change of focus during fiber counting. Pore sizes smaller than 0.8 µm are only used with line-operated pumps because of limited suction power available with personal sampling pumps.

Selection of the liquid for making filter transparent. A liquid is placed on the filter that closely matches the filter refractive index, yet has an index that is as far as possible from that of the fibers being detected. Rooker et al. showed that refractive index difference between cleared filter and fibers translated directly into detectability of small diameter fibers [20]. A viscous solution of dimethyl phthalate and diethyl oxalate mixed with cellulose filter material was commonly used in the 1970s and early 1980s. However, it did not result in a permanent

sample, with crystallization of the mount and movement of fibers often occurring several days after sample preparation. Permanent slides were needed for quality assurance purposes and the sample preparation technique was also slow and required some skill. A rapid acetone-based filter clearing technique was developed that could be used safely in field situations [21]. After clearing, filters were coated with triacetin to surround the fibers. This resulted in a longer lasting sample (typically months to years) and is currently specified in most methods. Another technique uses a resin called Euparal to surround the fibers and results in a permanent slide preparation [22].

Filter loading. The number of fibers on the filter is usually specified to be within a certain loading range to ensure consistent counting. Cherrie *et al.* demonstrated using a serial dilution technique that counting efficiency was a function of concentration of fibers on the filter [23]. At very low filter loadings (<100 fibers/mm^2) there was a tendency to count high relative to an intermediate range of concentrations (100-1300 fibers/mm^2), where the counts were a linear function of loading. This "overcounting" was apparently due to greater visibility of fibers in a clean visual field. This effect was noted for both human counters and an image analysis system. At high filter loadings (>1300 fibers/mm^2), undercounting occurred due to overlap of fibers with other fibers and with nonfibrous particles. Most published methods indicate that optimum counting occurs within the 100-1300 fibers/mm^2 range, while some restrict the range further to less than 650 fibers/mm^2.

Fiber counting rules. The basic fiber counting rules for most current methods indicate that a countable fiber should be longer than 5 µm, narrower than 3 µm, and have an aspect ratio greater than 3:1. These rules were selected because shorter fibers were difficult to detect by optical microscopy and the 3:1 aspect ratio was used to discriminate between fibrous and non-fibrous particles in occupational settings. There has been a great deal of controversy over these rules. The use of a longer fiber cutoff, e.g., 15 20 µm, has been suggested, based on two separate arguments: first, that most asbestos fibers are relatively long and thin (with high aspect ratio) and the longer fiber cutoff would discriminate better toward fibers that were truly asbestos fibers according to mineralogical definitions [24]; and second, that fibers that enter the lungs are removed readily by macrophages if they are shorter than about 15 µm [3]. Longer fibers cannot readily be engulfed by macrophages, thus staying in the lungs for a long period and causing continuing fibrosis.

The aspect ratio criterion has also been questioned because many non-asbestiform particles have shape distributions that include particles with aspect ratios greater than 3:1. Since asbestos and other minerals often contain single crystal particles not in the asbestiform habit, it has been argued that these single crystals, or cleavage fragments, should not be counted. However, the Occupational Health and Safety Administration (OHSA) has supported the 3:1 minimum aspect ratio through legal precedent. The National Institute for Occupational Safety and Health (NIOSH) has noted that because of the great difficulty in differentiating whether individual high aspect ratio particles are cleavage fragments or asbestiform fibers, all such particles should be counted. These high aspect ratio particles may cause disease whether or not they are asbestiform.

Other aspects of fiber counting have been investigated, including how to count non-standard fiber shapes, overlapping fibers, overlapping compact particles on fibers, and bundles of fibers. Each of these factors can have a noticeable effect on the final count. Cowie and

Crawford investigated the effect of some of these factors and estimated most of them made a difference in the final count on the order of 20% [25]. Many of the methods currently in use have slight variations in their interpretation of which fibers to count and thus can contribute to variation in results between countries and organizations.

NIOSH Method 7400 contains two sets of counting rules, the A and the B rules. The A rules are used for asbestos and are consistent with counting rules in previous NIOSH methods. The A rules are required for asbestos counting by OSHA because of legal precedent in regard to the 3:1 aspect ratio rule. The A rules do not have an upper diameter limit for fibers to be counted. The B rules were introduced as an alternative to the A rules when Cowie and Crawford found that these rules agreed best with previous PCM counts, yet had improved precision [25]. The B rules have been informally adopted for use with fibers other than asbestos because these rules include the upper diameter limit of 3 µm. This upper diameter limit significantly reduces the counting of typically large-diameter fibers, e.g., glass and cellulose, that are unlikely to deposit in the lungs [26].

c. Quality assurance schemes

Sample recounts. Most methods require individual counters to recount about 10% of the field samples to ensure consistent counting procedures and alert the analyst in the case of problem samples. It is also recommended that counters have samples that are routinely recounted to ensure consistent counting within a laboratory over time.

One of the difficulties in analyzing errors made by analysts during PCM counting is that individual fields are difficult to relocate after the analyst has finished counting a slide. Differences in counts between analysts have often been ascribed to local variations in loading on the filter. Pang's development of a slide coverslip that defines counting areas on the sample solves this problem [17]. Areas on the coverslip are vacuum coated with a thin layer of gold and platinum using an electron microscope grid as a mask. This leaves defined areas on the coverslip that can be located by grid index marks. Thus, specific fields in a sample can be readily located. Using this grid mapping approach, the location, orientation and shape of each fiber can be noted and differences in counts can be reconciled on a fiber-by-fiber basis. The coverslips have been used to study fiber counting accuracy by comparing routine counting of specified fields to counts agreed upon by a group of competent counters. It was found that the principal errors for chrysotile fiber samples were due to missing fibers close to the visibility limit, while the principal errors for amosite fiber samples were caused by incorrectly sizing fiber length near the 5-µm limit. The chrysotile samples were therefore typically undercounted (negative bias), while the amosite samples had increased variability with individual counters being biased either high or low. Both these errors can be reduced by training counters with pre-counted reference slides prepared using Pang's coverslips [17] (Omega Specialty Instrument Co. Chelmsford MA). In addition, these reference slides can be used on a routine basis to ensure consistency in counting. These coverslips or modified versions show great promise for training analysts and perhaps for improving quality assurance schemes.

Interlaboratory sample exchanges. Crawford *et al.* found that use of sample exchange programs was more important in ensuring agreement between laboratories than similarity in details of the counting rules [27]. Thus, exchange of field samples between laboratories is

commonly performed to improve consistency of counting. A description of several quality assurance techniques for asbestos fiber counting is described by Abell *et al* [28]. To fulfill Method 7400 requirements for an interlaboratory sample exchange, Tombes and Calpin have described a simple approach using appropriate statistical tests [29].

Quality check samples. In order to get agreement between laboratories within a country or internationally, several programs send out identical samples to participating laboratories to assess their relative performance [30-33]. These programs provide feedback, often tied to laboratory accreditation, which provides incentive for laboratories to ensure that their performance is similar to that of other laboratories.

d. Qualitative fiber analysis

In addition to simply counting the fibers, there are techniques available for providing at least tentative identification of fiber type; use of these techniques is commonly called differential counting. Fiber shape can be used to limit the type of fiber counted. For instance, glass fibers tend to be straighter, with smoother sides than chrysotile fibers. Polarizing light techniques can also be used to identify larger diameter (> 1 μm) fibers. These are based on the optical properties of the materials, including refractive index and crystallinity. These techniques can provide quite positive identification for the presence of certain types of fibers, but are limited in application to airborne fibers because they only work for the larger diameter fibers. These techniques are often used in analysis of bulk materials [34]. The use of identification techniques is not allowed in reporting fiber counts using Method 7400 so that the results are consistent between laboratories. Considerable confusion has been caused in the past by individual laboratories using some of these identification techniques to change the counting procedure and, hence, the final results.

Several PCM fiber counting methods have been published by national [35-36] and international organizations [37-38]. Most countries have methods very similar to the ones referenced here.

e. Sampling volume for asbestos abatement applications

Sampling for asbestos after abatement requires the selection of a sampling volume so that one can have high confidence that the air meets acceptable concentration standards. The following is an example of how to calculate this sampling volume.

The approach assumes that one wishes to select sampling parameters in order to have a high degree of confidence that a target exposure standard (e.g. NIOSH REL, OSHA PEL, EPA clearance standard) is met.

Several factors need to be established in order to perform this calculation if the target exposure standard involves clearance monitoring. The U.S. Environmental Protection Agency (EPA) authorizes the use of PCM for some clearance monitoring applications and specifies that a level of 0.01 fibers/mL be met. On the method synopsis page, Method 7400 indicates that the limit of detection (LOD) for PCM analysis is 5.5 fibers/100 fields. This is based on intralaboratory variability. A major difference between Method 7400 and other analytical methods in the NIOSH Manual of Analytical Methods (NMAM) is that there is no

reference method for Method 7400. Therefore, the consensus mean is the "true" value and the interlaboratory results effectively define the method accuracy. Under the heading "Evaluation of Method, B. Interlaboratory comparability," Method 7400 provides a means of calculating the confidence limits on a single analysis result (Equations 3 and 4). From Equation 3, the interlaboratory variability at the LOD is such that the upper 95% confidence limit on a measured value is 300% greater than (or 4 times) the measured value.

Using the upper confidence limit, the equation in Section 21 in Method 7400 can be used to estimate the sampling volume.

$$\frac{\frac{\text{number of fibers}}{\text{area of 100 fields}} \times \text{total filter area}}{\text{sampling volume}} = \frac{\text{target level}}{4}$$

With the appropriate values inserted, the equation becomes

$$\frac{\frac{5.5\,\text{fibers}}{0.785\ \text{mm}^2} \times 385\ \text{mm}^2}{\text{sampling volume}} = \frac{0.01\ \text{fiber/mL}}{4}$$

Solving this equation for sampling volume gives 1080 L. This is the minimum volume that will give a result allowing a single sample to indicate compliance with the 0.01 fiber/mL limit with 95% confidence. It requires that the sample give a result less than or equal to the LOD or 5.5 fibers per 100 fields. A higher fiber count may still indicate that the concentration meets the target level, but not with the same level of confidence. This is likely to be a conservative estimate of concentration and additionally ensure compliance with the standard because the fiber concentration is low and, as indicated above, low fiber loadings are usually overestimated. However, the background concentration of non-fibrous dust on the filter also must be low to ensure that fibers are not obscured.

f. Other techniques

Since fiber counting by human analysts produces relatively high biases and variability, several researchers have attempted to develop automated counting systems. With the increases in computer power over the last 25 years, it has been tempting to assume that fiber counting is a solvable problem and significant efforts have been made to develop such a system. The most intensive effort to produce a fiber counting system was carried out by Manchester University in collaboration with the Health and Safety Executive in the UK [39]. The Manchester Asbestos Program (MAP) was able to give reasonably good agreement with human counters for certain types of samples. It was used as a reference analyst for the US and UK reference sample programs for several years. Eventually, the MAP was dropped as the reference because it was not sufficiently consistent for all types of samples.

The principle problems with image analysis of asbestos fibers include: the complexity of many fiber shapes, including bundles, agglomerates, and split fibers; the fibers often go in and out of the plane of focus; the background includes many particles and other non-fibrous shapes; the phase contrast optics produces haloes around particles in the sample that can be detected as fibers; and finally, and perhaps most importantly, the contrast between the fibers and background is poor and many fibers are near the detection threshold. An evaluation of the MAP program indicated that a significant fraction of the fibers were misidentified as multiple fibers, not detected at all, and groups of compact particles or edges of large particles were detected as fibers [40].

Inoue and coworkers have more recently developed image analysis software using a microprocessor-based PC [41]. Initial tests indicate that it works approximately as well as human counters. Inoue also evaluated how well human counters and the image analyzer did in detecting the same fibers in a sample and found that only about 50% of the fibers were consistently counted by all counters, so the image analysis system did approximately as well as the human counters [42]. Further testing of the image analysis system is needed.

In addition to image analysis, optical microscopy can be enhanced using a personal computer to more easily observe the image and to mark and measure fiber dimensions, with automatic recording of the fibers counted [43]. This does not appear to improve the counting accuracy since the analyst still decides which fibers are to be counted.

4. POLARIZING LIGHT MICROSCOPY (PLM) OF BULK MATERIALS
(Adapted from Baron [44])

The asbestos fibers in bulk material can be released and become airborne when the bulk material is disturbed. For this reason, it is desirable to measure the asbestos content of bulk samples. PLM is often used to determine the percent asbestos in bulk material. The EPA [45] has defined asbestos containing material (ACM) as material containing more than 1% asbestos using the PLM method, which effectively estimates concentration by area observed. Some confusion exists regarding the units of asbestos percentage. EPA originally indicated that the limit for ACM was 1% by mass [45], but because of the difficulties in determining corrections for differences in material density and in determining particle volumes, the limit was changed to 1% by area as determined by the PLM method [46]. OSHA does not specify units for percent asbestos in its regulations [47].

Several PLM techniques are used for identifying fiber type as well as semi-quantifying the percent fibrous material (usually asbestos) in a sample [48-52]. These techniques depend on particle shape, the refractive index, and other optical properties of individual particles. Many of these PLM techniques require visual observation of color in the fiber and become less reliable for fibers thinner than about 1 µm [53].

a. Sampling

Several procedures have been suggested for obtaining representative bulk samples of ACM in a fashion that prevents unnecessary exposure to asbestos aerosol [54-56]. Representative sampling of commercial ACM materials is often problematic; these materials may vary significantly in asbestos concentration between nearby locations and even at different depths

at the same location. Sampling from multiple locations and compositing samples helps improve the likelihood of obtaining a representative sample.

The material should be wetted or sealed during sample removal. A small coring device, such as a cork borer, can be used to obtain a sample from the full depth of the material. At least three samples per 1000 ft^2 of ACM should be taken [45]. The sample should be placed in a well sealed, rugged container. Finally, the sampled area should be repaired or sealed to minimize further fiber release.

Surface sampling has been proposed by several groups, but there is no relationship between airborne fibers and those found on surfaces [57]. Therefore, surface sampling for fibers is not recommended.

b. Sample preparation and analysis

Sample preparation for a PLM analysis involves grinding the material to the optimum particle size range (1-15-µm diameter) and dispersing the particles in a liquid of known refractive index on a glass slide [51]. Particle size uniformity in the prepared sample is extremely important. A few large chunks of material may contain more asbestos than hundreds of much smaller particles. Friable material, i.e., that which is crumbly or can be crushed by hand, may readily release fibers and is considered more hazardous. Friable materials are generally easier to prepare for analysis than some other ACMs, such as vinyl asbestos floor tiles, which may require dissolution or ashing of the matrix material so that the fibers are separated and visible in the microscope. Before and after preparation, the sample is observed with a stereomicroscope at 10-100X magnification to evaluate sample uniformity and observe whether fibrous material is present.

Some materials that interfere with accurate fiber identification either by their similarity or by covering up the fibers can be removed by physical treatment of the sample. For instance, organic materials, such as cellulose fibers or diesel soot can be removed by low temperature, oxygen-plasma ashing [58]. Leather fibers and chrysotile have a similar appearance and refractive index. The leather can be removed by ashing at 400°C [59].

Fiber morphology, i.e. the structure and shape of the fiber, can be used to assist in its identification. Morphology of fibers can give some indication of fiber type. For instance, chrysotile fibers tend to be curly, while amphibole fibers are straight, especially when they are shorter than 50 µm. Asbestos fibers often have frayed or split ends, while glass or mineral wool fibers are typically straight or slightly curved with fractured or bulbous ends. Many plant fibers are flattened and twisted, with diameters between 5-20 µm. Note that it is not recommended to base identification solely on morphology.

Fiber refractive index and other crystalline properties can be used to identify fiber type with reasonable certainty. Several techniques for determining these properties can be used in a polarizing light microscope. When viewed in the microscope with crossed polarizing filters, isotropic (isometric or amorphous) fibers appear consistently bright when rotated, while anisotropic (uni- or biaxial crystal structure) fibers appear bright, but disappear when rotated to their extinction angle, which is a function of crystal structure. Thus, amorphous materials such as glass or mineral wool fibers can easily be discriminated from asbestos.

During PLM analysis, fibers are immersed in a fluid selected to have a known refractive index. When a fiber has a larger refractive index than the surrounding fluid medium, the bright halo (Becke line) around that fiber appears to move into it as the microscope focus is raised; when the fiber has a smaller refractive index, the Becke line move out of it. Placing the fibrous material into several different refractive index fluids allows the fiber refractive index to be bracketed.

Dispersion, or refractive index change with wavelength, of a fiber can be used for identification. When particles are placed in a liquid whose dispersion is different from that of the particle, the particle may exhibit a color caused by the refraction of light. This technique requires the use of special "dispersion staining" optics. By using several refractive index liquids in series, the refractive index and the dispersion of the fiber can be established and compared with those of standard materials or published data [12].

Once the sample has been uniformly dispersed on a slide in the appropriate refractive index liquid, specific fiber types, e.g., asbestos, can be identified and the percent fibers estimated. Two approaches are typically used: visual comparison with prepared reference slides or pictures and point counting. When attempting to estimate whether a material is ACM (i.e., > 1% asbestos), the visual comparison technique is adequate when more than about 10% of the particles observed are asbestos. Point counting is used for lower concentration samples to provide higher accuracy [60]. It involves observing 400 or more randomly selected "points" (identified with a reticle crosshair) in the sample. The number of points containing asbestos is divided by the total number of points observed to give the percent asbestos. A combination of these approaches balances the analysis time and accuracy of the results [61].

PLM also can be used for qualitative analysis of air sample filters by collapsing the filter and using low temperature plasma etching of the surface to expose the fibers. Various refractive index liquids can then be placed on the etched surface to surround the fibers, allowing techniques noted above to be used [53]. The smallest fibers that can be identified by this method are about 1-μm diameter.

c. Accuracy

PLM analysis is primarily used for qualitative identification of fiber type. Accurate identification of asbestos and other fibers requires proper training in the crystallographic properties of particles as well as training and familiarization with the PLM. As with fiber counting, a laboratory quality assurance program is necessary to ensure consistently accurate results. The National Voluntary Laboratory Accreditation Program (NVLAP) operated by the National Institute for Standards and Technology (NIST) inspects laboratories for proper practice as well as providing unknown samples four times a year to check their performance in fiber identification. Under a predecessor to this program, approximately 350 laboratories correctly classified 98.5% of the samples as asbestos and correctly identified the specific asbestos types in approximately 97% of the samples. A blind test of 51 laboratories resulted in 97.5% correct classifications and 79.1% correct identifications [62]. The American Industrial Hygiene Association Proficiency Analytical Testing Program provides similar PLM audit samples to laboratories. Some common interferences for bulk analysis by PLM include sepiolite, vermiculite, and cleavage fragments of non-asbestos amphiboles.

PLM has been cast in a quantitative measurement role by the EPA requirement of determining whether a school building material meets the 1% asbestos level defining ACM. Many variables including particle size, density and shape are not adequately controlled or measured in the analysis and contribute to errors in the percent mass estimate. Thus, PLM analysis is at best a semi-quantitative technique.

Chatfield indicated that the accuracy of PLM for low concentrations of asbestos was poor and described a set of procedures that concentrated the asbestos into a weighable fraction [63]. An EPA report describes, in addition to the PLM and Chatfield's gravimetry methods, a TEM and an X-ray diffraction method for bulk analysis of asbestos [63]. NIOSH Method 9000 describes an X-ray diffraction method for chrysotile.

5. ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) has not been the focus of as much method development as either light microscopy or transmission electron microscopy (TEM). PCM found favor because of the low equipment cost and lower training level required for analysis. TEM is preferred for environmental and research studies because it offers the highest resolution and the most positive identification capabilities. TEM allows visibility of all asbestos fibers down to the individual fibrils, electron diffraction for crystal structure identification, and energy dispersive x-ray analysis for elemental measurement. SEM has intermediate resolution, with many instruments of this type not able to see all asbestos fibers. However, many modern SEMs have the capability of detecting asbestos fibrils, though contrast with background may be poor for some fiber types, especially if a high contrast substrate is not used. Energy dispersive x-ray analysis is also available for many SEMs, providing some qualitative information of fiber type. However, since electron diffraction typically cannot be performed by SEM, this often leaves open the question of positive identification of fibers.

6. SCANNING ELECTRON MICROSCOPY (SEM)

Particles are observed in the SEM when a beam of electrons is focused onto the sample surface and scanned over an area. The electrons are scattered from the surface and detected above the surface synchronously with the beam scan rate and an image of the scanned surface is created. Thus, the SEM measures the surface of particles on a substrate. The best image can be obtained on conducting objects deposited on a smooth, conducting substrate. Particles are often deposited on aluminum or carbon planchets that fit directly into the SEM or onto polycarbonate membrane (track-etched, Nuclepore®) filters. The samples are usually coated with gold or carbon to increase conductivity.

There have been some SEM methods developed for fiber counting [65-68]. These methods are primarily used for inorganic man-made fibers that have larger diameter fibers than can occur with asbestos. Thus, all the fibers are potentially visible using the SEM.

7. TRANSMISSION ELECTRON MICROSCOPY (TEM)

The transmission electron microscope (TEM) allows detection of particle shape and structure down to the smallest asbestos fibers (Figure 2) and can be used to determine crystal structure from electron diffraction as well as determining elemental composition from energy

dispersive x-ray analysis. Although TEM analysis is potentially very powerful and accurate, the process of sample collection and preparation and details involved in sample analysis can degrade the quantitative accuracy of the technique. Several more specialized techniques, such as electron energy loss spectroscopy and secondary ion mass spectrometry, have been used for analyzing particles and can also be applied to fibers [69].

Airborne fiber samples for TEM analysis are typically collected onto a filter, usually a polycarbonate membrane or MCE membrane filter. For the latter filter type, the filter is chemically collapsed to form a smooth upper surface on which collected fibers are trapped. Sometimes the surface is etched using a low temperature asher to expose the fibers collected on or near the surface of the original filter. The filter is coated with a carbon film that entraps fibers exposed on the filter surface and the filter material is then dissolved away. The carbon film is transferred to a TEM grid (usually 3-mm diameter) and the sample can be placed in the TEM for analysis.

For Method 7402, the surface is not ashed because some fibers, e.g., cellulose, may be removed and give an inaccurate total fiber count [58]. Ashing can thus affect the measurement of the asbestos fiber fraction.

The above approach to preparing MCE filters for TEM analysis is called the direct-transfer approach, since fibers are transferred to the carbon film with minimum disturbance to the way they were collected. An alternative technique is to dissolve the entire filter in liquid, ultrasonicate the suspension to disperse the particles, and deposit an aliquot of the particle suspension onto a polycarbonate filter for final transfer to the carbon film. This is called the indirect transfer technique. With the indirect technique, the optimum particle loading of the TEM sample can be obtained and soluble particles can be removed from the sample. However, the suspension process can change the apparent size distribution of the particles and fibers by breaking apart agglomerates or even breaking apart asbestos fibers into smaller fibers or fibrils [70]. The breakup problem can be especially severe for chrysotile, causing a large increase in fiber count. Quality assurance is especially important with TEM analysis of fibers. The NVLAP program provides quality assurance accreditation for laboratories performing TEM analysis using the Environmental Protection Agency's Asbestos Hazard Emergency Response Act (AHERA) method. Note that data provided under the AHERA method, because of significant differences in counting rules, the types of structures counted as asbestos, and the size range of fibers, cannot be directly compared with counts by Methods 7400 or 7402.

The process of sample collection and preparation is a complex one that can introduce biases into the final measurement. Since only small portions of the filter are measured during TEM analysis, sampled fibers that deposit non-uniformly onto the filter due to inertial, gravitational, and electrostatic effects will be measured inaccurately [71]. Fibers that penetrate the filter surface and are not transferred to the carbon film will be lost. If the filter is incompletely dissolved away from the carbon film, the sample will be difficult to analyze.

Many of the sources of bias and variability noted in sampling and counting by PCM also apply to TEM analysis. Fiber counting in a TEM can also introduce biases and variability in the final result. There is a tendency to use the high magnification of the TEM to look for the smallest fibers, while ignoring some of the larger ones. Even so, fibers shorter than 0.5 µm tend to

be missed because they are difficult to see in the background clutter of the sample [72]. Taylor et al. found that TEM counting gave poorer precision than counting the same sample by PCM and recommended that the fraction of asbestos fibers counted by TEM be applied to the PCM count as indicated in Method 7402 [73]. This combined PCM/TEM approach gave better precision than counting by TEM alone.

In addition to recognizing fibrous shape and structure of the several asbestos minerals, qualitative analysis of fibers by TEM primarily involves two techniques, energy dispersive x-ray analysis and electron diffraction. X-ray analysis produces responses for each of the elements (typically atomic number > 6, but is instrument dependent) present in a particle; the responses occur as peaks in an energy spectrum. Specific asbestos minerals can be identified using peak intensity ratios observed in standard samples and as specified in the method.

The crystal structure of individual fibers is evaluated using electron diffraction. Focusing the TEM electron beam on a single fiber produces a diffraction pattern consisting of a number of spots. The spot locations depend not only on the particle crystal structure, but also on the geometry of the electron beam optics and other instrumental parameters. The diffraction spot locations relative to one another give a very specific identification of crystal structure. For easily recognized minerals, such as chrysotile, the visual identification of the diffraction pattern is often sufficient. However, to identify fibers not fitting the x-ray analysis pattern for standard asbestos minerals, careful measurement, or indexing, of the diffraction spots is important.

The combination of x-ray analysis and electron diffraction gives a highly definitive identification of specific minerals. However, as with any analytical methods, there are exceptions that require greater expertise to recognize potential interferences. Some minerals that are difficult to differentiate from regulated asbestos minerals include non-regulated amphiboles and fibrous talcs. There are several established methods for analyzing fibers, especially asbestos fibers, by TEM [45, 74-77].

8. OPTICAL DETECTION (LIGHT SCATTERING)

Two types of light scattering detectors are commonly used for measuring airborne dust concentrations: the optical particle counter (OPC), which detects and counts individual particles, and the photometer (sometimes called a nephelometer), which detects the scattering from all particles in a defined detection volume. A standard OPC was used to detect asbestos concentrations in a workplace where the aerosol was primarily fibrous and good correlation with fiber counts was obtained [78]. A nephelometer may also be used, but may have an even greater interference from non-fibrous dusts.

The fibrous aerosol monitor (Model FM-7400, MIE, Inc. Bedford MA) used an electrostatic alignment technique by applying a field that aligns and rotates individual fibers in a laser beam. The light scattered from the fibers uniquely identified the presence of individual fibers. This allowed specific detection of fibers [79] and was even used to measure fiber length [80].

Several field tests have indicated that the fibrous aerosol monitor agrees reasonably well with field measurements of fibers by phase contrast microscopy, though mostly at concentrations above ambient levels. It has been used at abatement sites to provide rapid feedback and ensure acceptable containment of airborne fibers during asbestos removal.

9. FIBER CLASSIFICATION

Several devices have been used to measure or separate fibers by diameter. A spiral centrifuge was used to separate fibers and reference spherical particles to estimate fiber aerodynamic diameter [81]. It was found that the aerodynamic diameter was directly proportional to physical diameter, proportional to the square root of the fiber density, and proportional to fiber length to the $1/6^{th}$ power. For mineral fibers having a density of about 3 g/cm^3, the aerodynamic diameter was approximately three to five times the physical diameter of the fiber. Behavior of glass fibers in a cascade impactor was investigated by Burke and Esmen [82]. A small correction to the aerodynamic diameter was developed to take into account interception of longer fibers with the impaction surface. An inertial spectrometer was used to measure fiber aerodynamic diameter and good diameter separation was achieved [83]. Baron and Deye developed a technique for separating fibers by length using dielectrophoresis [84, 85]. This technique was also shown to be useful for measuring fiber length and diameter distributions [86].

As with most airborne dusts, fiber settling will reduce the number of larger diameter fibers in a distribution as the distance from the source of the dust increases. Esmen et al. showed that average fiber concentration in workplaces decreased exponentially with an increase of fiber diameter, indicating that the larger diameter fibers settled out more quickly than smaller diameter fibers [87]. Cyclones, impactors and porous foam classifiers were evaluated for efficiency of removing airborne fibers not likely to deposit in the lungs [88].

The aerodynamic diameter of fibers is dependent primarily on fiber physical diameter and fiber density, with a minor dependence on fiber length [89]. The diseases caused by asbestos fibers are lung diseases and so it makes sense to measure only fibers that can enter the lungs, i.e., thoracic fibers. Identical conventions for thoracic samplers have been published by ISO, ACGIH [90], and CEN. Baron [89] showed that sampling fibers with a thoracic sampler was approximately equivalent to counting only mineral fibers with a physical diameter smaller than 3 µm. Jones et al. [91] reported that there appeared to be no impediment to using a thoracic sampler for fiber sampling; they found that several samplers matched the thoracic convention, the sample collected by these samplers could be analyzed by standard methods, and that field studies indicated equivalence to the current method. Maynard [92] also found that there appeared to be no variation in penetration through these samplers as a function of fiber length. The advantage to using a thoracic sampler, apart from adhering to conventional sampling practice, is that it would remove larger compact particles and fibers from the sample and result in a cleaner sample. Although current US practice does not use an upper diameter limit for asbestos fibers, such a limit is commonly used for man made fibers. Except for the United States, all national and international organization methods use an upper diameter limit of 3 µm for fiber counting of asbestos fibers.

It is likely that thoracic sampling will eventually be in routine use for measurement of asbestos and other fibers. This approach has several advantages. It places the fiber method in line with other dust sampling conventions. It removes some of the larger particles in the sample, resulting in a cleaner sample for the analyst. It removes the need for determining fiber diameter during counting and it is consistent with previous practice of using an upper diameter limit of 3 µm for fiber counting in some methods. Thoracic sampling has the disadvantage of requiring the flow rate for a specific sampler to be fixed. This reduces the flexibility to target the loading of the filter by adjusting the flow rate. However, several classifiers can be designed to operate at selected flow rates to allow some flexibility in sampling.

10. CONCLUSIONS

The capability for measurement of fiber size distributions is available through microscopy and, to a much lesser extent, through direct-reading instrumentation. Because of differences in counting rules, resolution capability, and ability to distinguish asbestos from interfering particles or other fibers, PCM, PLM, SEM, and TEM methods often do not produce results which are directly comparable. The traditional methods of microscopy are relatively inaccurate when compared to chemical analysis methods for most other analytes because of the many sources of error in the sampling and analysis procedure. To improve laboratory-to-laboratory agreement, counter training and quality control, including the exchange of samples among laboratories and proficiency testing, are important. Implementation of training through the use of Pang's coverslips allows investigation of counting errors and potential improvement of PCM counting accuracy. Thoracic sampling could eliminate interfering particles and thereby improve measurement methods in the future.

11. FIGURES

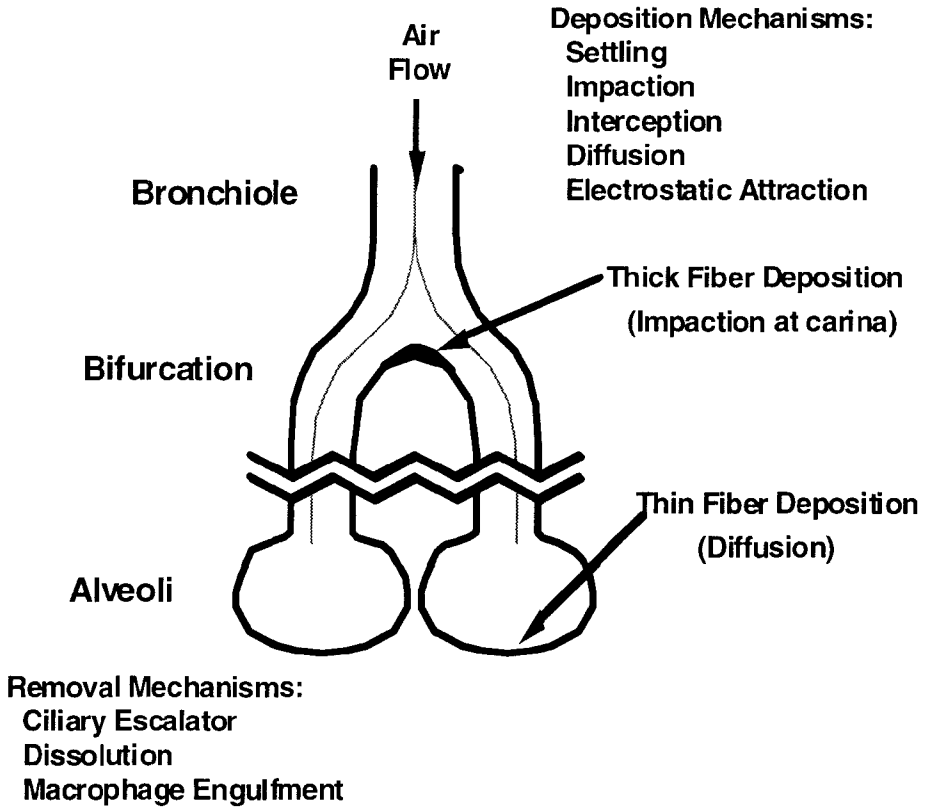

Figure 1. Schematic of mechanisms that affect fiber deposition and retention in the lungs. The deposition depends on all the indicated parameters in a complex fashion. However, larger diameter particles are affected more by gravitational settling, impaction, and interception, resulting in greater deposition further up in the respiratory tract. The saddle points, or carinae, in the branching respiratory tree are often a focal point for deposition of larger diameter fibers. Smaller diameter particles are affected more by diffusion and can collect in the smaller airways and gas exchange region (alveoli). Particle removal from the lungs is primarily effected by the cilia coating the non-gas exchange regions of the lungs; the cilia push mucus produced in the lungs and any particles trapped in the mucus out of the lung and into the gastrointestinal tract in a matter of hours or days. Some fibers are sufficiently soluble in lung fluid that they can disappear in a matter of months. Finally, white blood cells or macrophages roam the gas exchange regions and ingest particles deposited there for removal through the lymph system. Human macrophages are approximately 17 µm in diameter and can only ingest particles smaller than they are. Therefore, thin fibers are likely to deposit in the gas exchange region and, of these, the long insoluble fibers can remain in the lungs indefinitely.

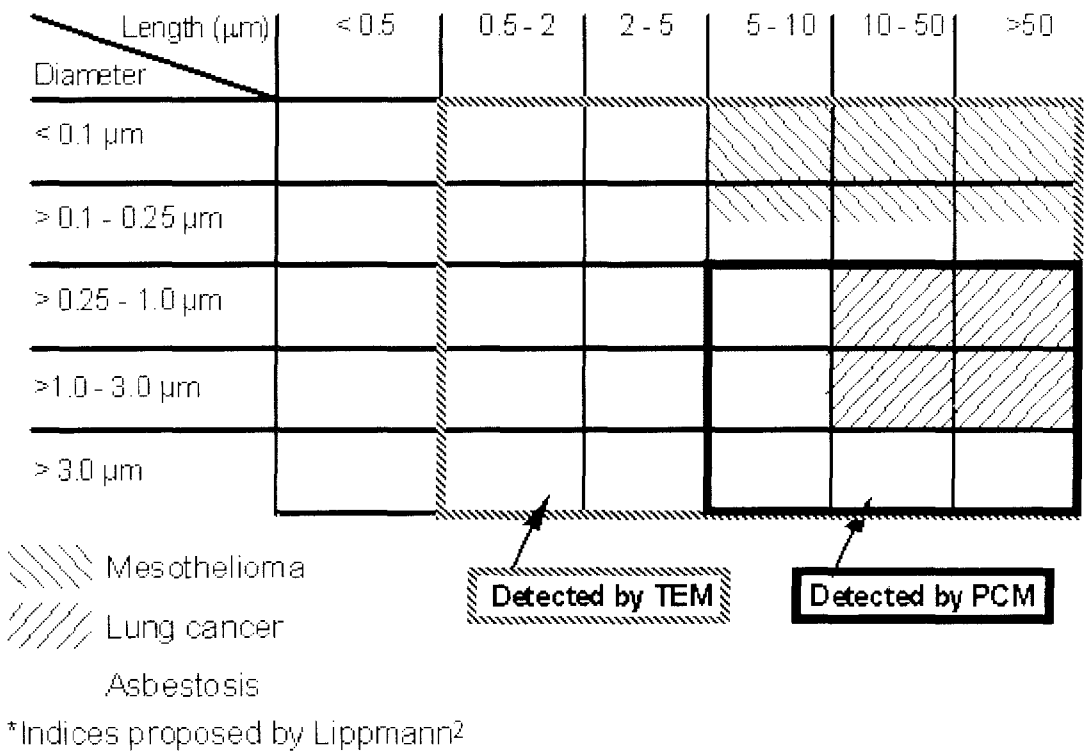

Figure 2. Comparison of proposed size ranges of asbestos fibers causing specific diseases compared with the fiber sizes detected using TEM and PCM techniques.

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M. SAMPLING AND ANALYSIS OF SOLUBLE METAL COMPOUNDS

by Kevin Ashley, Ph.D., NIOSH and Richard Fairfax, CIH, OSHA

Much of this chapter was adapted from: Fairfax, R and Blotzer, M [1994] TLVs-Soluble and Insoluble Metal Compounds [1], and Ashley, K [2001] International Standards for the Extraction of Metal Compounds Having Soluble Threshold Limit Values [2].

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1. INTRODUCTION

Workplace exposure standards have been established for several soluble metals and metalloids to take into account the increased bioavailability of some metal compounds. Exposure standards for soluble compounds can be up to 500 times lower than the exposure standards for less soluble compounds for the same metal. However, there is often confusion among chemists, industrial hygienists, and laboratories over what is meant by "soluble" when the metal species, extraction fluid, or solubility conditions are not specified in the exposure standard nor in the supporting exposure standard documentation [1]. In addition, the metals and metal compounds may interact chemically or physically with the sampling media or with each other. Such complications can affect the stability and speciation of the metals and their compounds, and must be addressed in order to obtain meaningful results. These issues are becoming more important in workplace airborne metals exposure monitoring.

The solubility of a metal will depend on the chemical form of the metal, the fluid used to extract the metal, and the conditions under which the extraction occurs (e.g., temperature, volume, time). Unfortunately, the degree of method specificity needed to obtain measurements that are reproducible among laboratories is generally either missing or is subject to a variety of interpretations from exposure standards and supporting documentation. The need for a better definition of what is meant by the term "soluble" in relation to exposure standards was first raised in 1994, but to date no significant improvement has occurred within United States exposure standard setting organizations. Therefore, to meet the needs of analysts, laboratories, and laboratory clients for better definition of the analyte of interest, and to improve measurement reproducibility among laboratories, various organizations are attempting to achieve international consensus on extraction of soluble metal compounds. New guidelines have been promulgated in an International Standard, [3] and this will serve to fill the void and improve the situation.

2. SOLUBLE AND INSOLUBLE METAL COMPOUNDS

The *American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs)* [4] list metals and metalloids having soluble TLVs; updates are published annually. Those from 2002 are listed in Table 1. For most of these elements, the TLVs for the soluble compounds are lower than for the corresponding insoluble forms (Aluminum [Al], Silver [Ag], Hexavalent Chromium [Cr^{VI}], Molybdenum [Mo], Nickel [Ni], Platinum [Pt], Rhodium [Rh], Tungsten [W]), while for the remainder (Barium [Ba], Iron [Fe], Thallium [Tl]) the TLVs for soluble and insoluble compounds are the same [3]. Several countries (e.g., France, Germany, UK, USA) have also adopted workplace exposure standards for various soluble metal compounds.

TABLE 1. METALLIC ELEMENTS FOR WHICH SOLUBLE COMPOUNDS HAVE BEEN ASSIGNED TLVs.[3]

Element and Soluble Compounds Thereof	TLV, Time-Weighted Average (mg/m^3)
Aluminum - Soluble salts, as Al	2
Barium - Soluble compounds, as Ba	0.5
Chromium - Water-soluble Cr^{VI} compounds	0.05
Iron - Soluble salts, as Fe	1
Molybdenum - Soluble compounds, as Mo	0.5
Nickel - Soluble compounds, as Ni	0.1
Platinum - Soluble salts, as Pt	0.002
Rhodium - Soluble compounds, as Rh	0.01
Silver - Soluble compounds, as Ag	0.01
Thallium - Soluble compounds, as Tl	0.1
Tungsten - Soluble compounds, as W	1
Uranium - Soluble compounds, as U	0.2

Solvent The term "solubility," as used by analytical chemists, ordinarily pertains to the dissolution of a material in pure water [5]. The subject of water solubility of metal compounds is covered in several references [5-8]. According to *Patty's Industrial Hygiene and Toxicology* [7] and the individual TLV documentation for these metals [6], the solubilities of metals and metal compounds are quite variable depending upon the solvent. Other pertinent references sustain the notion that solubility, regarding metals and their compounds, is generally identified in terms of their solubility in water [6]. The solubility and insolubility of numerous inorganic substances are presented in the Appendix. What is meant by "soluble" depends on the operational definition employed for the extraction conditions desired by the investigator.

Temperature. Temperature is another variable that directly affects solubility. Most current analytical methods specify deionized water, but not water temperature (some procedures call for hot water (37°C), but others use water at room temperature). Some important questions thus arise:

a. If using deionized water, should chemists assure that water temperature has been

heated to body temperature (i.e., 37°C)? For TLV purposes, should solubility be based upon body temperature?

b. Should the TLV documentation specify that analytical procedures use extraction media heated to body temperature?

3. HEALTH EFFECTS

From a health perspective, the solubility of a metal or metal compound is not the only consideration of interest. Ultimately, the most important consideration is the extent to which such soluble metals accumulate in body fluids or target organs, leading to toxic levels of the metal ion. This is of more concern than solubility in water, acids, or alkalies per se. Further complicating the solubility issue is the fact that the term "soluble" may have different meanings among industrial hygienists and chemists. Chemists generally use the term "soluble" as defined by the *CRC Handbook of Chemistry and Physics* [5]. According to the *Handbook*, a material is considered soluble if a saturated solution in water (at 25 °C) contains more than 1% (m/v); any material in which 1 percent or less is dissolved is considered insoluble. Unfortunately, a material listed as insoluble, using the CRC definition, could still dissolve in body fluids and produce a significant tissue concentration which is biologically detrimental. The point is that an occupational exposure limit (OEL) for an "insoluble"compound may not be sufficient to protect exposed workers. When asked in an informal poll to choose a solvent in which to measure the relative solubility of metals, industrial hygienists chose, in order of preference, water, body fluids, and a petroleum solvent [1].

Body Fluids. When considering the biological effect of the solubility of a material, we should ideally first consider body fluids. However, body fluids vary considerably in pH. For example, the pH of the stomach is acidic, the pH in the intestine is alkaline, the pH of blood serum is approximately neutral, some macrophages are highly acidic, and the pH of saliva is slightly acidic. Furthermore, body fluids contain a variety of solutes, including salts and polypeptides (proteins). Polypeptide molecules can wrap around metal ions in solution and often contain functional groups that can chelate metals. Polypeptides have strong chelating ability in body fluids and will account for the considerable difference between the solubility of a metal in body fluids versus that same metal in water. Metals, in turn, are bound to different proteins, depending upon where in the body they are located at a given time. In passing through the body, a metal ion is bound by different polypeptides. For each of them, a different reaction may be involved. Some reactions may increase or decrease the toxicity of the metal ion.

Because of the effect of proteins, pH, and other solutes in body fluids, the solubility of a metal compound in body fluids will be quite different than the metal's solubility in water [9].

4. SAMPLING CONSIDERATIONS

Filter Reactivity. The filter medium used must not react with the airborne particulate collected by the sampler so as to change the chemical form of the captured sample. This can occur if a soluble compound reacts with the filter material or a contaminant therein to produce an insoluble or less soluble compound. An example of this problem has been observed with silver, where a soluble silver compound, $AgNO_3$, can react with chloride in some mixed cellulose ester (MCE) or polyvinyl chloride (PVC) filters to form AgCl, which is much less

soluble in water. Thus, low recoveries of "soluble" silver will result unless an alternative filter medium, such as polytetrafluoroethylene (PTFE), is used. Another problem is illustrated by soluble forms of Cr^{VI}, which can react with the filter medium to form insoluble compounds and/or undergo reduction to Cr^{III} and, therefore, be lost to Cr^{VI} analysis. Hence, chemical compatibility issues must be investigated before samples meant for "soluble" extraction procedures are taken.

Membrane filters are appropriate for sampling aerosols for subsequent determination of soluble metal compounds. Such filters are manufactured from a variety of polymeric materials by a number of different processes. Choice of polymer material comprising the filter (e.g., MCE, PTFE, PVC) will depend on chemical reactivity issues discussed in the preceding paragraph. The metal content of the filters must be as low as possible, since it can make a significant contribution to the blank value.

5. ANALYTICAL CONSIDERATIONS

A number of analytical methods for soluble metal compounds in occupational hygiene samples have been published [10-13].

European Standard. Guidance on sample preparation methods for soluble metals and metalloids in workplace air has been promulgated recently in a European Standard [14]. In these published methods and guidelines [10-13,] two methodologies are generally favored for the extraction of "soluble" metal species: (1) extraction in pure water, or (2) extraction in diluted (~0.1 M) hydrochloric acid (HCl). In the European Standard [12,13], both strategies are given as options for the dissolution of "soluble" metals in workplace air samples. Extraction of metals and metalloids in water is meant to reflect the chemical definition of "soluble" (as mentioned above), while extraction in diluted HCl is designed to mimic the dissolution of "soluble" metal compounds in stomach acid, which is highly acidic (pH $\approx$ 1). A temperature of 37°C is recommended since this is normal body temperature.

Extraction Solvent. In a recent paper, [15] Hahn argued for the establishment of 0.1 M HCl in an operational definition for soluble metals in occupational hygiene samples and, also, specified mechanical agitation at 37°C for two hours prior to sample analysis. An exception is made for thallium, which can form insoluble TlCl, in which case HCl is replaced by diluted nitric acid (HNO_3). (A similar problem would arise if HCl were used as the extraction acid for soluble silver compounds.) The German extraction method for several soluble metal species [13] is consistent with the strategy outlined by Hahn, [15] which attempts to address bioavailability by choosing HCl as the extraction acid. However, in standard methods promulgated by the United States, [10] the United Kingdom, [11] and France, [12] deionized water is the solvent chosen in the operational definition of "soluble" for numerous metallic elements in workplace air samples. An exception to extraction in water is made for nickel, [10] where an ammonium citrate solution is specified as the leachate for soluble compounds of this element. Ammonium citrate provides buffering and chelating properties that are desirable for leaching soluble nickel compounds [11].

Operation Definitions. Operational definitions of "soluble" metal species have been promulgated for consumer products such as toys, paper products, paints and art materials [16-18]. Standard procedures for the extraction of metal compounds from consumer products are based on sample treatments in 0.07 - 0.14 M HCl (depending on the sample) for an hour

at a temperature of 37°C [15] or at room temperature [17]. An American Society for Testing Material (ASTM) procedure [16] is meant to provide an estimate of the bioavailability of several metals in art materials, using ~0.1 M HCl and extraction at body temperature.

Quantity of Solvent. Another uncontrolled variable is the quantity of solvent used in laboratory analytical procedures for soluble metals at different laboratories. Different laboratories may (and do) use different amounts of deionized water for extraction. For example, one laboratory might use 10 mL of deionized water to extract the metal from a sample, while another lab may use anywhere from 25 to 100 mL to extract the compound. Depending upon the amount of material present in the sample, the procedure using 25 to 100 mL can dissolve a larger mass of solute than that using 10 mL. A conservative analytical method for metals used 15 mL of deionized water for extraction. This volume was chosen as a convenience and may not bear any relationship to what the body might absorb. Thus, two identical samples could produce two different results depending on the volume of solvent and other analytical parameters. A further factor affecting solubility is the particle size distribution of the sample: smaller particles are ordinarily more easily dissolved than larger ones. Thus for two samples having the same mass, the sample comprised of small particles may be more easily dissolved than a sample having large particles.

6. ISO PROCEDURE FOR SOLUBLE METALS AND METALLOIDS

Various procedures for the extraction of soluble metals and metalloids have been used for years, based on different operational definitions of solubility. The International Organization for Standardization, Technical Committee 146 on Air Quality, Subcommittee 2 on Workplace Atmospheres, Working Group 2 on Inorganic Particulate Matter (ISO/TC 146/SC 2/WG 2) has attempted to standardize extraction procedures for "soluble" metal compounds by offering an operational definition in terms of a sample preparation method for metallic elements in industrial hygiene measurements.

Bioavailability. In 1994, Fairfax and Blotzer argued that the solubility in body fluids should be considered in the development of a new definition for soluble TLVs [1]. But since different body fluids have different solubility characteristics (e.g., pH, salts, polypeptides), such an operational and uniform definition for "bioavailable" cannot realistically be decided. Indeed, the meaning of "bioavailability" has been debated nationally and internationally for years, and it was not deemed practicable nor defensible to attempt to operationally define solubility based on biochemical arguments. Hence, it was decided by consensus within the ISO working group (ISO/TC 146/SC 2/WG 2) to describe procedures for soluble metal compounds in terms of strictly chemical, and not biochemical, criteria [19].

Laboratory Consistency. With regard to analytical methods for the extraction of soluble metals and their compounds, Fairfax and Blotzer suggested that the extraction media, temperature, and extraction volume should be consistent among all laboratories [1]. For an operational definition of "soluble" to be offered, delineation of these analytical parameters is necessary in order to fully standardize the extraction procedure for soluble metal species. Moreover, the apparatus used, as well as chemical compatibility issues, must be amply described. Matters that are outside of laboratory control, notably sampling, cannot always be adequately influenced; however, recommendations as to sampling media, sample handling, and transport requirements should be provided to the field industrial hygienist.

Development of ISO Procedure. The ISO working group responsible for the development of ISO 15202-2, ISO/TC 146/SC 2/WG 2, began its task in September 1995, not long after the publication of the Fairfax and Blotzer article [1]. Shown in Table 2 is a list of countries that participated in voting on the technical content of the draft international standard when it was circulated for balloting, from 1996 to 2000.

TABLE 2. "PARTICIPATING MEMBER"[1] COUNTRIES OF ISO/TC 146/SC 2 (DURING THE PERIOD OF DEVELOPMENT OF ISO 15202-2 [1996-2000])

Belgium	Korea
	Turkey
Germany	Netherlands
	United Kingdom
India	Poland
	United States
Italy	Spain
Japan	Sweden

1"Participating,"or P-Member, countries are those nations able to vote on Draft International Standards, and therefore may provide comments on the technical content of the documents during voting. "Observing," or O-Member, nations (not listed) may also offer comments and can participate in the development of ISO standards. However, in the formal ISO voting process, O-member nations can vote only on Final Draft International Standards, which allows only for editorial, and not technical, changes at this stage.

Because of the various operational definitions for "soluble" metal compounds, a significant challenge was presented to the ISO working group responsible for the development of an international standard method to describe a procedure for extracting soluble metals and metalloids for subsequent atomic spectrometric analysis. Two choices were available based on the standard methods mentioned above: (1) extraction in pure water, or (2) extraction in 0.1 M HCL. It was decided by consensus of ISO delegates present at the earlier working group meetings to follow the former course, where solubility of metal compounds in occupational hygiene samples is defined in chemical terms. This decision was upheld during the later international voting process, which involved those countries listed in Table 2. Nevertheless, text within the International Standard [3] states that individual countries may specify alternative procedures for the measurement of soluble metal species in workplace air samples. This, then, leaves open the option to use other extraction media, such as 0.1M HCl.

The ISO procedure for soluble metals and metalloids assumes that samples were collected using the new International Standard for the collection of workplace air samples for subsequent multi-element analysis, ISO 15202-1 [20]. However, the choice of filter material used for the collection of samples targeted for the "soluble" metals procedure is important. Annex A of ISO 15202-1 [20] and Annex B of ISO 15202-2 [3] provide useful guidance on this subject.

The "soluble" metals procedure described in ISO 15202-2 [2] lists all of the elements in

Table 1 except for Cr^{VI} and Fe. Nevertheless, the sample preparation protocol described in this International Standard is certainly applicable to these other two metallic elements as well. The ISO "soluble"metals method [3] calls for treatment of collected workplace filter samples in 5 mL of deionized water (or ammonium citrate leach solution in the case of Ni) and mechanical agitation in a water bath at 37 ± 2 °C for 60 min. Undissolved material is thereafter separated from the sample solution using a suction filtration apparatus or a syringe filter, and ensuring use of filtration materials that are unreactive towards the soluble metal compounds of interest. After filtration, the sample solution is acidified with nitric acid in order to stabilize the dissolved metallic elements within the extracted sample. This test sample is then ready for analysis by ICP-AES (or ICP-mass spectrometry if very low detection limits are required). Of course other analytical techniques, e.g., atomic absorption spectrometry [19,20] or electrochemical analysis [22,23] can be used as analytically equivalent alternatives.

7. SUMMARY

The exposure standards for some metals vary up to a factor of 500 to take into account the increased solubility and bioavailability of some compounds. Even compounds generally considered by chemists as being "insoluble" may have sufficient solubility in body fluids to be of biological importance. Exposure standards for soluble metals such as ACGIH TLVs are not specific with regard to extraction fluid, fluid temperature, agitation and other factors affecting solubility. Since these factors significantly affect solubility, some standardization or adoption of an operational definition is necessary if there is to be reproducibility among laboratories conducting soluble metal analyses. In some countries (e.g., nations in the European Union), the national requirements provide this specificity. In other instances, including exposure monitoring standards in the United States, formal national guidelines are not available.

Therefore, adherence to international extraction guidelines or methods such as those described in ISO standards is necessary to produce measurements that are reproducible with other laboratories, and have utility to the laboratory client when exposure standards or national guidelines are vague. ISO 15202 has the advantage over other guidelines and standards in that it has had input from more than (don't forget that "O" members also have input) 13 participating countries (Table 2). Thus the use of ISO 15202 is encouraged until either exposure standards or national guidelines provide better specificity.

Laboratories cannot recover soluble metal data if inappropriate sample media are used. Sample stability is a problem that must be addressed when sampling for silver (Ag), chromium (Cr) and other soluble metal compounds. Although the ISO procedure has not been validated for all soluble metal species, the standard recommends that method validation be carried out using representative soluble metal compounds for target elements. ISO 15202 provides guidance on sample media selection for soluble metals that can be a useful guide for industrial hygienists and other laboratory clients.

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9. APPENDIX Solubilities of Selected Metals and Metal Compounds[1]

Aluminum and compounds

Aluminum metal reacts with dilute hydrochloric acid, sulfuric acid, potassium hydroxide, and sodium hydroxide.

The salts of aluminum, including sodium aluminate, aluminum fluoride, aluminum chloride, and cryolite, are all soluble in water.

Arsenic and compounds

Arsenic Insoluble in hot and cold water; soluble in nitric acid.

Arsenic trioxide and pentoxide Soluble in cold and hot water, alcohol, alkalies, and hydrochloric acid; arsenic pentoxide is soluble in acids.

Lead arsenate Insoluble in cold water; soluble in hot water, nitric acid, and caustic alkalies.

Calcium arsenate(s) Insoluble in water and acids.

Sodium arsenate(s) Very soluble in water.

Arsenic acid Soluble in water and alcohol.

Arsenic trisulfide Practically insoluble in water.

Barium and compounds

Barium metal Insoluble in water; soluble in alcohol.

Most of the compounds of barium are soluble in (cold or hot) water, for example, barium chloride, barium oxide, barium acetate, and barium cyanide. Barium hydroxide is slightly soluble in water. Barium carbonate is insoluble to slightly soluble in water, and is soluble in acids.

Beryllium and compounds

Beryllium Slightly soluble in hot water; insoluble in cold water; soluble in dilute alkalies and acids.

Beryllium oxide Insoluble in water; soluble in some acids and alkalies.

Beryllium hydroxide Insoluble in water; soluble in acids and alkalies.

Beryllium fluoride Soluble in cold and hot water, alcohol, and sulfuric acid.

Beryllium sulfate Soluble in water and concentrated sulfuric acid.

Chromium and compounds

Chromium reacts with dilute hydrochloric acid and sulfuric acid, but not with nitric acid.

Chromium metal Insoluble in hot and cold water.

Hexavalent chromium compounds, including chromium trioxide, the anhydride of chromic acid, chromates, dichromates, and polychromates, tend to be of low solubility in water and can be subdivided into two subgroups:

1. Water-soluble hexavalent chromium compounds include chromic acid, its anhydride, and the monochromates and dichromates of sodium, potassium, ammonium, lithium, cesium, and rubidium.
2. Water-insoluble hexavalent chromium compounds include zinc chromate, lead chromate, barium chromate, and sintered chromium trioxide.

   NOTE: Depending on the reference [5,8], both calcium chromate and strontium chromate are listed as soluble and insoluble in water.

Iron and compounds

Iron, ferrous oxide, ferric oxide, and iron oxide Insoluble in hot and cold water.
Ferric chloride, ferric nitrate, ferric sulfate, ferrous sulfate and ferrous chloride Soluble in hot and cold water.
Ferric chloride Soluble in ethanol, methanol, and ether.
Ferric nitrate and ferrous chloride Soluble in ethanol and acetone.
Ferric sulfate Sparingly soluble in ethanol; insoluble in acetone.
Ferrous sulfate Ins oluble in ethanol.

Molybdenum and compounds

Molybdenum Insoluble in hot or cold water; soluble in nitric, sulfuric, and hydrochloric acids.
Molybdic oxide Sparingly soluble in water; soluble in acids and alkalies.
Molybdenum disulfide Insoluble in hot or cold water and dilute acids; soluble in hot sulfuric acid, aqua regia, and nitric acid.
Ammonium molybdate Soluble in hot or cold water, acids, and alkalies.
Calcium molybdate Insoluble in cold water; soluble in hot water.
Lead molybdate Insoluble in water and alcohol; soluble in acid and potassium hydroxide.
Sodium molybdate Soluble in hot and cold water.

Nickel and compounds

Nickel Insoluble in hot and cold water; soluble in nitric, sulfuric, and hydrochloric acids.
Nickel oxide Insoluble in hot and cold water; soluble in ammonium hydroxide and acids.
Nickel acetate Soluble in cold water; insoluble in alcohol; [4] soluble in alcohol.[7]
Nickel carbonate Soluble in cold water; insoluble in hot water.
Nickel hydrates Some forms soluble, others insoluble (in water).
Nickel sulfate Soluble in hot and cold water.

Platinum and compounds

Platinum Insoluble in hot or cold water and single mineral acids; soluble in aqua regia; attacked by halogens, alkali cyanides, and caustic alkalies.
Platinum forms are series of complex chloroplatinate salts that are water soluble.

Rhodium and compounds

Rhodium Insoluble in hot or cold water; soluble in hot sulfuric acid plus hydrochloric acid; slightly soluble in acids and aqua regia.
Water-soluble rhodium compounds include rhodium trichloride, sodium chlororhodite, and rhodium carbonyl acetylacetonate.

Silver and compounds

Silver Insoluble in water and inert to most acids; reacts readily in dilute nitric acid or hot concentrated sulfuric acid; soluble in fused alkali hydroxides in the presence of air.
Silver oxide Soluble in hot and cold water, acids, and alkalies.
Silver acetate Soluble in hot or cold water and nitric acid.
Silver bromide Insoluble in hot or cold water and nitric acid.
Silver chloride Soluble in hot water; slightly soluble in cold water and ammonium hydroxide.
Silver cyanide Soluble in cold water, nitric acid, and ammonium hydroxide.

Silver nitrate Soluble in hot and cold water.

Thallium and compounds

Thallium Insoluble in hot and cold water; soluble in nitric, sulfuric, and hydrochloric acids.
Thallous oxide Soluble in water, acids, and alcohols.
Thallic oxide Insoluble in hot or cold water; soluble in acids.
Thallous acetate and thallic chloride Soluble in cold water and alcohol.
Thallous bromide and chloride Slightly soluble in water.
Thallous sulfate Soluble in hot or cold water.
Thallous sulfide Soluble in cold water.

Tungsten and compounds

Tungsten Insoluble in hot or cold water, hydrofluoric acid, and potassium hydroxide; soluble in mixtures of hydrofluoric and nitric acid; slightly soluble in sulfuric acid.
Tungsten trioxide Insoluble in hot or cold water and acids; soluble in hot alkalies and hydrofluoric acid.
Tungstic acid Insoluble in cold water and most acids; soluble in hot water, alkalies, hydrofluoric acid, and ammonia.
Sodium tungstate Soluble in hot and cold water; slightly soluble in ammonia; insoluble in acids and alcohol.
Tungsten carbide Insoluble in water; soluble in mixtures of hydrofluoric and nitric acid, and in aqua regia.
Tungsten diboride Insoluble in hot or cold water; soluble in aqua regia.
Tungsten hexachloride Soluble in hot water.
Tungsten oxytetrachloride Soluble in hot or cold water.
Tungsten hexafluoride Soluble in hot or cold water and alkalies.
Tungsten disulfide Insoluble in cold water and in alcohol; soluble in mixtures of hydrofluoric and nitric acid.
Phosphotungstic acid Soluble in cold water, alcohol, and ether.
Ammonium paratungstate Soluble in water; insoluble in alcohol.

Uranium and compounds

Uranium Insoluble in hot or cold water, alcohol, and alkali.
Uranium dioxide Insoluble in hot or cold water; soluble in nitric acid and concentrated sulfuric acid.
Triuranium octoxide Insoluble in hot or cold water; soluble in nitric acid and sulfuric acid.
Uranium tetrafluoride Insoluble in cold water, dilute acids, and alkalies; soluble in concentrated acids and alkalies.

N. AEROSOL SAMPLING: MINIMIZING PARTICLE LOSS FROM CASSETTE BYPASS LEAKAGE

by Paul Baron, Ph.D., NIOSH/DART

Adapted from Baron [1]

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1. INTRODUCTION

The plastic two- and three-piece cassettes commonly used for collection of personal samples of airborne dust in the Americas are prone to bypass leakage if the cassettes are not properly assembled. A cross sectional view of these cassettes is given in Figure 1 [2]. If the pressure used to put the cassettes together is insufficient, or not properly applied, the base and mating piece may not make a proper seal with the filter, permitting sampled aerosol to leak around the filter as illustrated in Figure 2 [2]. Leakage around the filter will result in a loss of dust that should have been collected on the filter, resulting in a measurement that underestimates the concentration of the aerosol sampled. Anecdotal indications of this bypass leakage have cropped up from time to time, indicating that bypass leakage continues to be a problem when these cassettes are improperly assembled.

Van den Heever, in an investigation of the leakage problem, presented data on cassettes using a pressure drop measurement to indicate leakage [3]. The average pressure drop for a specific cassette/filter combination was measured for a number of "good" cassettes and then any decrease in pressure drop observed for assembled cassettes was attributed to bypass leakage. The decrease in pressure drop correlated well with reduced sample collection. Establishment of this baseline pressure drop when only assembling a few cassettes was cumbersome and a more direct measure of leakage was needed. A nylon cassette designed to replace the 37-mm cassette for the South African market was shown to have reduced likelihood of leakage; the nylon cassette had a rubber seal for the filter edge and a base that screwed to the cap.

Recently, Baron and coworkers developed and evaluated a leak test using ambient aerosol to assess bypass leakage [1, 2, 4]. The test, performed with an optical particle counter or a condensation particle counter, enabled the aerosol concentration upstream and downstream of a cassette to be measured. The specific procedure was as follows:

a. Using the optical or condensation particle counter, measure the ambient particle number concentration at the test location for a fixed time period (1-2 min). The particle counter should be capable of detecting submicrometer particles.

b. Attach cassette to be tested to inlet of the particle counter and make a second concentration measurement. Keep connections to minimum volume and leak free.

c. If the percent downstream concentration relative to ambient concentration is >1%, the cassette is poorly sealed. A value of <0.2% can routinely be achieved with a good assembly technique. The only exception appears to be for fibrous (e.g., glass, ceramic) filters without binder. The leak test still works in that a leak is detected, but fibers released from the filter cause overestimation (as much as 20-fold) of the leak rate.

The approximate cost required to setup the pressure drop leak test system is about $500 (the cost of the micromanometer), while the cost to setup the optical or particle count systems is >$1900. Although particle count systems are more expensive, they require less initial setup time and can be used for other industrial hygiene purposes, e.g., environmental monitoring and respirator fit testing (PortaCount, TSI, Inc. St. Paul, MN).

The particle leak test does not provide a direct measure of the airflow through the leak because particles contained in the sampled aerosol can be collected on the edge of the filter, on the cassette walls, or on the backup pad as illustrated in Figure 2. The particles lost from the filter can bounce or be re-entrained from the filter surface or they can stick if the particles are liquid. Therefore it is difficult to use the leak test results to predict the amount of material lost during sampling with a leaking cassette. Under a worst case scenario, the loss from the filter can be about 4 times the percent leakage by the particle count leak test. Thus, with a 1% measured leak rate, about 4% of larger (> 2 μm) solid particles can be lost in or through the leak.

Filters normally used for industrial hygiene sampling are efficient enough to collect particles from the sampled air with very high efficiency (>99.9%) [1]. Any particles detected downstream are assumed to be from leakage. The test will not work if low efficiency filters or polycarbonate straight-pore (Nuclepore) filters are used, because these will allow some particles to pass directly through the filter. Glass or ceramic fiber filters without binder will release fibers inside the leak and result in an overestimate of the leak size. With relatively large leaks using these fiber filters, the downstream concentration can be larger than the upstream concentration.

Assembly of press-fit cassettes should be performed using a press. This allows an even, selected, and repeatable pressure to be applied across the surface of the cassette. Too high a pressure will cut the filter or crack the cassette, while too low a pressure will result in a bypass leak around the filter. Approximately 70 lbs pressure was found to produce a good seal in 25-mm acrylic-copolymer cassettes [2], but optimum pressure must be established for each cassette/filter/backup pad combination. A pneumatic press designed for cassette-closing (APCSCLSR-2, about $2200, Omega Specialty, Chelmsford MA) has been used successfully for this purpose, though other pneumatic or hydraulic presses can also be used.

Tests of several manufacturer's pre-assembled cassettes indicated these are well-sealed. However, hand assembly of cassettes and even press-assembled cassettes of unusual combinations of filters and backup pads produced high rates of leakage [1]. In these cases, a quality control process including leak testing should be implemented to ensure proper cassette assembly.

The appropriate sample size for testing batches of items are described in MIL-STD-105E [5]. If leak test is treated as a pass/fail test of cassette quality, tables are available to determine

the sample size necessary to achieve an acceptable failure rate for an entire batch. For example, to achieve a one percent "average outgoing quality" (average failure rate of one percent) for a batch of 51 to 90 cassettes, a sample of 13 should be tested and produce no failures. If one or more of the 13 cassettes fail, the entire batch of cassettes must be tested or the batch discarded.

The leak test results in a small quantity of background aerosol (typically from less than 3 L of air) being collected on the filter. Field blanks should also be leak tested in the same manner to correct for this small amount of background material.

The particle count leak test should be performed prior to sampling. It was found that soot particles can clog the leak and prevent detection of particles downstream even though loss of material from the filter occurred during sampling. Thus, a negative leak test after sampling is not a guarantee that leakage did not occur. Another approach sometimes used to check for leakage after sampling is to observe the sealing area at the edge of the filter for improper compression or for particle deposits. These post-sampling tests can indicate when samples should be rejected, but are not generally recommended because they are subject to false negative results.

2. FIGURES

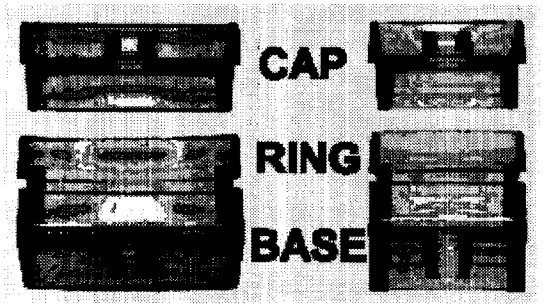

Figure 1. Picture of a 37-mm and a 25-mm cassette cut in half. The cut cassette surfaces are colored black for easier visualization. Bypass leakage can occur around the filter edge where the seal is formed [2].

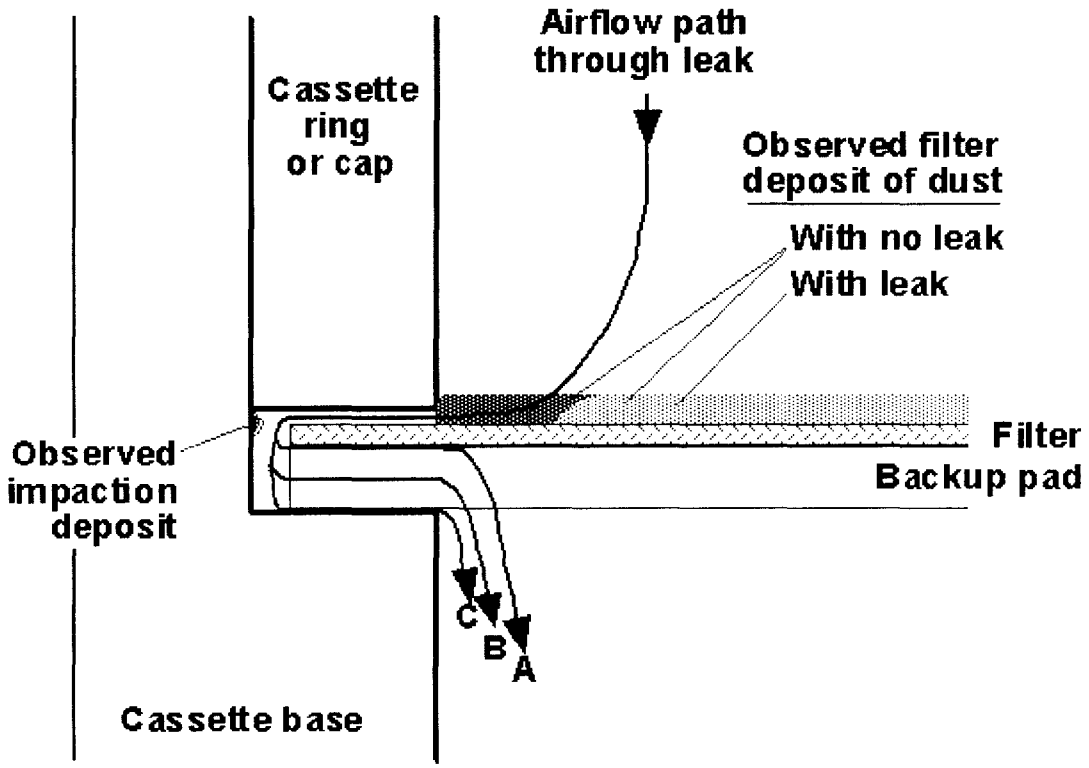

Figure 2. Schematic of filter seal region showing paths of airflow through leak. When a leak is present, the observed dust deposit indicates loss of material near edge of filter. Some of this lost material is found deposited on the cassette wall. The flow path through or around the backup pad appears to take some combination of Paths A, B, and C [2].

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O. FACTORS AFFECTING AEROSOL SAMPLING

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

This chapter adapted from Baron [1].

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1. INTRODUCTION

The American Conference of Governmental Industrial Hygienists (ACGIH) [2], the International Organization for Standardization (ISO) [3], and the European Standardization Organization (Comité Europeén de Normalisation, CEN) [2,3] have adopted identical particle size-selective sampling conventions for inhalable, thoracic, and respirable aerosols (Figure 1). The purpose of these conventions is to provide a scientific basis for a new generation of particle size-selective occupational exposure limits (OELs) for aerosols. Such OELs can therefore be matched to the relevant sites of aerosol deposition after inhalation into the respiratory tract, and in turn to the health effects of interest in a given exposure assessment. These sampling conventions are used throughout this manual unless otherwise specified. The criteria presented in this manual are used to determine the most appropriate aerosol sampling equipment. The type of sampling to be performed determines which criteria are important for estimating the adequacy of the sampler and determining aerosol concentration levels. For example, "total dust" samplers generally do not have a size selective particle classifier preceding the filter media and fall under the inhalable sampling convention. Alternatively, sampling for regulatory or voluntary compliance with aerosol exposure standards usually requires greater accuracy, increased efficiency, size-specific selectivity, and good analytical precision. Furthermore, regulations may require the use of a specific sampler and sampling conditions to standardize sampling results (eliminate bias) and reduce uncertainty among laboratory reports. See Chapter P, Measurement Uncertainty and NIOSH Method Accuracy for further discussion on standardization and aerosol measurement error.

Over the past two decades, researchers have pointed out strengths and weaknesses with several types of aerosol samplers (Figures 2a-j). Some of these samplers were adapted from

existing devices used for other purposes, e.g., the 10-mm nylon cyclone and the 37-mm cassette, without the benefit of current testing technology and understanding of particle behavior. More recently developed aerosol samplers were designed to either maximize the information gained regarding aerosol concentration levels or to minimize any inherent losses associated with the sampler design. Thus, each sampler design may have been based on some of the following criteria: inlet efficiency, classifier accuracy, cassette assembly (bypass leakage), electrostatic losses, particle deposition uniformity, collection media stability, sampler surface losses, and sampler field comparisons. These criteria are discussed in the following sections of this chapter.

2. INLET EFFICIENCY OF THE SAMPLER

An important review of sampling theory and practice was compiled in a book by Vincent [4]. The inlet efficiency of several samplers has been evaluated including thin-walled tubular inlets [5], a cyclone [6], an asbestos sampler [7], total aerosol sampling cassettes [8], and inhalable aerosol samplers [9,10]. All samplers have an inlet efficiency that varies as a function of particle aerodynamic diameter, inlet velocity, inlet shape and dimensions, dimensions of the body it is attached to, external wind velocity, and external wind direction. The *aspiration efficiency* of an aerosol sampler can be defined as

$$A = c_s / c_0$$

where c_s is the concentration of particles passing directly through the plane of the sampling orifice and c_0 is the ambient concentration. This is true for aerosol samplers for which the entire amount of aerosol that enters the plane of the sampling orifice is quantified, as is the case for the IOM sampler (SKC, Inc., Eighty Four, PA). However, it is important to note that many commercially available aerosol samplers use only the aerosol collected on the filter that is housed in the sampler, while any particles deposited on the inner surfaces upstream of the filter are disregarded. Performance of this type of sampler is therefore best characterized by its *sampling efficiency*, in which the aspiration efficiency is modified by the particle size-selective losses prior to the filter. The aspiration or sampling efficiency of a particular aerosol sampler, whichever is the most relevant, expressed as a function of particle aerodynamic diameter, is the primary index of sampler performance and should match the appropriate health-based criterion (e.g., the inhalability criterion) so that it may be said to provide a valid health-based assessment of personal aerosol exposure.

As an aerosol is being sampled, the large-particle trajectories are more affected by external flow fields than those of small particles. Thus, the shape, orientation, and inlet flow field will be most critical for inhalable aerosol sampler inlets; they will be less important for thoracic samplers and unlikely to be important for respirable samplers, except at very high wind velocities. The flow field near the inlet of a sampler is different when the sampler is mounted on a person (or in laboratory simulations using a mannequin) than when it is freestanding. Therefore, it has been recommended that measurement of inhalability be determined from mannequins in wind tunnels [11-14]. Flow field studies using mannequins in wind tunnels indicate that the air is slowed down by the body, resulting in an enrichment of large particles in the upstream side of the body [15]. When intended for use at low wind speeds (less than about 1 m/s [200 ft/min], representing most indoor workplaces), it may be possible to test the

samplers as freestanding devices if it can be shown there is no effect from the mannequin body [16]. However, if the sampler is to be used at higher windspeeds, which frequently occur outdoors, personal aerosol samplers should be evaluated on a mannequin in a wind tunnel [16].

Respirable aerosol samplers generally do not have problems with inlet effects because the particles being sampled have low enough inertia and settling velocity. However, Cecala et al. [6] found that the 10-mm nylon cyclone operated free-standing in a wind tunnel oversampled at external air velocities greater than 4 m/s when the inlet faced the wind and undersampled at 90° and 180° to the wind at velocities greater than 1 m/s. The maximum sampling error of about 40% was observed at 10 m/s. It is expected that these errors would be reduced if the sampler were located on a person, because the air velocity decreases near the body surface. It should be noted that the Cecala *et al.* work was conducted in the context of aerosol sampling in underground mining environments. Here, windspeeds of the magnitude quoted are not uncommon. However, in industrial workplaces more generally, windspeeds are much lower. Two surveys of a wide range of workplaces [17,18] revealed that actual indoor windspeeds rarely exceeded 0.2 to 0.3 m/s and more typically were less than 0.1 m/s.

The EPA PM-10 standard for environmental sampling specifies a sampler that has a 50% cutpoint at 10.6 µm, approximately the same as that for the thoracic sampler [19]. Although the requirements for environmental PM-10 samplers stipulate wind tunnel testing, similar work on personal PM-10 and thoracic samplers has yet to be performed. It is expected that these samplers will be more susceptible to wind effects than respirable samplers because larger particles are more susceptible to inertial and gravitational effects.

The most extensive comparison of available inhalable aerosol samplers was that carried out under the auspices of the European Commission (EC) [9]. Eight samplers were tested: CIP-10 (foam-based, French); 37-mm closed-face cassette (Spain and US) (Figure 2a); 37-mm open-face cassette (Sweden) (Figure 2a); PAS-6 (Netherlands); PERSPEC (Italy); GSP (Germany, sold as CIS sampler in US; BGI, Inc. Waltham MA); IOM (United Kingdom; (Figure 2b); and the Seven-Hole Sampler (United Kingdom; Casella CEL, Inc., UK) (Figure 2c). Conditions of the experiment included measurement of sampler collection efficiencies on a mannequin for aerosol particles with diameters as large as 100 µm at a wind speed of 0.5 m/s, 1.0 m/s, and 4 m/s. Samplers were positioned on a mannequin rotating within a wind tunnel. The samplers were all conductive; the 37-mm cassette samplers were painted with an external conductive coating. The aerosol was, however, not neutralized. The results of this experiment indicated high inter-sampler variability, but permitted estimates of bias relative to the inhalable convention. The EC study also indicated that most samplers work reasonably well at low wind speeds (<1 m/s) for particle median diameters below 25 µm [20]. The study indicated that experiments of this type were difficult, expensive, and generally had poor precision. Perhaps better understanding of the flow field near the body may lead the way to improved and simplified sampler testing. Recent work suggests ways of making the wind tunnel testing of inhalable samplers simpler and less expensive, e.g., by using a compact body to simulate the chest of a mannequin [21] and by using miniaturized mannequins and samplers that are calculated to be aerodynamically equivalent [22].

The orientation and diameter of an inhalable sampler inlet may affect the collection of very large particles (generally >100 µm), since these may be thrown into the inlet as projectiles. The current definition of inhalable aerosol only covers particles up to 100-µm aerodynamic diameter.

In situations where large particles can be generated (e.g., abrasive blasting, wood working, and grinding operations) excessive collection of particles up to the millimeter range is likely to occur. There have been some attempts to modify inlets with shields to provide a barrier against the collection of large particles, but these modified inlets have not been demonstrated to provide the same agreement with the inhalable convention as the unmodified ones.

Another potential problem with inhalable samplers is the collection of passively sampled particles. Measurements when the sampler airflow is turned off indicate that IOM samplers, which pointed outward from the body and had a large inlet diameter (15-mm), can collect quite significant amounts of dust, with median values of 9 to 32 percent of the mass collected during active sampling [23]. Open-faced cassettes had only 2 to 11 percent of the mass passively collected. These samplers have a larger inlet (37-mm), but point downward, reducing the likelihood of particle settling onto the collection surface. The mechanism of collection is unclear, but the dust may be transported into the inlet by turbulence and deposited by settling or turbulent diffusion. How this passively collected dust modifies the amount collected during active sampling remains under investigation.

A comparison of measurements obtained with the 37-mm closed face cassette (4-mm inlet diameter) to the IOM sampler (15-mm inlet diameter) in several workplaces gave similar results when the material on the interior walls of the 37-mm cassette were added to the analyte deposited on the filter [24]. This suggests that the two samplers can have similar inlet efficiencies in spite of differences in inlet size and orientation if the median particle size sampled is not too large. Other studies did not include wall deposits in evaluation of the 37-mm cassette.

3. CLASSIFIER ACCURACY

The theory of classifier separation is based on particle aerodynamic diameter, which is defined as the diameter of a 1 g/cm^3 density sphere having the same settling velocity as the particle in question. If the particle is markedly non-spherical, the aerodynamic diameter may not be well defined, possibly resulting in sizing errors. For example, fibers and plate-like particles settle slightly differently depending on orientation. Thus, the sampling conventions, based on aerodynamic diameter of particles reaching specified parts of the respiratory system, become somewhat ambiguous for these types of particles. For such non-ideal particles, further testing of classifiers to simulate particle behavior in the respiratory tract may be necessary. For instance, Maynard [25] found that plate-like particles may orient differently in elutriators, impactors, and cyclones. This preferred orientation in a cyclone produced a collection efficiency 15% below that estimated to occur in the respiratory system. Improved understanding of fiber [26] and plate-like particle [25] behavior in the respiratory tract is needed to aid in development of more accurate samplers for these types of particles.

Various types of classifiers have been constructed to meet the ACGIH/ISO conventions. For example, respirable samplers have used cyclones [27], impactors [28-30], elutriators [31], and porous foam [32,33] to remove non-respirable particles from the aerosol prior to filter collection. The technology for testing these samplers has improved in recent years through use of a real-time aerodynamic sizing instrument and resulted in quicker and more precise measurements [34,35]; this technique has allowed the accuracy of these samplers to be investigated more carefully [36]. However, a round-robin comparison of 50% cut-point measurements from six

laboratories using an aerodynamic sizing instrument to test the same cyclone agreed within a range of 11% [37]. Further work on the testing protocol is needed to improve interlaboratory agreement. Many current classifiers do not match the shape of the respirable convention exactly and produce biases that depend on size distribution. Two comparisons of several respirable samplers have been performed using the aerodynamic sizing technique [38,39].

The introduction of the thoracic fraction in the ACGIH/ISO conventions has spurred interest in thoracic classifiers for certain types of aerosols, e.g., cotton dust, asbestos and sulfuric acid [19]. The performance characteristics of the vertical elutriator (operated at 7.4 L/min) used for cotton dust approximately meets the thoracic definition [40]. Laboratories in many countries perform asbestos fiber measurement using the technique of counting only fibers with diameters of 3 µm or less; this size selection was shown to be approximately equivalent to thoracic sampling [41]. Further tests indicate that several thoracic samplers may be appropriate for asbestos sampling [42,43]. Thoracic sampling is also recommended for sulfuric acid [44] and metal working fluids [45].

Several samplers based on inertial, cyclone and foam separators have been specifically developed to meet the thoracic definition [46-49]. The CIP-10 sampler has been used for thoracic sampling in Europe [50], but is not applicable to aerosols with a significant submicrometer fraction [46]. Several of these samplers have been tested to compare with the thoracic convention [42,43]. The GK2.69 cyclone (Figure 2i) has been used for metal working fluids [45]. The other samplers referenced are in the development stage and need further testing. The PM-10 standard for environmental sampling is very similar to the thoracic convention and impactors with a 10 µm cutoff size have been used for personal PM-10 sampling [51]. A cascade impactor, e.g., the Andersen personal cascade impactor (Figure 2j), can be used to calculate the thoracic fraction of an aerosol. Although a thoracic sampler is commercially available (Figure 2i), further work is needed to determine its applicability for specific types of aerosol. For example, a thoracic sampler for fibers must result in a uniform deposit of the particles on the filter for accurate analysis results.

The overall accuracy of a classifier with respect to sampling in accordance with the one of the sampling conventions can be estimated using a bias map (Figure 3). The bias map displays the percent difference between the predicted mass collected by the sampler and the mass expected according to the convention as a function of the parameters of a lognormal particle diameter distribution for a range of likely workplace distributions. Such a bias map can be used for selecting a sampler for a workplace having a certain range of particle sizes or for developing samplers that agree more closely with the sampling conventions.

The bias map in Figure 3 was created by: (a) fitting the penetration curve for the 10-mm nylon cyclone (Figure 2g [35]) at 1.7 L/min with a lognormal curve (a logistic curve also can be used), (b) calculating the bias between the respirable convention and the curve from the previous step for a range of lognormal size distributions, and (c) plotting the bias contour lines as a function of the size distribution mass median aerodynamic diameter (MMAD) and geometric standard deviation (GSD). The 10-mm nylon cyclone shows significant negative biases, especially at large MMADs and small GSDs because the cyclone penetration curve drops off more rapidly with size than the curve for the respirable convention. The "best" flow rate to use in a workplace when sampling according to one of the conventions becomes a matter of judgment, depending on the size distribution typically encountered in that workplace. A cyclone that fits

the convention more exactly will exhibit smaller biases throughout the entire size distribution range. Bias maps are available for several respirable samplers [38, 39]. It should be mentioned that in some cases, e.g., coal mine dust sampling, a single sampler is specified by regulation. This sampler specification eliminates the question of bias for that type of measurement.

Investigation of the effect of changing the physical dimensions of a commercial cyclone resulted in modifications that improved the match to the respirable sampling convention [52]. Chen and coworkers developed a virtual cyclone that appeared to give excellent compliance with the respirable curve [53]. It is possible to make samplers that have predicted biases less than 10% over the entire range of likely workplace size distributions. While the behavior of certain samplers, such as impactors, can be predicted theoretically, it is still important to measure penetration curves experimentally to ensure correct application of the theory. Bias maps based on these data then allow estimation of accuracy for a specific workplace application. As improved samplers are tested and become commercially available, more accurate thoracic and respirable aerosol measurement on a routine basis will be possible.

As mentioned above, several inhalable samplers were investigated in a wind tunnel to evaluate their sampling efficiency compared to the inhalable convention [9]. Based on these data, sampler performance (maximum bias confidence limit) was ranked [Bartley 1998] and the IOM, GSP, and CIP-10 samplers were rated the best.

As interest in the new particle size-selective conventions by standards setting bodies has grown, efforts have been made to define protocols to guide the testing and validation process for available samplers. One approach was developed by the CEN [54, 55]. In the CEN model, for any given sampler to be tested, the first step is a critical review of the sampling process for the instrument in question. This is intended to identify factors that may influence the performance of the sampler, including particle size, windspeed, aerosol composition, filter material, etc. This is essential in the process of sampler evaluation, determining under what conditions the sampler will need to be tested. Three options are then presented for the testing of samplers: (a) the laboratory testing of samplers to compare performance with the sampling conventions, (b) the laboratory comparison of instruments, and (c) the field of comparison of instruments. Research projects have been conducted in recent years to define testing protocols (option a), funded both by the European Community and by NIOSH, to consolidate the scientific basis for such protocols and to identify improved and more cost-effective methods.

4. SAMPLER ASSEMBLY

Some samplers are designed such that improper assembly can result in internal leakage, i.e., aerosol particles bypassing the filter. This bypass leakage has been noted in the 37-mm closed-face cassette [56,57]. Although at least one study found no problem with hand assembly of these cassettes [58], NIOSH and others [59] have occasionally observed, after sampling black or colored dusts, streaks of dust on the filter's compression seal region or an incomplete compression mark, indicating aerosol leakage bypassing the filter. An airtight seal in these cassettes is achieved by compression of two plastic parts that must be parallel and joined with the proper force. If this seal is not compressed with sufficient force, the vacuum behind the filter may pull the filter from the seal, especially at high flow rates. Too high a compression force results in cracking the cassette or cutting the filter, also producing leakage.

Prudence dictates that a check of cassette integrity and the seal area on each filter should be made after sampling to ensure that the cassette was properly assembled; otherwise, the sample may underestimate the actual exposure.

At least two approaches to eliminating the sealing problem with press-fitted cassettes have been taken. One was to assemble the cassette using a press. Pressing the cassette together by hand often produces misalignment of the cassette parts, resulting in bypass leakage. Frazee and Tironi designed a mechanical press that held the two cassette pieces in proper alignment, while applying just enough pressure to effect a seal, but not so much as to cause cracking of the plastic [56]. This press was designed to allow motion of the cassette pieces to compress to a certain distance. A commercial pneumatic press (Accu-Press, Omega Specialty, Chelmsford MA) used a selected pressure to compress the cassette components. For additional information on bypass leakage and bypass leak test procedures see Chapter N: Aerosol Sampling: Minimizing Particle Loss from Bypass Leakage. The second approach was to redesign the cassette to provide a more positive filter seal [57]. In a well-designed sampler, opening the seal should not cause tearing and loss of the filter or collection medium during removal from the sampler.

The 37-mm closed-face cassette is usually sealed with tape or shrink bands around the outside. There is a common misconception that this seal prevents bypass leakage in the cassette. These external seals primarily cover the joint between the cassette components to prevent deposited particles on the external surface of the cassette from contaminating the sample during filter removal. The tape or shrink band also aids in holding the cassette together and preventing external air leakage. However, Puskar, et al. [58] found that even by using this precaution, a significant amount of dust was found downstream of the filter. The authors hypothesized that this dust was deposited during filter removal.

Three other commercial samplers, the IOM (figure 2b), the CIS, and the coal mine dust sampler (MSA, Inc, Pittsburgh) use a cartridge to hold the filter. For the first two samplers, an external threaded cover applies pressure to the cartridge to ensure a good seal around the filter. This prevents twisting at the filter surface while creating positive, even contact around the filter edge.

5. ELECTROSTATIC LOSSES

Most aerosol particles generated in workplaces have electrostatic charge levels considerably higher than the minimum level [60]. Minimum charge (Bolzmann equilibrium) levels are usually achieved after particles are suspended in the atmosphere for an hour or so because of the presence of naturally occurring ions. When freshly generated particles are sampled in an electric field, as when a sampler is highly charged [61], the particle trajectories may be modified to such an extent that the particles are inefficiently sampled. No electrostatically induced particle motion occurs when either the particle charge or electric field during sampling is zero; when both the sampler and particle are highly charged, particle acceleration is much greater than that caused by gravity, inertia, diffusion or other mechanisms.

Samplers can achieve a high charge level when they are electrically insulated from ground and are triboelectrically charged (i.e., by contacting or rubbing against other surfaces); this sampler charging, as well as particle charging, tends to occur more frequently at low (<20% RH) humidity levels. Certain plastic materials, such as polycarbonate, polytetrafluoroethylene,

polyvinyl chloride (PVC), and polystyrene readily retain high charge levels; others, such as Tygon®, retain relatively little charge [62]. The PVC/polystyrene copolymer used in the 37 mm closed-face cassette is an excellent electrical insulator and can retain high charge levels on its surface. These charges can be incorporated in the bulk plastic during manufacture or accumulated on the surface by handling or contact with other objects; the charge levels and polarity are highly localized and variable. Such samplers can exhibit particle losses to the internal walls of the cassette and negative sampling biases [63]. Non-conductive plastic asbestos samplers were shown to produce large negative biases and variable results [61, 63, 64].

Conductive samplers have demonstrably lower losses when sampling charged particles. Metal samplers obviously have high conductivity. Samples collected using nylon cyclones were shown to exhibit higher variability [65, 66] and negative biases [66] when sampling charged dusts. However, the degree of conductivity required is not high; as long as charges can move over the sampler surface and reach equilibrium in seconds, the effect of charges transferred to the sampler is likely to be minimized. Materials with this low level conductivity (surface resistivity < 10^8 ohms/square) are often termed "static-dissipative." Graphite-loaded plastics were developed that have adequate conductivity to distribute charges over the surface of the cassette (e.g., the 25-mm asbestos sampler). A simple test to ensure adequate conductivity of these samplers can be performed by attaching a good quality multimeter at any two points on the sampler surface. Resistance readings in the range of tens of megohms or less indicate sufficient conductivity for sampling purposes.

Some metals are coated with a thin, non-conductive layer, e.g., anodized aluminum. These coatings may retain a surface charge, but this charge will induce an opposite charge in the conductive layer beneath the surface, effectively canceling out the field produced by the surface charge. Recent measurements at NIOSH using a non-contacting electrostatic voltmeter (Model 300, Trek Inc. Medina NY) indicated that no significant external field (< 50 volts) could be produced near an anodized surface by rubbing the surface with various plastics or other materials. Plastic or cellulose-based materials rubbed in a similar manner produced electrostatic potentials measured in the hundreds to thousands of volts. Thus, metals with a thin, insulating surface layer are not likely to produce significant external fields that would affect aerosol sampling.

A further electrostatic problem not specifically associated with the cassette is the use of filters made of highly nonconductive materials, such as PVC, polytetrafluoroethylene, or polycarbonate. In addition to having desirable chemical properties, these filters have the advantage of not absorbing water from atmosphere, leading to improved weight stability [67-69]. However, these filters can retain a high electrostatic charge level, resulting in non-uniform particle deposition and even repulsion of particles from the filter surface. Such filters are also more difficult to handle during weighing because of charge effects. Even filters that are normally more conductive, such as cellulose-based filters, can become non-conductive and exhibit non-uniform particle deposition and particle losses at very low humidity levels (< 10% RH) [70]. A treatment was developed to make filters more conductive without significantly affecting weighing accuracy or moisture absorption [71]. In one study, it was found that applying this treatment to the filter decreased particle losses from 14% to 2% [72]. Anti-static sprays are available that leave a temporary static-dissipative coating on surfaces.

6. SAMPLE DEPOSITION UNIFORMITY

Some analytical methods require that sampled particles be deposited uniformly on the filter surface. For instance, asbestos fiber analysis by microscopy requires uniform deposition of fibers on the filter for accurate results. Direct silica analysis of collected filter samples also is improved with uniform particle deposition. Classifiers using inertial or gravitational forces tend to stratify the aerosol stream. A small, high velocity inlet in a sampler, such as the 4-mm opening in the 37-mm closed-face cassette, can also result in the larger particles being deposited in a small central area on the filter. Even sampling at high flow rates through more open inlets can cause a non-uniform deposit [73]. This results in particle deposits that vary in uniformity as a function of particle size. Such deposition patterns are visible when sampling colored particles [74]. Open-pore foam classifiers may improve the uniformity of particle deposits on the filter, but have not been thoroughly evaluated [75, 76]. Careful design of classifiers to ensure mixing of the aerosol prior to deposit on the filter may result in adequate uniformity [47]. Even inhalable samplers or samplers that have no classifier may be prone to non-uniform deposits under certain conditions of sampler orientation relative to gravitational settling, orientation relative to external winds, or when sampling charged particles [61, 62, 64, 70]. Flaring the inlet of such a sampler, as in the commercial "bell-mouth cowl," (Figure 2f, Envirometrics, Charleston SC), is one approach to improving sample uniformity under anisokinetic conditions [73]. In another study, a sampler having an inlet screen (button sampler, Figure 2d, SKC, Inc. Eighty Four PA) exhibited improved filter deposit uniformity when compared to a closed-face cassette [77].

The filters in some samplers require support to prevent tearing or distortion of the filter. The support device may cause occlusion of parts of the filter surface, resulting in non-uniform particle deposits [78].

On occasion, it was observed that poorly-sized tubing connectors protruded into the 37-mm cassette and touched the filter surface. This caused all the airflow to pass through the filter adjacent to the small area of the connector opening. When undetected, this caused low sampling efficiency and pump failure because of the high pressure drop.

7. SAMPLER WALL LOSSES

Particle deposits on internal surfaces (i.e., wall losses) of the 37-mm closed-face cassette for several hundred field measurements were found to be large and highly variable (2 - 100% of dust collected in the cassette) [79]. Another study found only 22% of the dust on the filter, 65% on the upstream portion of the cassette, and 22% downstream of the filter [58]. In a study of an in-line cassette of similar shape, it was found that the internal wall deposition of particles could be largely eliminated by: (a) making the cassette conductive, (b) creating an aerodynamically smooth surface having no corners for eddies to form, and (c) decreasing the diameter of the filtration area so that dust does not deposit on the filter adjacent to the upstream walls of the cassette [72]. By incorporating these three corrective measures, the wall losses in the latter cassette were reduced from 25-30% to 5%. These losses appear to be caused by a combination of electrostatic, inertial, gravitational and diffusion mechanisms.

Another solution to the problem of not capturing 100% of the sampled particles on the filter is to use an internal cartridge sealed to the filter. All the particles collected in the combined

filter/cartridge are analyzed. The air stream entering the cassette is surrounded by the cartridge and any deposition on the walls of the cartridge is retained for analysis. The IOM sampler for inhalable dust uses this approach by having the cartridge form the inlet of the sampler (Figure 2b). This approach also has been used in the in-line cassette of the coal mine dust personal sampling unit (MSA, Pittsburgh PA) where an aluminum foil cover is crimped onto the filter. A similar cartridge was designed for the 37 mm closed-face cassette in measurements of pharmaceutical dust [80]. Another cartridge made of "static dissipative" plastic is commercially available (Accu-Cap, Omega Specialty Instruments, Chelmsford MA). However, it is important that cartridge material be compatible with the analytical method. For instance, the plastic material used in the first version of the IOM sampler cartridge (Figure 2b, SKC, Eighty Four PA) was found to absorb milligrams of water over periods of days, making the accuracy of gravimetric measurements problematic [81-83]. Demange et al. more recently demonstrated significantly improved agreement between inhalable sampling using the IOM sampler and the 37-mm cassette by including all deposits inside the cassette [23]. This suggests that the accuracy and precision of the 37-mm cassette can be improved by including internal sampler deposits by wiping or washing, or by using an internal cartridge such as the Accu-Cap.

8. COLLECTION MEDIA AND ANALYTICAL ISSUES

The sampling medium should be compatible with the analytical method. Some analytical methods require specific filter properties. For instance, atomic absorption and inductively coupled plasma analyses typically require complete ashing of the filter material; organic compound analyses require that no reaction or adsorption of the compounds occur at the filter surface. Several studies have dealt with gravimetric stability of filters and recommended specific procedures [67-69, 84, 85]. Generally, plastic materials that do not absorb water (polycarbonate, polyvinyl chloride, polytetrafluoroethylene) are more weight stable than natural cellulose-based materials; uncoated glass fiber filters also may absorb water [67-69, 84, 85]. Note, however, that the more weight stable materials also tend to be more highly charged, resulting in more charged particle repulsion and deposit non-uniformity. When a plastic (Tyvek®) backup pad is crimped into a cartridge together with a filter, the weight stability of the cartridge may suffer [86]. To improve the weight stability of coal mine dust sampler cartridges, stainless steel backup pads have been used by MSHA. The IOM sampler can be purchased with either a plastic or a stainless steel cartridge. The plastic cartridge has been shown to exhibit poor weight stability and should not be used for gravimetric analysis [81, 83].

Lawless and Rodes investigated the use of modern electronic balances to determine factors affecting the accuracy of gravimetric measurements and found that balance stability, balance leveling, vibration and thermal drafts, electrostatic charge reduction, positioning of the filter in the balance so that the filter did not hang over the edge of the pan, and temperature and humidity control were all important in achieving accurate results [87].

Although not strictly a problem with the collection medium, the sampler construction material should not outgas vapors that can condense on the collection medium and affect the analysis. Early (circa 1970) versions of the closed-face cassette were made of a plastic called "tenite," which resulted in weight gain of the filter over time. This currently does not appear to be a problem.

Impactors have been used as samplers and, especially with cascade impactors, the deposits on the impaction stages are measured. Particle bounce from the collection substrates on the impaction plates can be severe, especially for solid particles impacting onto a smooth metal plate. Several modifications to the collection substrate are available to improve collection efficiency of each stage. These modifications should be compatible with the analytical method. Oil can be placed on the collection substrate that wicks up over collected particles and continually provides an oiled surface. A filter or sintered metal can be used to provide a reservoir for this oil. For gravimetric analysis, this oil must have a low vapor pressure and not migrate off the collection substrate. Alternatively, grease can be used, but after the surface is coated with collected particles, additional particles are more likely to bounce. Filters have also been used as substrates and provide a convenient substrate that is somewhat better than a smooth metal surface. Selection and use of an impactor is a complex issue and has been described in reviews [88, 89]. Accurate analysis of cascade impactor data can also be difficult and simple regression analysis of the data may not provide the best answer [89-91].

9. SAMPLER FIELD COMPARISONS

Direct field comparisons of various samplers are frequently reported in the literature. Because of the typical high variability of aerosol concentrations and size distributions in workplaces, it is difficult to use these situations for accurate assessment of sampler performance. However, field studies are important to verify the overall performance of a sampler and to indicate specific sampler issues. The problems with samplers as discussed above can be highlighted with some examples observed in field studies.

a. Sampler Bias Affected By Internal Deposits

A study of wood dust sampling comparing collocated free-standing samplers indicated that an MSA cassette (having an aluminum cartridge crimped onto the filter) used as a sampler gave two times better precision and collected 2.6 to 3.5 times more dust than the standard 37-mm closed-face cassette [92]. Both these samplers have the same size and shape of inlet. The same study showed that the IOM sampler collected 1.3 times more dust than the MSA cassette, indicating that the particle size, inlet shape and inlet orientation are important factors in inhalable sampling. Among a number of inhalable samplers in current use around the world, the IOM sampler appears to agree the best with the inhalable dust sampling convention [9, 93]. Several studies have shown that the IOM sampler collects anywhere from slightly more to 3.5 times more dust than the closed-face cassette [94-98]. However, Demange et al. showed that for several work sites with relatively small MMAD particles (about 15 μm), the 37-mm cassette results agreed well with the IOM results if the deposits on the internal surfaces of the cassette were added to the filter analyte [23]. Measurements with the 37-mm cassette are not expected to agree as well with the IOM when the particle sizes are much larger because of differences in aspiration efficiency. However, by including all aspirated material, i.e., all material entering the 37-mm cassette inlet, in the analysis, it appears that agreement with the inhalable convention is improved.

b. Sampler Precision Affected By Internal Deposits

Internal wall deposition in a sampler can also contribute to variability of results. In a field study of lead dust, it was found that the results from a closed-face 37-mm cassette gave a coefficient

of variation (CV) of 1.0 and 0.33 when sampling at 2 L/min and 10 L/min, respectively, while the button sampler gave a CV of 0.10 under the same conditions [77]. The button sampler has few internal surfaces for wall deposition, suggesting that elimination of this type of loss would improve the precision of the 37-mm cassette. Demange et al. found improved precision for the 37-mm cassette data when the wall deposits were added to the analyte [23].

In spite of some of its drawbacks, the 37-mm cassette is likely to be used for some time. It appears that from the standpoint of improving agreement with the inhalable convention and improving precision, the inhalable sampler wall losses should be minimized through sampler design (use of a cartridge such as the AccuCap or in the MSA coal mine cassette) or the wall deposits should be added to the analyte.

10. CONCLUSIONS

Clearly, when proper features are incorporated in the sampler design, significant improvements in bias and precision can be achieved for some currently used aerosol samplers. Several recommendations regarding the application of these samplers are listed:

a. Classifiers used to select respirable, thoracic, or other fractions should be evaluated based on bias maps obtained from experimental data and combined with size distributions from workplace measurements to evaluate their applicability.

b. Further research and development is needed to improve sampler design to better match ACGIH/ISO conventions and reduce inter-laboratory variability in conducting aerosol sampling. It is important to report the sampler and flow rate used to allow evaluation of potential biases due to sampling.

c. The filter cassette and fittings should be air-tight and have no by-pass leakage. A pneumatic or mechanical press should be used to assemble the cassette and a leak test should be used to establish appropriate pressure and proper assembly procedures. See chapter entitled: Aerosol Sampling Cassette Assembly: Leak Testing

d. The sampler should be made of conductive or static-dissipative materials.

e. Internal deposits in sampling cassettes should be included in the analysis. One approach to improving the closed-face cassette is to use an internal cartridge that collects all the sampled dust entering the cassette. The cartridge must be compatible with the analytical method. Another approach is to wipe or wash the internal surfaces of the cassette and add this material to the filter analyte.

11. DISCLAIMER

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

12. FIGURES

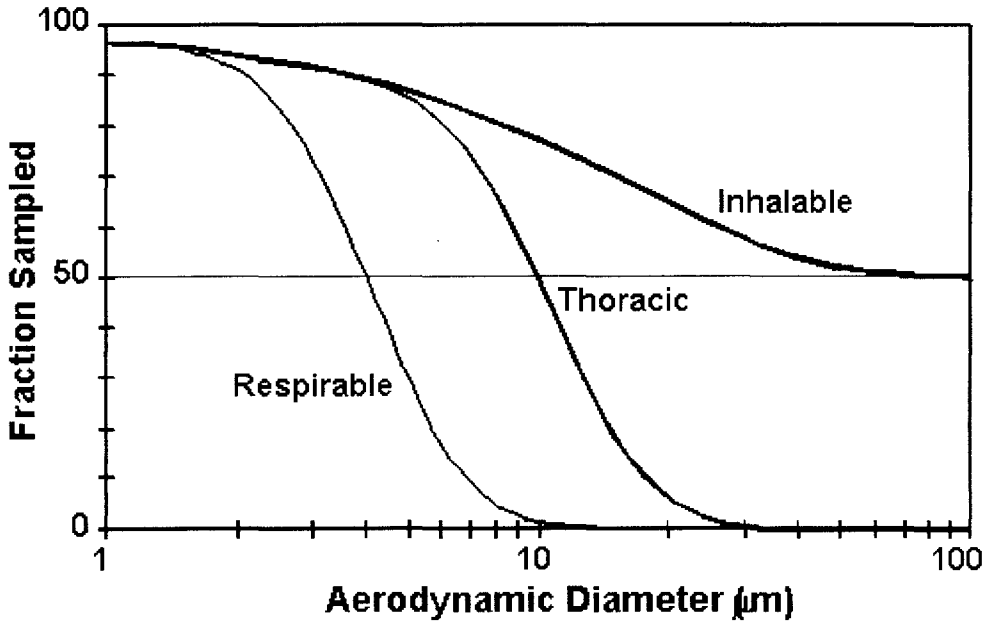

Figure 1. ISO/ACGIH/CEN sampling conventions. An ideal sampler should have a sampling efficiency curve that matches one of these curves as closely as possible under all wind directions and velocities. The 50% cutpoints for the respirable and thoracic conventions are 4 and 10 µm respectively.

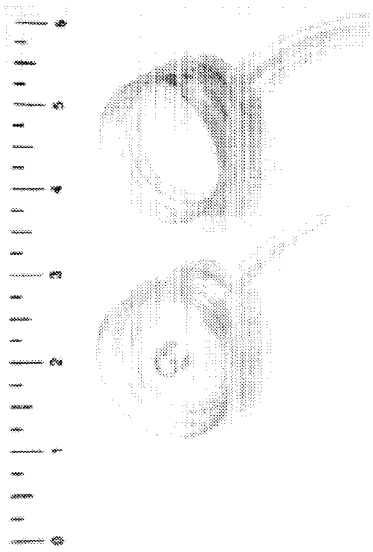

Figure 2a. Examples of personal aerosol samplers. a. Open faced (top) and closed face (bottom) 37 mm cassette samplers. These are shown in acrylic copolymer (clear, non-conducting) material and are more prone to electrostatic losses. Other construction materials are available, including conducting plastic. Sampling flow rates range from 0.5 to 10 L/min.

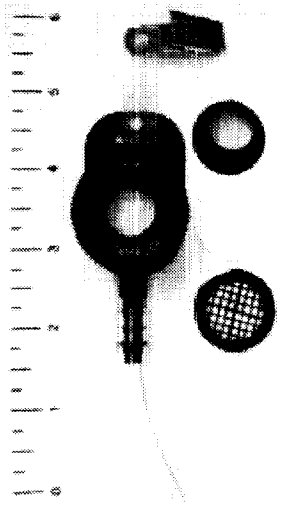

Figure 2b. IOM inhalable sampler. This is the first sampler designed specifically to match the inhalable sampling convention. The sampling cartridge is shown on the right with the inlet, filter, and support grid from top to bottom. All dust entering the cartridge is collected and analyzed. Sampler is made of conductive plastic and operates at 2 L/min.

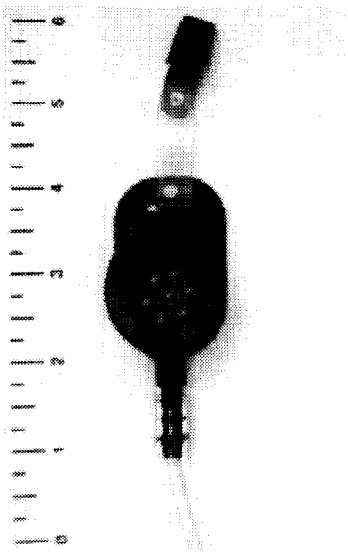

Figure 2c. Seven hole sampler used for inhalable dust sampling in the UK. Sampler is made of conductive plastic and operates at 2 L/min.

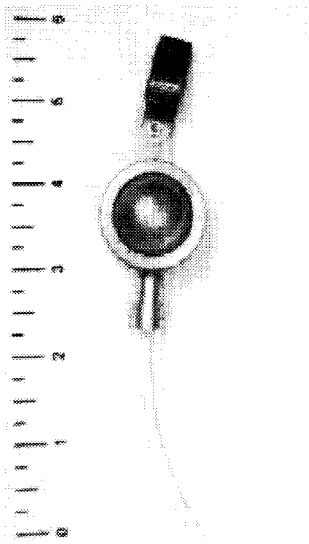

Figure 2d. Button sampler. So-named because the inlet, a hemispherical screen with ~380 µm diameter holes, resembles a large button. Developed as an inhalable sampler with reduced wind direction response and improved filter deposit uniformity. Uses metal construction and operates a 4 L/min.

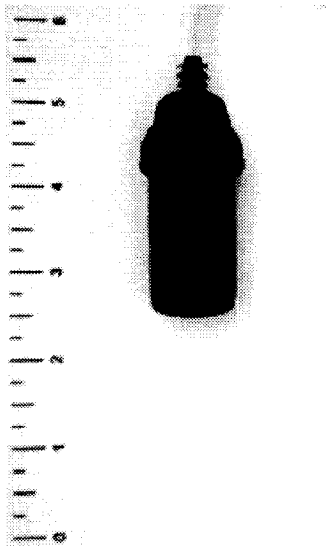

Figure 2e. Asbestos sampling cassette. The long (50 mm) inlet was designed to prevent incidental contact with the filter surface and, when facing downward, acts to a certain extent as an elutriator, preventing larger particles from reaching the filter surface. Made of conductive plastic and is operated at a flow rate between 0.5 L/min to 16 L/min.

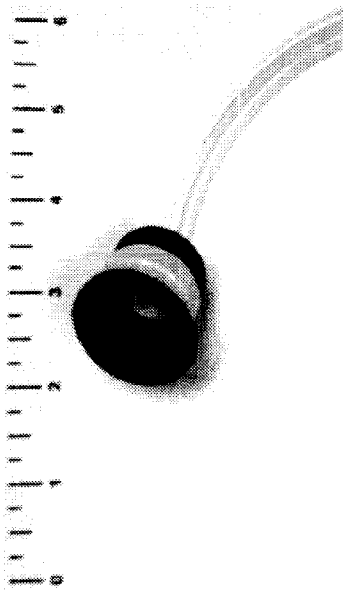

Figure 2f. Bell mouth cowl sampler. An alternative to the standard asbestos sampling cassette. The inlet is flared to reduce the effect of external air motion on sample uniformity. Made of conductive plastic and is operated at a flow rate between 0.5 L/min to 16 L/min.

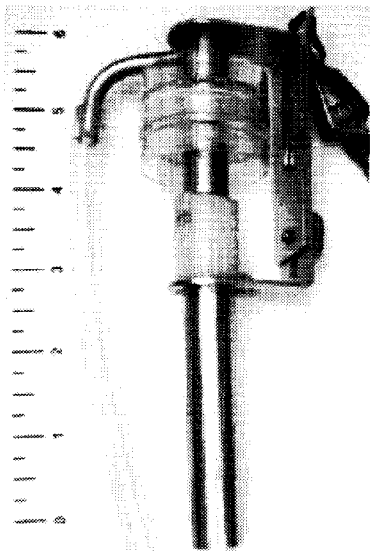

Figure 2g. Dorr-Oliver 10-mm nylon cyclone. Used as a respirable sampler most often at 1.7 L/min. A version of this sampler is used at 2 L/min in coal mines with a 1.38 correction factor applied to the resultant mass. The holder encases body of the cyclone so that only the inlet section is visible just below the connection to the 37 mm cassette. The coal mine dust sampler version uses a cassette with an aluminum cartridge encasing the collection filter.

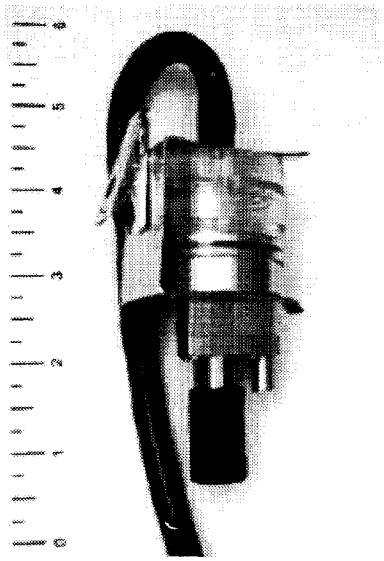

Figure 2h. Higgins-Dewell cyclone. Developed and used primarily as a respirable sampler in the UK. This version provides an interface directly to a 37-mm cassette. Cyclone construction is steel and operates at 2.2 L/min.

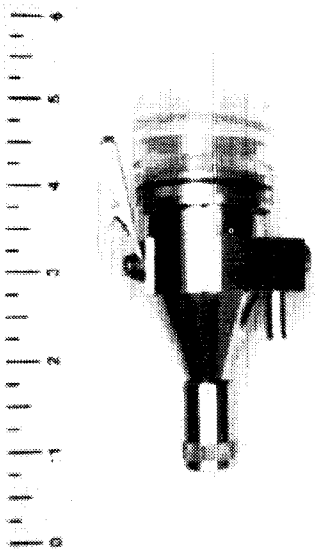

Figure 2i. GK2.69 cyclone. This cyclone was designed to match the slope of the thoracic and respirable conventions more closely than other sampling cyclones. Cyclone construction is stainless steel and operates at 4.2 L/min as a respirable sampler and 1.6 L/min as a thoracic sampler.

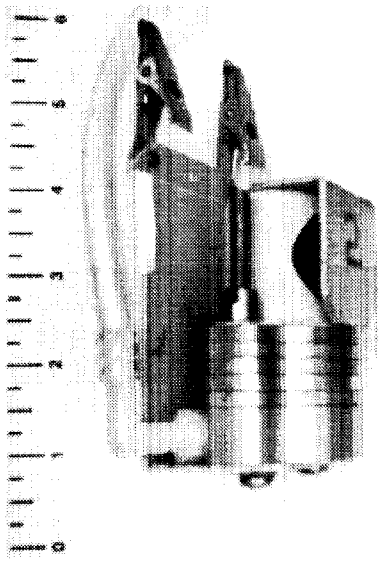

Figure 2j. Personal cascade impactor sampler (model Marple 290, Thermo Andersen, Atlanta). The sampler has five stages in the version shown and an additional three stages are available to provide cutpoints from 0.4 µm to 21µm. The flap over the inlet reduces direct projection of large particles into the inlet. This sampler allows measurement of aerosol size distribution and calculation of respirable and thoracic fractions. Aluminum construction and operates at 1.7 L/min.

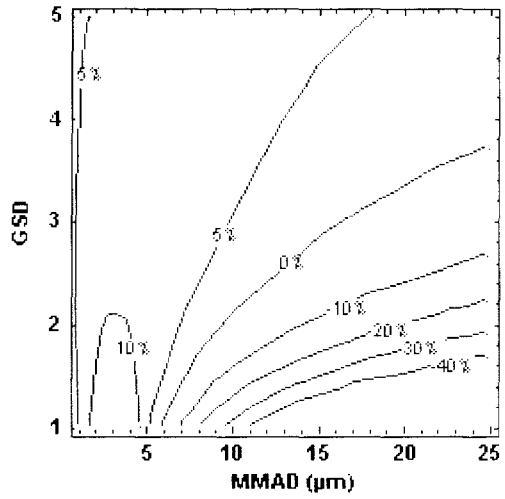

Figure 3. Bias map for the 10-mm nylon cyclone (operated at 1.7 L/min) compared with the respirable convention [33]. The contour lines represent percent bias for specific lognormal size distributions. The calculation of this map is based on laboratory measurement of cyclone penetration and can be used with measured field size distributions to estimate sampling bias.

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P. MEASUREMENT UNCERTAINTY AND NIOSH METHOD ACCURACY RANGE

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1. INTRODUCTION

Recently, the *ISO Guide to the Expression of Uncertainty in Measurement* (GUM) has come close to being universally adopted as the standardized way to characterize and document measurement uncertainty [1-5]. Since the mid-1970s, accuracy criteria have been an integral part of the evaluations of the sampling and analytical methods used by the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), the Mine Safety and Health Administration (MSHA), and others. NIOSH has previously published extensive discussions addressing the issue of accuracy as a factor in the development, evaluation, and characterization of analytical methodology. Both traditional method accuracy and new measurement uncertainty concepts are intended to communicate measurement limitations to laboratory clients. Naturally, laboratories are interested in how NIOSH accuracy requirements [6-7] relate to measurement uncertainty.

This chapter provides guidance for achieving consistency in determining measurement uncertainty by those laboratories using NIOSH methods. Minor modifications to NIOSH accuracy measures, and an expansion of ISO GUM to cover situations unique to workplace atmosphere measurement can improve consistency and utility.

ISO GUM proposes pooling estimated variance components from diverse error sources. The square root of the pooled variance estimate is termed the *combined uncertainty* u_c . Multiplication of u_c by a *coverage factor k* (generally in the range of 2 to 3) results in an *expanded uncertainty U*. The purpose of the expanded uncertainty is for each measurement to provide an interval bracketing the *measurand* (the true value of what is to be measured)

to account for errors in both the measurement and the determination of the uncertainty components themselves.

ISO GUM is somewhat sketchy about the coverage factor k. Furthermore, the coverage factor can be interpreted in several ways. Most straightforward is the limited case where the uncertainty components can be re-evaluated each time the method is used (resulting in k proportional to a Student-t quantile). In this case, the covering intervals bracket the measurand for (for example) 95% of the measurements.

Alternatively, the coverage factors based on the Student-t quantile specify intervals containing measurand values at levels of evaluation confidence in the *mean* (i.e., averaging over many method evaluations). In other words, for roughly 50% of method evaluations, intervals used at each measurement contain the measurand value greater than (for example) 95% of the time. The concept is consistent with the statistical theory of tolerance or prediction intervals.

This approach is important to industrial hygiene since workplace air concentrations vary spatially and over time to such a degree that a method cannot be evaluated by simply taking replicate measurements [8]. However, industrial hygiene measurement methods have traditionally required confidence levels greater than 50% in the method evaluation. Generally, 95% confidence in a method validation is required. The different types of confidence levels are reflected simply in the numerical value and interpretation of the coverage factor.

Of equal importance in the industrial hygiene field are details needed to handle systematic error (bias) relative to reference concentration measurements found during method evaluation. For example, the sampling rate of a given diffusive sampler for gases or vapors is generally measured once by the diffusive sampler manufacturer prior to use by multiple clients. As the samplers are not re-calibrated for each use, residual bias exists in the measurements due to uncertainty in sampling rates used [9]. (NIOSH methods typically do not cite performance for passive samplers because agreement among diffusive monitor manufacturers on test protocols has not yet been achieved, and a system of third party evaluation of diffusive monitor manufacturers sampling rates is not available.) Similarly, the calculation of desorption efficiencies may be performed only once or infrequently and can, therefore, introduce residual bias in measurements that use sorbent-captured samples, e.g., charcoal tubes.

In aerosol sampling, detailed knowledge of the particle size-dependent bias of a sampler relative to a sampling convention, such as adopted by ISO/CEN/ACGIH/ASTM [10] for defining respirable dust, is often necessary to judge the usefulness of a given sampler. Each

type of aerosol sampler is characterized by specific particle collection characteristics, and some analytical methods (e.g. silica) may also exhibit particle size effects. Typically the issue of aerosol sampler bias is avoided or minimized in the industrial hygiene field by narrowing use to a specific aerosol sampler. For example, common industrial hygiene practice establishes a single sampler type, such as the 1.7 L/min 10-mm nylon Dorr-Oliver cyclone, for respirable dust sampling in a particular application.

Sensitivity to other environmental factors, referred to in ISO GUM as *influence variables,* must be acknowledged. Suppose a sampler is sensitive to temperature changes that are impractical to measure in the field; i.e., sampler estimates are not temperature corrected. Then, suppose during method evaluation in the laboratory, measurement of this sensitivity is combined with knowledge of the expected temperature variation for a given field application. Putting together both would determine the uncertainty associated with the effect. Examples of the important effects of influence variables - such as wind velocity, temperature, pressure, and fluctuating workplace concentrations - on diffusive monitor uptake rates are common.

2. ISO GUM

ISO GUM presents several concepts. One of these calls for the identification of sources (labeled j = 1, 2,...) of uncertainty u_j (standard deviation estimate components) in a measurement method and for their classification into Type A or Type B uncertainties. Type A uncertainty is one that has been characterized by a statistically sound approach. In this case, u_j^2 is given by s_j^2, an unbiased estimate (with υ_j degrees of freedom) of variance σ_j^2. On the contrary, Type B uncertainty generally requires professional judgment. See Table 1 for examples of possible uncertainty components.

A common example of Type B uncertainty is the conservative assignment (Chapter E) of a 5% relative standard deviation component (without error, i.e., with infinite degrees of freedom) as the random sampling pump uncertainty. As described in ISO GUM, such an assignment would be a result of sampling pump random errors that had a uniform distribution and fell within $\pm \sqrt{3} \times 5\%$ of zero with a probability "for all practical purposes equal to one". Therefore, if it is judged that sampling pump variations are *within* these bounds, then the assignment of 5% as the relative standard deviation component is conservative. Other similar ways of handling Type B uncertainties are found in ISO GUM.

TABLE 1. EXAMPLES OF POTENTIAL UNCERTAINTY COMPONENT SOURCES.

Sampling

personal sampling pump flow rate: setting the pump and subsequent drift
sampling rate of diffusive sampler
sampler dimension (aerosol and diffusive sampling)

Sample handling

sample preparation (e.g., handling silica quasi-suspensions)
sample loss during transport or storage

Analytical

aerosol weighing
recovery (e.g, GC-based methods)
Poisson counting (e.g., in XRD methods)
sensor variation
operator effects giving inter-lab differences (if data from several labs are to be used)

Evaluation

calibration material uncertainty
evaluation chamber concentration uncertainty
other bias-correction uncertainty

Environmental influence parameters

temperature (inadequacy of correction, if correction is made as with diffusive samplers)
atmospheric pressure
humidity
aerosol size distribution (if not measured by a given aerosol sampling method)
ambient wind velocity
sampled concentration magnitude itself (e.g., sorbent loading)

Within the field of industrial hygiene, the quantities u_j are often standard deviation component estimates obtained from a *single* measurement-method evaluation, rather than from replicates. When the estimates are independent, a *combined uncertainty* u_c may be computed (through the propagation of uncertainty approximation) as:

$$u_c = \sqrt{u_1^2 + u_2^2 + \ldots} \quad . \qquad (1)$$

Through a *coverage factor k*, generally approximated conservatively (e.g., see *Technical Note 2* at end of chapter), as equal to 3 for a single method evaluation, an *expanded uncertainty U* may be computed as:

$$U = k \times u_c \quad . \qquad (2)$$

The purpose of the expanded uncertainty U is to provide intervals, which generally contain measurand values (often referred to as the *true* values). In particular, given a concentration estimate $\hat{c}$ (hats, as here, indicate estimates), the measurand value C is bracketed at better than 95% confidence by intervals of the type:

$$\hat{c} - U < C < \hat{c} + U \,, \qquad (3)$$

at 95% confidence in the method evaluation. The coverage factor k is intended to account for both (1) the fluctuation of the measurement about the measurand value and (2) the uncertainty in the assessment of this fluctuation.

Note: Requiring only *mean* confidence in the evaluation leads to k given in terms of a *Student-t* quantile. Here, however, in fixing the method evaluation confidence (e.g., at 95%), the *chi-square distribution* takes the place of the Student-t distribution. Double confidence levels (in the measurement and evaluation) directly relate to a well-developed [11-19] statistical theory of *tolerance* or *prediction intervals.*

Another point of ISO GUM is semantic. *Uncertainty*, as in common usage, covers only what is *unknown* about a measurement. The *known* but uncorrected systematic deviation or *bias* relative to reference concentrations does not enter into measurement uncertainty.

A related concept, *accuracy*, is defined qualitatively within ISO GUM as the "closeness of agreement between the result of a measurement and a true value of the measurand". Accuracy can have both random and systematic components. It is not surprising then that if a bias correction is made and if accuracy is quantified reasonably, the expanded uncertainty and an accuracy confidence limit can be equivalent.

As mentioned above, another aspect of ISO GUM deals with *influence factors.* If measurement results are expected to be sensitive to an environmental factor (e.g., ambient temperature), then the effect of such a factor on the measurement method must be measured in the laboratory. Given estimates of the environmental variations expected during method application, influence components of the combined uncertainty can be estimated for inclusion in the uncertainty budget of Eq. 1. Table 1 lists several *influence factors*, which may or may not be significant.

3. THE SYMMETRIC ACCURACY RANGE *A* AS USED BY NIOSH

a. Definition and its Approximation

The *symmetric accuracy range A* is defined as the fractional range, symmetric about the true concentration C, within which 95% of sampler measurements $\hat{c}$ are to be found. Another way of saying this is:

$$C \times (1 - A) < \hat{c} < C \times (1 + A) \qquad \text{for 95\% of measurements } \hat{c} \qquad (4)$$

It is clear from this simple definition that the accuracy range function *A* must increase with both random effects and bias magnitude and therefore, is one means of quantifying accuracy as defined above according to ISO GUM.

More specifically, suppose that estimates $\hat{c}$ are normally distributed about population mean *c* with standard deviation σ. Then we may characterize random measurement effects in terms of the (true) relative standard deviation *TRSD* and *bias* of the mean concentration estimate *c* relative to the true concentration *C* as:

$$\begin{aligned} bias &= (c - C)/C \\ TRSD &= \sigma / C \end{aligned} \quad . \qquad (5)$$

The descriptive definition of Eq. 4 implies that the symmetric accuracy range *A* increases with both *TRSD* and bias magnitude |*bias*|. This feature can be seen directly in the following close approximation to the accuracy range function *A*, which follows [Ref. 11, 12 for derivation] from the definition in Eq. 4:

$$\begin{aligned} A &= 1.960 \times \sqrt{bias^2 + TRSD^2}, \ if\ |bias| < TRSD / 1.645; \\ A &= |bias| + 1.645 \times TRSD, \ otherwise. \end{aligned} \qquad (6)$$

This expression is simple enough for calculation by most hand-held calculators, and it is also a useful starting point for estimating the 95% confidence limit $A_{95\%}$ on the accuracy range as measured during a method evaluation, accounting for evaluation errors.

b. Uses of the Symmetric Accuracy Range

method validation. One application of the symmetric accuracy range is for evaluating measurement methods. As mentioned in Chapter E, a method evaluation consists of a number of measurements taken from replicate samplers at each of several controlled and known concentrations covering the range of expected method application. This type of experiment gives information about the samplers' random errors and also the bias relative to reference concentrations. A confidence limit on the accuracy range can then be computed. One objective in a method suitable for NIOSH application is that the 95% confidence limit $A_{95\%}$ not exceed 25%. *A* includes both the uncertainty (as the term is used by ISO GUM) and the systematic deviation or bias, so that correction of the bias by the sampler vendor or developer is encouraged by the very statement of this objective. See Eqs. 9-11 below for computing $A_{95\%}$ when bias is negligible.

measurement uncertainty. Suppose then that bias correction has been made. For example, suppose that following evaluation, the sampler is used for future measurement with bias corrected on the basis of its measurement during the evaluation itself. Then computation of the confidence limit $A_{95\%}$ is possible accounting for the residual bias which is uncorrectable due to evaluation limitations, but nevertheless will be present in all future measurements. The quantity $\hat{c}\, x\, A_{95\%}$ in this case forms the counterpart to the expanded uncertainty *U* of ISO GUM for specifying evaluation confidence at 95%.

The relationship between $\hat{c}$ x $A_{95\%}$ (with corrected bias) and expanded uncertainty U can be seen most clearly in the case that $A_{95\%}$ is significantly smaller than 100%. In this case, Eq. 4 can be rewritten as the approximation:

$$\hat{c} - \hat{c} \times A_{95\%} < C < \hat{c} + \hat{c} \times A_{95\%}, \tag{7}$$

which means that at 95% confidence in the method evaluation, the inequality bracketing the measurand value C holds at probability > 95%. A study using 10,000-point simulations indicates that $A_{95\%}$ can be as large as 25%, with method evaluation confidence close to 95% using the approximation of Eq. 7. As can be seen directly, Eq. 7 is the analogue to Eq. 3 when $\hat{c}$ x $A_{95\%}$ is adopted as the *expanded uncertainty U*:

$$U = \hat{c} \times A_{95\%} . \tag{8}$$

In the case that bias is known to equal zero (*Technical Note 1* at the end of this chapter), $A_{95\%}$ (at 15 degrees of freedom in the evaluation experiment) is simply:

$$A_{95\%} = 2.8 \cdot \hat{TRSD}. \tag{9}$$

Eq. 8 then gives:

$$\begin{aligned} U &= 2.8 \cdot \hat{TRSD} \cdot \hat{c} \\ &= 2.8 \cdot u_c. \end{aligned} \tag{10}$$

Therefore, the coverage factor k is

$$k = 2.8, \tag{11}$$

consistent with the use of $k = 3$ as a conservative but not excessive value.

The user of a method then may report the expanded uncertainty U in a concentration estimate $\hat{c}$ using Eq. 8, knowing the accuracy range confidence limit $A_{95\%}$ as reported in the method. Of course, this approach relies on the sense of double confidence—in the evaluation and also in the subsequent application.

Note: The European Assessment of Workplace Exposures Technical Committee, CEN TC 137, has adopted a similar viewpoint regarding method performance [20]. In this case, an *overall uncertainty*, defined as |*bias*| + 2 × *RSD*, is used to quantify accuracy. When compared to Eq. 6, the overall uncertainty can be regarded as an approximation to the symmetric accuracy range.

4. UNCERTAINTY AND ANALYTICAL LAB PROCEDURES

Interest in measurement uncertainty and ISO GUM is currently finding its way into the criteria for the accreditation of analytical labs [4]. The result will no doubt be high confidence in understanding one component of the combined or expanded uncertainty namely the analytical component. Several general approaches to controlling and characterizing analytical uncertainty in routine lab practices seem reasonable.

a. Validated Method Adoption

One possibility is for a lab to adopt a published, evaluated method. Such an adoption would require an initial establishment of the method within the lab's capabilities. Equivalence to the published method would be established during this initial phase. Thereafter, the method's uncertainty as documented in the original publication would be claimed for the lab results. Ongoing analysis of a limited number of quality control samples would provide evidence that the method as implemented in the lab remains stable.

An example of this approach is the current practice in some labs that handle sorbent tubes to analyze about 4 lab blanks per set of field samples analyzed. The variability in the blank results are then continually compared to past lab performance so as to detect problems which may occur in analysis. Though the small number of degrees of freedom (= 3) does not give a tight figure on the uncertainty, it nevertheless gives assurance that the method is stable.

As a specific example of method evaluation data and documentation of an uncertainty budget, data from n = 16 exposures of diffusive samplers in a controlled environment are shown in Table 2. The evaluation is somewhat simplified for this example; a more comprehensive evaluation would also measure effects of wind velocity, humidity, temperature, and concentration time-dependence (potentially significant to diffusive monitoring). Analysis of these data can be handled by an ordinary calculator capable of computing means and standard deviations.

Note that the uncertainty ($\hat{r}RSD/\sqrt{n}$, where n = 16 is the number of measurements) in the bias is the value that accounts for residual bias due to imperfect correction. Very similarly, the uncertainty in the reference concentration is pooled to arrive at a combined uncertainty. Interestingly, neither of these two contributions corresponds to quantities that vary during sampler application subsequent to its initial evaluation. The background for documenting residual (uncorrectable) bias can be seen in *Note 2* at the end of this chapter.

Table 2. Example of Method Evaluation and Uncertainty Budget

Evaluation experimental results

The following are results from a simplified evaluation of a specific diffusive sampler for o-xylene. There were four experimental runs with four samplers each. The reference concentration set within the exposure chamber is denoted as $\hat{C}$ having an assigned (Type B) relative uncertainty = 1%.

Run 1 $\hat{C}$ (ppm) = 123	replicates (ppm)	$\Rightarrow \hat{TRSD}_{inter}$ [$s / \hat{C}$]	$\hat{bias}$
	139.2		
	138.2		
	138.6		
	145	2.6%	14.0%
Run 2 $\hat{C}$ (ppm) = 101.1	replicates (ppm)		
	108.3		
	110		
	110.7		
	112.8	1.8%	9.2%
Run 3 $\hat{C}$ (ppm) = 12.7	replicates (ppm)		
	14.2		
	15.3		
	12.9		
	14.6	7.9%	12.2%
Run 4 $\hat{C}$ (ppm) = 91.3	replicates (ppm)		
	109		
	109.2		
	107.1		
	105	2.1%	17.8%

Averaging the above bias estimates and pooling the inter-sampler estimates $\hat{TRSD}^2_{inter}$ results in:

Mean bias estimate: $\hat{bias}$ = 13.3% from average of 4 × 4 = 16 data points.

The TRSD estimate is $\hat{TRSD}_{inter}$ = 4.4% having 4 × 3 = 12 degrees of freedom.

Uncertainty budget

The following includes bias correction by dividing future concentration estimates by (1 + *biâs)* as in *Technical Note 2.*

Source	*Component*	*Category*
Inter-sampler	3.9% [= 4.4% / (1+.133)]	Type A
Bias Correction Uncertainty	0.97% [= 3.9%/$\sqrt{16}$]	Type A
Ref Concentration Uncertainty	0.5% [1% / $\sqrt{4}$, but not /(1 + $bi\hat{a}s$)]	Type B

Combined (Relative) Uncertainty $u_c = \sqrt{3.9\%^2 + 0.97\%^2 + 0.5\%^2} = 4.0\%$

Expanded (Relative) Uncertainty $U = k \times u_c = 12.1\%$ ($k = 3$).

Notes: Here $k = 3.0$. A more accurate determination based on the chi-square quantile at 12 degrees of freedom and prob = 0.05, gives $k = 2.97$, which is consistent with conventional use of 3 as a conservative value.

Again, an expanded (relative) uncertainty *U* means that with greater than 95% of future bias-corrected estimates $\hat{c}$, true concentrations *C* are bracketed by:

$$\hat{c} \times (1 - U) < C < \hat{c} \times (1 + U)$$

at 95% confidence in the above evaluation experiment. Generally, a quality control program is required to ensure that the method remains stable following evaluation.

Note that many methods (e.g., those based on sorbent tubes) employ personal sampling pumps, in which case normally a 5% (Type B) component representing sampling pump uncertainty would be included in the uncertainty budget.

Note also that the inter-sampler component includes both analytical and sampling sub-components. Further refinement of the inter-sampler component may perhaps be useful for improving a method, but is not needed for establishing confidence intervals around (true) measurand values.

Note further that storage effects require estimating and inclusion in the budget if considered significant.

b. Pooled Quality Control Results

Another approach utilizes a large number (e.g., 50) of the most recent quality control sample results. By pooling uncertainty values, a running method evaluation can be effected. The result is (1) a direct measure of the analytical uncertainty of the method as implemented in the lab, and (2) a means of detecting any problems that may creep into a method during routine use. Note that a running uncertainty average is similar to a partial method evaluation and not to a method re-evaluation at each measurement because consecutive running averages are strongly correlated.

This approach is adopted within a current MSHA procedure for the analysis of silica. A sampling filter is dissolved and re-deposited onto an analysis filter where the silica is quantified by infrared absorption. From each batch of samples to be analyzed, an analysis filter is retained for re-dissolution, re-deposition, and re-analysis within a subsequent batch. The result is a large number of pairs of nearly identical samples, which can give a running estimate of the method's analytical uncertainty.

c. Continual Method Re-Evaluation

A third possibility, the closest to the original measurement approach of GUM uses a large number (e.g., 30) of *independent* control samples for each application measurement. This is the most expensive approach, but also may give the best estimate of the analytical uncertainty, especially in cases where uncertainties may be measurement-dependent. Because many more evaluative measurements per application measurement are needed, this approach is not easily implemented for most industrial hygiene applications.

As an example of this approach [2], suppose that a lab estimates only a 30-day average concentration of a given gas or vapor. Further, every day a measurement is taken of a known calibration gas concentration. Then, if the method is expected to behave similarly for measurements of gas and field samples calibrations, the 30 control samples give analytical uncertainty estimates that differ month-to-month and from field measurement to field measurement.

d. Limit of Detection and Detection Limit

When the concentration is low, approaching the method uncertainty u_c, concepts of the limit of detection (*LOD*) and a related detection limit L_D may be useful. *LOD* is used for controlling false positives when asserting the presence of a substance. On the other hand, the detection limit specifies what measurand value (e.g., concentration) is required so that the false negative rate is negligible when the substance is actually present. The limits can refer to the analytical measurement only or, as in this section, to the entire sampling and analytical measurement method.

In the following examples, several often realistic assumptions are made. The standard deviation in concentration estimates is assumed constant (i.e., independent of the sampled concentration), unlike the commonly occurring constant *relative* standard deviation at larger concentrations. Also, bias (or uncertainty in its correction) is assumed to be negligible. More

complicated cases generally have specific difficulties that are best be approached by a statistician.

With these assumptions, in terms of the combined uncertainty u_c the limit of detection is traditionally [23, 24] taken to be:

$$LOD \equiv 3 \times u_c \quad , \tag{12}$$

and the detection limit may be defined as

$$L_D \equiv 2 \times LOD \, . \tag{13}$$

Note that u_c includes the uncertainty associated with correction, if any, with blank subtractions. See Ref. [5] for a detailed example.

After *LOD* and L_D have been determined for a method they may be used as follows. A substance may be asserted as present if an estimate $\hat{x}$ exceeds *LOD*. Moreover, if unknown (true) concentration *X* exceeds L_D, an estimate $\hat{x}$ is likely to exceed *LOD*. Given the above definitions and assumptions, the false positive rate *r* on asserting presence is closely equal to the non-detection rate.

Note: If the combined uncertainty u_c is determined from a method evaluation providing an effective number υ (as in Technical Note 2) degrees of freedom, then at 95% confidence in the method evaluation, the false positive rate r is limited by:

$$r < 1 - \Phi[3 \times \sqrt{\chi^2_{0.05,\upsilon} / \upsilon}], \tag{14}$$

where Φ is the cumulative normal function. For example, if $\upsilon = 15$, then $r < 3.5\%$.

5. DISCUSSION

The approach presented here to document method accuracy range and uncertainty relates to the statistical theory [11, 16-22] of *tolerance or prediction intervals*. This theory was originally developed in simplified form to predict the range of future measurements of a normally distributed random variable on the basis of *n* initial measurements. The *initial measurements* are analogous to the method evaluation, whereas the *future measurements* represent method application subsequent to evaluation.

Because of measurement cost, workplace assessments cannot at present be conducted in such a way that continual re-evaluation is done at each measurement. The prediction interval approach given here shows a less costly way to document measurement uncertainty in those cases where a method has been initially evaluated and then used many times without re-evaluation. The approach closely follows ISO GUM. Of course, for such an approach to actually make sense, an adequate quality control program must be instituted so that the measurement method remains stable during the time of its application following evaluation.

Several generalizations and variations of the material presented in this chapter are possible. The relative standard deviation and relative bias sometimes depend on the concentration sampled in a complicated way, requiring special attention. See, for example Ref. [24]. Also, asymmetric confidence intervals are sometimes required. Single-sided intervals are useful in some instances, e.g., alarm systems, as well as in quantifying limits of detection or quantitation, described briefly above. Ways to handle environmental influence parameters may also be complicated. See, for example Ref. [9]. In any case, despite the complexities possible, the examples given in this chapter may help to characterize method uncertainty in a reasonable manner.

6. TECHNICAL NOTES

Note 1: *Mainly for the statistically minded.*
Example of accuracy range confidence limit:

Suppose it is known that the bias is zero. For example, an exposure standard may be set that specifies a given sampling and analytical method. In this case, the hazardous concentration may be said to be *operationally defined.* Operationally defined methods include NIOSH Methods 7400 and NIOSH 5040.

If the bias is zero, Eq. 6 simplifies to:

$$A = 1.960 \times TRSD \ .$$

Furthermore, if the relative standard deviation is estimated as $\hat{TRSD}$ with υ degrees of freedom (computed using the Smith-Satterthwaite approximation [1,13-14] if *TRSD* has more than one component), then the 95% confidence limit on *TRSD* is:

$$TRSD_{95\%} = \hat{TRSD} \times \sqrt{\upsilon / \chi^2_{\upsilon,0.05}} \ ,$$

where $\chi^2_{\upsilon,0.05}$ is a 5% quantile value for the chi-square distribution, which can be read from a table in most elementary statistics texts. This determines the 95% confidence limit on the accuracy range itself as:

$$A_{95\%} = \hat{A} \times \sqrt{\upsilon / \chi^2_{\upsilon,0.05}} \ .$$

If υ = 15, $\sqrt{\upsilon / \chi^2_{\upsilon,0.05}} = 1.44$, giving coverage factor k = 2.8 (Eq. 11).

Note that $TRSD_{95\%}$ can be interpreted as a conservative estimate of *TRSD* and therefore can be treated as a Type B uncertainty with infinite number of degrees of freedom as described following Table 1.

Note 2: For statisticians only.
Single-evaluation correction of bias:

Details are given here illustrating the tolerance interval approach, bias correction, imprecise reference concentrations, and the use of the symmetric accuracy range function. The derivation is not entirely general, but is given here for guidance in handling the myriad possibilities in measurement uncertainty. Though the derivation is slightly complicated, the result obtained is simple.

Suppose that estimates $\hat{c}$ having an as-yet-unknown constant *bias* relative to true concentrations C (not necessarily constant) may be modeled as:

$$\hat{c} = C \cdot [1 + bias + \hat{\varepsilon}],$$

where the random variable $\hat{\varepsilon}$ is approximately normally distributed about zero with variance $TRSD^2$. For evaluating the method, assume that reference concentration measurements $\hat{C}$ can be made simultaneously and modeled by:

$$\hat{C} = C \cdot [1 + \hat{\varepsilon}_{ref}],$$

where $\hat{\varepsilon}_{ref}$ has variance $TRSD_{ref}^2$, assumed known accurately. Measure n values of the ratio $\hat{\theta}$:

$$\hat{\theta} \equiv \hat{c} / \hat{C} = 1 + bias + \hat{\varepsilon}_c$$

and compute estimates $\hat{bias}$ and $\hat{TRSD}_c^2$ at $\upsilon = n - 1$ degrees of freedom, where the approximately normally distributed random variable $\hat{\varepsilon}_c$ has variance $TRSD_c^2$ given by:

$$TRSD_c^2 = TRSD^2 + (1 + \hat{bias})^2 \times TRSD_{ref}^2$$

(to the order of $TRSD$, neglecting Cauchy effects of reciprocals of random variables).

Future bias-corrected measurements $\hat{x}'$ of unknown concentration X can be defined in terms of raw measured values $\hat{x}$ as:

$$\hat{x}' \equiv \hat{x} / (1 + \hat{bias}).$$

The residual corrected $bias'$ is then given by:

$$bias' = (bias - b\hat{i}as)/(1 + b\hat{i}as).$$

If n is large enough, $|bias'|$ will be small enough that the corrected symmetric accuracy range A' can be accurately approximated (Eq. 6) as:

$$A'^2 = a^2 1.960^2 / (1 + b\hat{i}as)^2,$$

where the unknown a^2 is:

$$a^2 = (bias - b\hat{i}as)^2 + TRSD^2,$$

whose confidence limit is now required.

First note that the expected value of the first term is:

$$E[(bias - b\hat{i}as)^2] = TRSD_c^2 / n .$$

Therefore, an estimate $\hat{a}^2$ for a^2 can be constructed as:

$$\hat{a}^2 \equiv T\hat{R}SD_c^2 / n + T\hat{R}SD^2$$
$$T\hat{R}SD^2 \equiv T\hat{R}SD_c^2 - (1 + b\hat{i}as)^2 \times TRSD_{ref}^2 .$$

Expressed in terms of $T\hat{R}SD^2$, $\hat{a}^2$ is

$$\hat{a}^2 = T\hat{R}SD^2 + \frac{1}{n} T\hat{R}SD^2 + \frac{1}{n} \cdot (1 + b\hat{i}as)^2 \times TRSD_{ref}^2 .$$

Each term can now be identified, forming the basis for an uncertainty budget: the first is the (uncorrected) method uncertainty (squared); the second and third reflect the bias-correction uncertainty owing to finiteness of the validation experiment and the uncertainty in the reference concentration (as here measured n times).

A confidence limit a_β^2 at confidence level β (e.g., 95%) on a^2 is now constructed using $\hat{a}^2$:

$$a_\beta^2 = K^2 \cdot \hat{a}^2,$$

where the constant *K* is to be determined so that

$$prob\{a_\beta^2 < a^2\} = 1-\beta\,.$$

First of all, the distribution of $\hat{a}^2$ is approximated as chi-square:

$$\upsilon_{eff}\frac{\hat{a}^2}{E[\hat{a}^2]} \approx \chi^2,$$

where υ_{eff} is determined as with the Smith-Satterthwaite [23-24] approximation, forcing variances to agree; often $\upsilon_{eff} \approx n-1$.

Now,

$$a_\beta^2 < a^2 \Leftrightarrow \hat{a}^2 < K^{-2}a^2\ ,$$

or, in other words:

$$\chi^2 < \upsilon_{eff}\,(K^{-2}a^2) \,/\, E[a^2]\,.$$

[Note that $E[\hat{a}^2] = E[a^2], but \neq a^2$, unlike *Note 3.*]

Remembering that a^2 depends on the estimate $bi\hat{a}s$, *K* is given as a solution of the following integral equation:

$$1-\beta = \int_{-\infty}^{+\infty} d\,bi\hat{a}s\,P[bi\hat{a}s] \int_0^{\upsilon_{eff}\cdot K^{-2}\cdot a^2 / E[a^2]} d\chi^2 P_{\upsilon_{eff}}[\chi^2]$$

$$= \int_0^{\upsilon_{eff}\cdot K^{-2}} d\chi^2\,P_{\upsilon_{eff}}[\chi^2]\times(1+O[1/n^2])\ ,$$

where the correction $O[1/n^2]$ is easily proved by expanding the integrand about $TRSD_c^2$ in $(bi\hat{a}s - bias)^2$. Therefore, the following simple asymptotic expression for K^2 results:

$$K^2 \approx \upsilon_{eff} \,/\, \chi^2_{1-\beta,\upsilon_{eff}}\,.$$

Thus, the coverage factor *k* is approximated as:

$$k \approx 1.960 \cdot \sqrt{\upsilon_{eff} / \chi^2_{1-\beta,\upsilon_{eff}}} ,$$

which is less than and close to 3.0, if the effective number of degrees of freedom $\upsilon_{eff} \geq 12$, and $\beta = 0.95$.

In summary, the bias uncertainty is pooled together with the uncertainty components in $T\hat{R}SD^2$.

It should be remembered, however, that only $T\hat{R}SD$ refers to quantities, which vary at each of the future measurements following the initial evaluation.

Note 3: *For statisticians.*
Characterizing effects of uncorrected bias:

If the systematic error (bias) is non-zero, confidence limits on the accuracy range *A* may be approximated as follows. The Smith-Satterthwaite approximation is generalized in approximating estimates $\hat{A}$ in terms of a chi-square random variable χ^2_υ for the two cases in Eq 6 by:

$$\hat{A} / A = \begin{cases} \sqrt{\chi^2_\upsilon / \upsilon}, & if \ |bias| < RSD / 1.645; \\ \chi^2_\upsilon / \upsilon, & otherwise \end{cases}$$

The effective number of degrees of freedom υ is determined by forcing the variance of χ^2_υ to reproduce the estimated variance of $\hat{A}^2$ or $\hat{A}$ in their respective cases:

$$\upsilon = \begin{cases} 2A^4 / \mathrm{var}[\hat{A}^2], & if \ |bias| < RSD / 1.645 \\ 2A^2 / \mathrm{var}[\hat{A}], & otherwise \end{cases}$$

Calculation of $\mathrm{var}[\hat{A}^2]$ or $\mathrm{var}[\hat{A}]$ is generally straightforward and depends on specifics of the evaluation experiment and on significant influence parameters. The confidence limit $A_{95\%}$ is then determined as in Eq 9:

$$A_{95\%} = \begin{cases} \hat{A} \times \sqrt{\upsilon / \chi^2_{0.05,\upsilon}}, & if \ |bias| < RSD / 1.645 \\ \hat{A} \times \upsilon / \chi^2_{0.05,\upsilon}, & otherwise \end{cases}$$

This expression has been found [12] quite accurate, exhibiting negligible effects from the discontinuity: The chi-square approximation is expected to be worst when $|bias|$ is large relative

to $TRSD$. As an example, suppose the uncertainty has the following components: 5% from pump error and also a 5% analytical relative standard deviation. Suppose $bias$ = 20%. Suppose bias and the analytical uncertainty are measured with υ = 15 degrees of freedom. Then 10,000-point simulations indicate that the calculated $A_{95\%}$ is slightly conservative, giving 96% confidence.

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7. TERMINOLOGY

A — *symmetric accuracy range*, relative (%) range of 95% of a method's measurements about the (true) measurand

$A_{95\%}$ — 95% confidence limit on the symmetric accuracy range

$bias$ — mean concentration estimate *bias* relative to the (true) measurand

$\hat{bias}$ — bias estimate

$\hat{c}$ — concentration estimate

C — true concentration

$\hat{C}$ — reference concentration (estimate)

k — *coverage factor*, a constant containing confidence information for obtaining the expanded uncertainty U as a factor of the combined uncertainty u_c

L_D — *detection limit* (for controlling false negatives)

LOD — *limit of detection* (for controlling false positives)

n — number of measurements in a method evaluation

s_j^2 — unbiased estimate of variance σ_j^2

σ_j^2 — jth population variance component

$TRSD$ — (true) relative standard deviation

$TRSD_{ref}$ — (true) relative standard deviation in reference concentration (estimates)

u_j — jth *uncertainty* component, an estimated standard deviation

u_c — *combined uncertainty*, pooled uncertainty components

U — *expanded uncertainty*, a value giving intervals bracketing the (true) measurand at given confidence in the measurement and method evaluation

υ_j — degrees of freedom in an estimate s_j^2

$\chi^2_{\upsilon,0.05}$ — chi-square quantile. This quantity by definition exceeds the chi-square variable at probability = 5%. Note that many tables use the notation $\chi^2_{\upsilon,0.95}$ for this quantity.

In general, hats represent estimates. Primes indicate bias-corrected quantities.

Q. MONITORING OF DIESEL PARTICULATE EXHAUST IN THE WORKPLACE
by M. Eileen Birch, NIOSH/DART

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1. INTRODUCTION

a. Health Effects

In the United States alone, over a million workers (e.g., trucking, mining, railroad, agriculture) are occupationally exposed to diesel exhaust [1]. The widespread and growing use of diesel-powered equipment has raised concern because workers exposed to diesel exhaust show an elevated (20% to 50%) risk of lung cancer [2]. While environmental exposure is a concern, occupational exposure is a greater one because workplace exposures to diesel exhaust are generally much higher. The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen and recommends that employers reduce workers' exposures [1]. This [1988] recommendation was based on five independent animal studies in which rats exposed to unfiltered exhaust showed an increased incidence of benign and malignant lung tumors [3]. Other organizations, including the International Agency for Research on Cancer (IARC) [3], the World Health Organization (WHO) [4], the California Environmental Protection Agency [5], the U.S. Environmental Protection Agency (U.S. EPA) [6], and the National Toxicology Program [7] have reviewed the animal and human evidence, and each has classified diesel exhaust as a probable human carcinogen or similar designation.

Noncancer health effects have also been associated with diesel exhaust exposure, including immunologic, respiratory, and cardiovascular effects. Diesel exhaust particles can act as nonspecific airway irritants at relatively high exposures. At lower levels, they can trigger release of mediators (cytokines, chemokines, immunoglobulins, and oxidants) of allergic and inflammatory responses [8]. Diesel particles may promote expression of the immunologic response phenotype (Th2) associated with asthma and allergic disease and appear to have greater immunologic effects in the presence of environmental allergens. Internationally, the prevalence of asthma (and related hospitalizations and mortality) continues to rise in adults and children. Children may be more vulnerable than adults [9-12]. Studies indicate children living along major trucking thoroughfares are at increased risk for asthmatic and allergic symptoms. In the United States, the number of individuals with self-reported asthma increased by 75% from 1980 to 1994 [13]. The immunologic evidence is consistent with results of epidemiologic studies that associate traffic-related air pollution, especially diesel exhaust particles, to an increase in respiratory diseases.

Studies have consistently found positive associations between particulate air pollution and daily mortality [14 23]. The traditional U.S. air quality standard for particulate matter is based on particles having diameters $\leq$ 10 µm (PM_{10}) [24]. In 1997, EPA proposed a new standard (see http://www.epa.gov/airlinks/airlinks4.html) based on particles having diameters $\leq$ 2.5 µm ($PM_{2.5}$). These smaller particles originate mainly from combustion sources. The new standard was proposed because recent studies show higher correlation between fine particle pollution and adverse health effects. In an analysis [19] of data from six U.S. cities, fine particles were consistently associated with increased risk of death from chronic obstructive pulmonary disease, pneumonia, and ischemic heart disease. Positive associations between fine particle pollution and hospital admissions due to respiratory and cardiovascular illness also have been found [25 27]. Particles produced by combustion sources have been implicated in these findings. In addition to asthma, chronic inhalation of diesel exhaust particles may play a role in these adverse health outcomes. Comprehensive reviews on the health effects of diesel exhaust can be found elsewhere [1-7, 28, 29].

b. Composition

Diesel engine exhaust is a highly complex and variable mixture of gases, vapors and fine particles. The amount and composition of the exhaust vary greatly, depending on factors such as fuel and engine type, maintenance schedule, tuning, workload, and exhaust gas treatment. The gaseous constituents include hydrocarbons and oxides of carbon, sulphur, and nitrogen. Particulate components consist of liquid droplets and soot particles bearing organic compounds, sulfates, metals and other trace elements. The organic fraction (droplets and particle adsorbed) is mainly unburned fuel and oil, but also contains thousands of compounds (e.g., aldehydes; polycyclic aromatic hydrocarbons [PAH]) some of which are genotoxic. Detailed information on the composition of diesel exhaust has been published previously [1-4, 28].

c. Analyte Choice

Because diesel exhaust is a highly complex mixture, a surrogate of exposure must be selected. In the early nineteen-nineties, NIOSH researchers considering potential surrogates sought an overall measure of the particulate fraction because animal studies linked lung tumor induction to unfiltered diesel exhaust [1,3], and most (90% in one study) [30] of the exhaust's mutagenic potency was associated with the particulate fraction. At the time, gravimetric methods for respirable combustible and submicrometer dusts were being used in mines, but gravimetric methods lack selectivity and are not suitable for low-level (e.g., < 200 $\mu g/m^3$) measurements. Methods for characterization of the soluble organic fraction of diesel particulate matter also were available; others have since been developed. Although measurement of specific organic compounds, particularly genotoxins, may be relevant in characterizing the potential toxicity of diesel exhaust, a single compound or compound class would not reflect exposure to the particulate fraction even if unique markers are found because the composition of the exhaust is highly variable.

Carbon is a logical exposure surrogate to monitor because diesel particulate matter is predominantly (typically more than 80%) carbon [31-33], but carbon in the organic fraction (i.e., *organic carbon,* or OC) of diesel particulate matter is not a selective measure because other sources of OC (e.g. cigarette smoke and other combustion aerosols, asphalt fumes) are present in many workplaces.

Elemental carbon (i.e., carbon in the soot particle core, or EC) is a better surrogate [34] to monitor because it is a more selective measure of particulate diesel exhaust and still constitutes a sizable fraction (30% 90%) (see reference [28], Part I, Section 1) of the particulate mass. Fine EC particles are derived primarily from the combustion of fossil fuels, and diesel engines are major sources of these particles. Carbonaceous aerosols such as cigarette and wood smokes contain little, if any, EC [34, 35]. Gasoline engines emit far less EC than diesels, so the contribution of this source is relatively small. Other sources such as coal combustion, incinerators, and tire debris can contribute to the background (environmental) levels of EC, but diesel engines are the primary emitters (see reference [2]: Sawyer and Johnson; Cass and Gray). In occupational settings, where diesel equipment is used in relatively close proximity to workers, the contribution of these remote sources is negligible, especially when EC levels are well above background. Environmental EC concentrations typically range from about 1 3 $\mu g/m^3$ [34]; workplace levels are generally much higher [36 43]. Although higher background levels (near 5 $\mu g/m^3$) have been reported for more polluted U.S. cities (e.g., Los Angeles), the higher levels were attributed to diesel vehicles [44, 45] (see also reference [2], Cass and Gray). At one monitoring site (Glendora, CA), examination of the data collected at 1-minute intervals revealed that emission plumes from diesel vehicles located 50 meters from the site contributed up to 5 $\mu g/m^3$ above the background level [46].

Materials such as coal dust contain EC (content depends on coal rank), but mechanically generated particles are larger (generally > 1 µm diameter) than combustion-based particles. Therefore, coal dust, and other mechanically generated dusts, can be effectively excluded

from the diesel sample on the basis of size. Only low levels of EC ($\leq$ 15 $\mu g/m^3$) were found in electric-powered (i.e., nondieselized) coal mines when impactors with submicrometer cutpoints were used for air sampling [47]. Guidance on air sampling is discussed in a following section.

In addition to selectivity, potential health effects were considered when an EC surrogate was proposed [34, 48, 49]. Diesel particles and other types of insoluble fine particles are inhaled deeply into the lungs, where they can induce an inflammatory response. Further, EC particles increase the long-term retention [50, 51] of adsorbed genotoxins and other chemical toxins because the particles have a high affinity for them [52]. The adsorbed organic fraction results from rapid cooling of the exhaust mixture, which causes enrichment of some species on the particle surface [53 5 5]. Enrichment by this mechanism is associated with compounds of moderate to low volatility [54, 55]. For example, PAHs having four or more rings are generally associated with particulate matter [56]; this is important because these higher-ring condensates are expected to be the most carcinogenic or mutagenic [57, 58]. In combination with an inflammatory response induced by the particles, genotoxic agents may promote tumorigenesis. Ultrafine particles (< 0.10 µm) may pose an even greater health risk. Results of toxicological studies on solid particles having aerodynamic diameters in this size range indicate ultrafine particles are especially toxic, even those not having an organic fraction and consisting of materials considered relatively nontoxic (e.g., carbon black, titanium dioxide). In a recent study (see reference [23], Donaldson et al.) of rats, a 10-fold increase in inflammation was seen with exposures to ultrafine particles, relative to the same mass of fine particles. This is significant because, by mass, the majority of diesel particles are in the fine particle range, and most are in the ultrafine range by number (see reference [28], Kittleson et al.). Given the physical and chemical nature of EC particles emitted by diesel engines, monitoring and controlling exposures to these particles is prudent.

2. ANALYTICAL METHOD

a. Background

A monitoring method for diesel particulate matter was published as Method 5040 in the NIOSH Manual of Analytical Methods (NMAM). The method is based on a thermal-optical analysis technique for particulate carbon. Both OC and EC are determined by the method, but EC is a better surrogate of exposure. Rationale for use of an EC surrogate is summarized in the previous section (see Analyte Choice). Method updates have been published [59, 60] to include data (e.g., round robin results) obtained since the initial publication (1996) of the method. NMAM 5040 has been used in numerous industrial hygiene surveys, [36 43] and it was recently applied to an ongoing epidemiological study (NIOSH/National Cancer Institute [NCI]) of miners. Details on method operation and performance are provided in this chapter. Recently proposed exposure criteria also are discussed.

b. Instrumentation

Of the possible approaches for OC-EC analysis, a thermal-optical technique was investigated because it offers greater selectivity (a pyrolysis correction for char) and flexibility (automated analysis, programmable parameter files) than previously used methods. While thermal-optical methods have not been widely used in the industrial hygiene field prior to its proposed use for diesel exhaust monitoring, they have been routinely applied to environmental monitoring of particulate carbon air pollution.

The thermal-optical analyzer has been described previously [34, 59]. Design improvements have since been made, but the operation principle remains unchanged. The analyzer (Figure 1) is equipped with a pulsed diode laser and photodetector that permit continuous monitoring of the sample filter transmittance. This optical feature corrects for the char formed during the analysis of some materials. As in samples where EC is initially present, char strongly absorbs light, particularly in the red/infrared region. Char is formed through pyrolysis, which is a thermal decomposition process. When some organic substances are heated to elevated temperatures in an inert (non-oxidizing) atmosphere, carbonization (conversion to carbon) occurs. Both volatile products and char (decomposition product containing mostly carbon) are formed in the process, which can begin at temperatures as low as 300 °C.

In the thermal-optical analysis, a filter portion (punch) of known area (typically 1.5 cm^2) is placed in the sample oven, and the oven is tightly sealed. Quartz-fiber filters are required because temperatures in excess of 850 °C are employed. The analysis proceeds in inert and oxidizing atmospheres. In both, the evolved carbon is catalytically oxidized to carbon dioxide (CO_2). The CO_2 is then reduced to methane (CH_4), and CH_4 is quantified with a flame ionization detector (FID).

OC (and carbonate, if present) is first removed in helium, as the temperature is increased to a preset maximum (about 870 °C, NMAM 5040). If charring occurs, the filter transmittance decreases as the temperature is stepped to the maximum. After OC is removed, an oxygen-helium mix is introduced to effect combustion of the remaining material. As light-absorbing carbon is oxidized from the filter, the filter transmittance increases. The split (Figure 2) between the OC and EC is assigned when the initial (baseline) value of the filter transmittance is reached. All carbon removed before the OC-EC split is considered organic, and that removed after the split is considered elemental. If no charring occurs, the split is assigned prior to removal of light-absorbing carbon. If the sample chars, the split is not assigned until enough light-absorbing carbon is removed to bring the transmittance back up to its initial value. In general, char is more readily oxidized than diesel-particle EC. The delay (i.e., the transit time from sample to FID) between the laser and FID signals is considered in the split assignment. Ordinarily, the split is assigned in the oxidative mode of the analysis.

EC and OC results are reported in micrograms per square centimeter ($\mu g/cm^2$) of the sample deposit. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous deposit is assumed. For triplicate analyses, the precision (relative standard deviation) is normally under 5%, and it is typically

2% or better [60]. The total carbon (TC) in the sample is the sum of OC and EC. If carbonate is present, the carbon in it is quantified as OC, unless a carbonate-subtracted value is requested by the client. Additional details about carbonates are given in a following section.

c. Standards

Currently, a reference material is not available for determining the OC and EC content of a complex carbonaceous aerosol. For this reason, only the accuracy of the method in the determination of TC could be examined. No discernable differences in the responses of five different organic compounds were noted. Linear regression of the data (43 analyses total) for all five compounds gave a slope and correlation coefficient (r) near unity [slope = 0.99 (± 0.01), r^2 = 0.999, n = 43]. In addition to the OC standards, eight different carbonaceous materials were analyzed. Three different methods (including the thermal-optical method) were used, and laboratories reported the TC contents of the samples. The samples analyzed included diesel particulate matter and other types of carbonaceous matter (coals, urban dust, humic acid). Thermal-optical results agreed well with those reported by the two other laboratories. The variability in TC results for the three laboratories ranged from about 1% 7%. These findings [34, 59] indicate that the carbon in a sample is accurately quantified, irrespective of sample type.

To estimate the method's limit of detection (LOD), a set of low-level calibration standards (ethylenediaminetetraacetic acid [EDTA]) was analyzed [34, 59]. The standards covered a loading range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter). Results of linear regression of the low-level calibration data were then used to calculate a 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 LOD estimated through the linear regression results was 0.24 µg C, or 0.15 µg/cm^2. This value showed good agreement with the LOD estimated as $3\sigma_{blank}$ (three times the standard deviation for blanks), which gave a value of about 0.3 µg C. The mean (n = 40) instrumental blank was 0.03 ± 0.1 µg C. With a 960-L air sample collected on a 37-mm filter and use of a 1.5 cm^2 sample portion, this LOD translates to an air concentration of about 2 µg/m^3. As with all analytical methods, the LOD is a varying number. Other values can be expected, depending on the individual instrument and means by which the LOD is calculated.

d. Air Sampling

In the initial evaluation of the thermal-optical method, a set of laboratory-generated air samples was analyzed. A dilution tunnel equipped with a dynamometer was used for generation of diesel particulate samples. Four EC concentrations, ranging from 23 to 240 µg/m^3 (EC loadings from 2.7 to 27 µg/cm^2), were generated. The analytical results [59] indicated that the method met the NIOSH accuracy criterion [61]. The variance was roughly proportional to the mean concentration; therefore, the relative standard deviation (RSD) decreased with increasing concentration. The accuracy was calculated accordingly. The accuracy was ± 16.7% at the lowest loading (2.7 µg/cm^2), with an overall precision (RSD) of 8.5%. On the basis of a method evaluation, the NIOSH accuracy criterion requires a confidence limit on the accuracy less than 25% at the 95% confidence level. Restated, the

criterion dictates that greater than 95% of the measurements fall within ± 25% of the true value at 95% confidence in the method's validation experiments. The method was considered unbiased (i.e., considered the reference method), and the overall precision reflected method accuracy. Sample generation and collection, not analysis, was the main source of variability.

When only combustion-source EC is present, different samplers can be expected to give comparable EC results because particles from combustion sources are generally less than 1 µm (diameter). As such, the particles are evenly deposited on the filter and collected with the same efficiency (near 100%). To confirm this assumption, seven different sampler types (open-faced 25-mm and 37-mm cassettes; 298 personal cascade impactor [7 stages, 0.9-µm cutpoint]; 4 prototype impactors) were used to collect diesel aerosol at the loading dock of an express mail facility. The RSD for the mean EC concentration was 5.6% [39]. Based on the 95% confidence limit (19%; 13 degrees of freedom, n = 14) on the accuracy, results of this experiment also indicated that the NIOSH accuracy criterion [61] was fulfilled. The amount of EC collected (240 µg per sample) would have been equivalent to sampling an air concentration of 250 µg/m^3 for 8 h at 2 L/min. Variability in the OC results was higher (RSD = 12.3%), which is to be expected when different samplers are used to collect aerosols that contain semivolatile (and volatile) components because these can have a filter face velocity dependence.

Similar performance was obtained from collected samples in an underground molybdenum mine. Five different sampler types were used (closed-face 25-mm and 37-mm cassettes; 298 cascade impactor [7 stages, 0.9-µm cutpoint]; cyclone with filter; in-house impactor). The RSD for the EC results (mean EC = 297 µg/m^3) was 7%. The EC deposits obtained with all five sampler types were homogeneous, even when the ore deposit was visually heavier in the center of the filter (e.g., with the closed-face 37-mm cassette). Although the dust loading was higher in the center of the filter, portions taken from the center gave equivalent EC results, indicating the ore contained no EC component. The TC results for the center portions were only slightly higher, so this particular ore was mostly inorganic. EC concentrations found with three different sampler types (nylon cyclone, open-faced cassette, and impactor with sub-micrometer cut) also were comparable in a study of railroad workers [42].

If high levels of other dusts are present, a size classifier (e.g., impactor and/or cyclone) should be used to prevent filter overloading, particularly if the dust is carbonaceous. In the latter case, a size classifier provides a more selective measure of the diesel-source OC. It also provides a better measure of the diesel-source EC if the dust contains an EC component, which is less common. A finely ground sample of the bulk material can be analyzed to determine whether a specific dust poses potential interference [34]. Depending on the dust concentration, size distribution, and target analyte, an impactor may be required.

For mines, the Mine Safety and Health Administration (MSHA) recommends a specialized impactor to minimize collection of carbonates and other carbonaceous dusts [62]. An impactor can greatly improve the selectivity of the TC measurement in some cases, but it may exclude a small amount of the diesel particulate matter. Then, too, some OC interferences cannot be excluded on the basis of size (e.g., condensation aerosols, fumes, wood and cigarette smokes). If present in the sampling environment, these materials can positively bias

the OC (TC) results to some degree, depending on their relative concentrations and the sampling location. Although a 37-mm cassette is often suitable for general industry, the sampler required must be dictated by the sampling environment.

e. Carbonates

The presence of carbonate is indicated by a narrow peak during the fourth temperature step in helium (Figure 2). Its presence is verified by exposing a second portion of the filter to hydrogen chloride (HCl) vapor prior to analysis. When the acidified portion is analyzed, a diminished (or absent) peak during the fourth temperature step is indicative of carbonate in the original sample. (Note: Acid treatment may sometimes alter the appearance of the EC profile in the thermogram [output signal of thermal-optical instrument], but the EC result itself should not be affected significantly.)

A desiccator containing concentrated HCl (added to the desiccator or a petri dish placed at the bottom of it) can be used to acidify the sample portions. The desiccator, or alternative vessel, should be used in a well-ventilated hood. The filter portions are placed on the desiccator tray, and the tray is placed in the desiccator. A wetted pH indicator stick can be used to check acidity. A wetted indicator stick inserted between the desiccator lid and base should give a pH near 2. Portions should be exposed to the acid vapor for about 1 hour (large particles can require more time). After acidification, the tray is placed on a clean, inert surface inside the hood. The residual acid on the portions should be allowed to volatilize in the hood for at least an hour prior to analysis.

Environmental samples typically contain little (if any) carbonate, but levels in some occupational samples can be quite high. For example, respirable dust samples collected in limestone and trona mines can contain high levels of calcium carbonate and sodium sesquicarbonate, respectively. In such cases, acidified samples give a better measure of the diesel-source OC (TC). If the carbonate loading is relatively high (e.g., carbonate carbon > 10% of the TC), the difference between the TC results (before and after acidification) gives an estimate of carbonate carbon (CC). Estimation of CC by difference assumes the carbonate is evenly deposited on the filter, which may not always be the case. It also assumes that OC loss through acidification is negligible. The latter assumption is generally true for workplace samples, but depends on sample composition and loading.

Alternatively, a carbonate-subtracted OC (TC) result can be obtained through separate integration of the carbonate peak. This applies only to carbonates (e.g., calcium carbonate) that can be removed as a single peak during the fourth temperature step in helium. The carbonate of interest should be analyzed to ensure this is the case. A minor adjustment (lower) to the third temperature step may be necessary to prevent partial loss during this step. Sodium sesquicarbonate (trona) is removed over multiple temperature steps. Samples containing trona should be acidified if a carbonate-subtracted result is desired. (Note: *At elevated temperature, trona and other compounds containing sodium can etch the quartz oven wall and sample holder. An etched surface can reduce laser throughput. Avoid direct contact of these materials with the oven wall and sample holder.)*

The presence of a small 'peak' during the fourth temperature step is not necessarily due to carbonate. Other carbonaceous matter (e.g., char) is sometimes removed during the fourth step. Unlike carbonates, which produce a relatively sharp peak, other materials typically evolve as a small, broad peak. If determination of relatively low (e.g., CC < 10% of TC) amounts of CC is desired, a second portion of the sample should be acidified and analyzed to verify the presence of carbonate and reveal any underlying baseline features contributed by other materials. A more accurate estimate of CC can then be obtained by integrating the first (non-acidified) sample over the missing peak area (i.e., area removed through acidification).

f. Sampling Artifacts: Organic Aerosol

Face velocity. Quartz-fiber filters are routinely used to collect airborne particulate matter for carbon determination. Quartz filters have high collection efficiency for particulate carbon, but collection of organic aerosol is artifact prone [63 67]. Particulate carbon (EC and nonvolatile OC) results should not depend on filter face velocity. This is true for EC, but OC (and TC) results can have a face velocity dependence due to sampling artifacts. Namely, adsorption of organic vapor can positively bias the results, while evaporative losses have the opposite effect. Although both processes may occur, recent studies indicate vapor adsorption is the dominant artifact [65, 67]. In one study [65], the OC (TC) results for air samples collected at face velocities of 20, 40, and 80 cm/sec had a face velocity dependence before, but not after, correction for adsorbed vapor. Lack of dependence after correction supports adsorption as the dominant artifact. At the much lower face velocities typical of occupational monitoring (e.g., about 4 cm/sec with a 37-mm filter and 2 L/min flow rate), OC losses induced by pressure drop across the filter are expected to be minor relative to adsorption. OC sampling artifacts were acknowledged when the thermal-optical method was proposed [48, 49], but this issue was not investigated prior to publication of NMAM 5040 because an EC surrogate was recommended. In view of the MSHA-proposed air standard for TC, and the fact that both OC and EC are determined by the method, the issue has since been addressed.

Adsorbed OC. Correction for adsorbed organic vapor through use of traditional blanks (media or field) may not be accurate because the amount of vapor adsorbed by them is variable [68]. More importantly, traditional blanks collect vapor passively, while the samples collect it actively (during sampling). A more representative correction for adsorbed organic vapor can be made through use of two filters in tandem [65, 67]. The air sample is collected with a sampler containing a Teflon or quartz upper filter and a bottom quartz filter. After sampling, the bottom filter is used to correct for adsorbed vapor. The vapor adsorbed on the bottom filter more closely represents that adsorbed on the sample filter (quartz) because both are collected actively. Use of two quartz filters is preferable to Teflon and quartz because the filter used to correct for adsorbed vapor is in the same sampler; however, the second (bottom) quartz filter may underestimate the amount of adsorbed OC relative to a quartz filter under Teflon [65, 67]. These results have been attributed to depletion of the vapor concentration by the top quartz filter, which presents a lower concentration to the bottom one. A shorter equilibration time (for partitioning between gas phase and adsorbed state) is expected with Teflon filters because they have less surface area and are more inert than quartz. Thus, less adsorption is expected on Teflon relative to quartz. Because differences in the amount of adsorbed OC have been reported for the two sampling configurations, both were examined.

Six sets of air samples were collected. Two precleaned quartz-fiber filters were loaded into each of eight 37-mm cassettes. In four of the these, a Teflon filter was then placed on top. The bottom quartz filters in all eight cassettes, as well as the four directly under the Teflon filters, provided measures of adsorbed OC. Filters in four additional cassettes served as passive field blanks, which meant that no air was pulled through them. The second (bottom) quartz filter in the cassettes with the Teflon filters were compared to the bottom quartz filters in those having only a quartz pair. If negligible adsorption occurs on Teflon, the bottom quartz filters in the two different sampling configurations should give equivalent results. To avoid possible variability due to lot-to-lot differences [67], filters from the same lot were used to collect a given sample set.

Portable dust chamber. A portable dust chamber [69] designed for sampling in mines was used for sample collection. The chamber allowed simultaneous collection of up to eighteen samples. Twelve cassettes were mounted inside the chamber in a symmetrical fashion. Samples were collected on six different days, five days in a loading dock area and a sixth near an outside smokers' shelter. A diesel truck was operating in the loading dock, over different periods, on three of the days. Personal air pumps were programmed to run at 2 L/min over an 8-hour period. In one case, the pumps were stopped after 23 minutes. The short sampling period provided a low loading of diesel exhaust (a light deposit was visible) and was of interest with respect to the amount of adsorbed carbon collected in the short time frame.

Results for the six sample sets are shown in Table 1 and Figure 3. The QQ2 results correspond to the bottom quartz filters in the four cassettes containing quartz pairs only. The TQQ1 results are for the four filters directly beneath Teflon filters; TQQ2 results are for quartz filters beneath the TQQ1 filters (i.e., top Teflon, middle TQQ1, bottom TQQ2). The mean carbon on the bottom quartz filters ranged from 1.35 to 3.44 $\mu g/cm^2$, and the variability (RSD) ranged from about 4% to 12% on a given day. The loading found on the two sets of bottom filters (QQ2 and TQQ2) was not statistically different, so all bottom filters were pooled in the calculation of the mean. The pooled means for the bottom quartz filters (BQ), the means for the quartz under Teflon (TQQ1), and the corresponding OC and EC loadings are plotted in Figure 3. Results for the TQQ1 filters were only slightly higher than those for the bottom quartz filters, even with the 23-minute sampling period (set 4). Thus, using a separate cassette that has a top Teflon filter appears unnecessary. Although differences between the amount of carbon adsorbed on a quartz filter under another quartz and on one beneath a Teflon filter reportedly can be significant [65, 67], these studies concerned environmental monitoring at much higher flow rates. The negligible differences reported here most likely relate to the lower flow rates and filter face velocities used.

TABLE 1. RESULTS FOR SIX SETS OF AIR SAMPLES COLLECTED IN TWO OUTDOOR LOCATIONS. SEE TEXT FOR DETAILS.

Set	Location	TC, µg/cm²								Adsorbed fraction (%)
		QQ1		TQQ1		Bottom quartz mean				
		mean, SD	RSD %	mean, SD	RSD %	QQ2	TQQ2	pooled, SD	RSD %	
1	shelter	4.81, 0.47	9.77	3.66, 0.43	11.75	3.46	3.41	3.44, 0.30	8.80	76
2	dock	3.52, 0.25	7.10	2.82, 0.36	12.77	2.48	2.33	2.43, 0.23	9.57	80
3	dock	3.61, 0.05	1.39	2.89, 0.04	1.38	2.41	2.42	2.41, 0.18	7.45	80
4	dock	4.59, 0.18	3.92	1.79, 0.24	13.40	1.41	1.36	1.38, 0.09	6.46	30
5	dock	8.43, 0.33	3.91	1.84, 0.35	19.02	1.35	1.36	1.35, 0.16	12.03	22
6	dock	22.78, 0.35	1.54	3.62, 0.18	4.97	3.10	3.18	3.14, 0.13	4.09	16

The mean carbon loading (Table 1) on the sample filters (QQ1) was about 4 $\mu g/cm^2$ on four different days (sample sets 1-4). A diesel truck was operating briefly on one of these days (set 4). On two other days (sets 5 and 6), the truck was running for longer periods, as evidenced by the higher EC loadings (Figure 3). The corresponding TC loadings on these two days were about 8 $\mu g/cm^2$ and 23 $\mu g/cm^2$. Over the loading range, the amount of adsorbed OC had no dependence on the TC loading, and the OC results for the bottom quartz filters (1.35 to 3.44 $\mu g/cm^2$) were higher than those for the passive field blanks (0.17 to 0.74 $\mu g/cm^2$). Two of the results (sets 4 and 5) were slightly lower than the others. In one case (set 4), the sampling period (23 minutes) was shorter, but the adsorbed OC results for the bottom filters in both sampling configurations (i.e., QQ2 and TQQ2) were equivalent and comparable to the upper quartz filters (TQQ1), below the Teflon. This implied that partitioning [65] (between gas and adsorbed states) on the sample filters (QQ1) had reached equilibrium; thus, the lower result was not due to lack of equilibration. In large part, the results for passive blanks provided a likely explanation for the lower value. The mean blank (passive) for this set was 0.17 ($\pm$ 0.10) $\mu g/cm^2$, which was the lowest value obtained. Passive blank results for the other sets (excluding set 5) ranged from 0.25 ($\pm$ 0.07) to 0.74 ($\pm$ 0.14) $\mu g/cm^2$. It is not known whether the same explanation applied to set 5 because passive blanks for this set were accidentally contaminated (results voided). As in sets 1 3 and 6, set 5 was collected for an 8-hour period, but it was collected during the spring, while the other sets were collected during mid-summer. Changed weather conditions may explain the lower value.

On three days, the adsorbed OC fraction (calculated as the TQQ1 TC mean divided by QQ1 TC mean) constituted about 80% of the TC on the sample filters (QQ1). On three other days (sets 4, 5, and 6), the adsorbed OC fraction was 39%, 22%, and 16% of the total. A backup quartz filter provided a better correction for adsorbed carbon than a traditional blank would have. Traditional blanks (media and field) underestimated the adsorbed OC, causing overestimation of the true particulate OC (TC) concentration. The need for this correction, and the number of backup filters analyzed, depends on the sampling strategy and environment. The lower the OC loading, the greater the influence of adsorbed vapor on the particulate OC measurement. If the EC loading also is low, the same holds true for the TC result. Thus, when carbon loadings are low, correction for adsorbed OC is important for accurate measurement of particulate OC and TC concentrations. However, the correction addresses adsorbed vapor only not interference of less volatile materials (e.g., components in cigarette and wood smokes, oils) collected primarily on the top filter. Depending on vapor pressure, sampling conditions (temperature, flow rate, sampling period), and filter loading, these materials also collect on the bottom filter to some extent. The bottom filter cannot correct for this interference. If high OC loadings are found on the bottom filter, less volatile OC interferences should be suspected.

g. EC Oxidation in Helium

In the NMAM 5040 analysis, oxidation of original EC (as opposed to char) is sometimes seen during the last temperature step in helium, but this is generally not common. If early removal occurs, it is important to ensure that oxygen contamination is not responsible. This check can be performed by analyzing a sucrose standard solution applied to a clean, unused filter punch. Although char loss is sometimes observed with sucrose, the filter transmittance normally does not reach its initial value until after oxygen is introduced. If oxygen

contamination can be ruled out, the early EC loss is most likely due to oxidants in the sample. In our laboratory, EC loss in helium has been observed with samples from a few mines [70]. With these samples, the filter transmittance exceeded its baseline (initial) value during the last temperature step in helium. No sample pyrolysis was apparent, so the increase in transmittance was not caused by char loss. Moreover, analysis of sucrose standards revealed only a minor increase in transmittance in helium, and no increase was seen with samples from other mines. For these reasons, oxygen contamination was ruled out. On average, about 10% of the EC was removed at 870 °C in helium, but the carbon removed was included in the EC result because the OC-EC split was assigned when the initial transmittance was reached (in helium). Reducing the maximum temperature to 750 °C was recommended [59] for these types of samples (i.e., *no sample charring and early splits in helium*). Early EC loss was not seen at this temperature. A lower (< 750 °C) temperature may be required, depending on the type and amount of internal oxidant present. Our analytical result and precision were not affected by the early splits, but a reduced temperature was recommended in the interest of interlaboratory precision, which might be adversely affected. Interlaboratory testing was not conducted to determine if this is indeed the case, and, if so, whether a lower temperature would improve precision.

h. Reference Materials

Unfortunately, a suitable reference material for OC and EC is not yet available. A new Certified Value (17.68% g/g) for the TC mass fraction of an urban dust standard (SRM 1649a, formerly SRM 1649) was recently reported by the National Institute of Standards and Technology (NIST), but only Information (not Certified) Values are provided for the EC content. The EC content (as EC:TC fractions) was determined by a variety of methods. As expected from past studies [35, 71 74], the results were quite variable. The EC:TC fractions found by 13 methods ranged from about 7% to 52%, and the data were distributed in three clusters. Method bias was not evaluated. The reported range is obviously too broad to use this material as an analytical standard. According to the Certificate of Analysis (1649a), the reported values may be useful for comparison with results obtained by similar methods, but this may not be the case for methods with optical corrections because filter samples are not available. Depending on its placement, bulk dust on a filter can present different optical properties, which may increase variability. Preparation of a reference material deposited on quartz filters is being investigated at NIST.

Sample composition is an important consideration in the production of an analytical reference material. As is true with many standards, no single OC-EC material can be representative of all samples because there are many sources of particulate carbon and many different monitoring sites both occupational and environmental. Production of an OC-EC reference material is further complicated by the variability between methods (SRM 1649a provides only Information Values for different methods), and the need of a filter-based material for thermal-optical methods.

Because sample components that char pose a potential interference in the determination of EC, and interlaboratory variability is greater when samples contain them, analysis of organic materials that char provides an important quality assurance check. Sucrose serves as both an analytical standard and a check of the method's char correction, but sucrose is a simple

carbohydrate (a disaccharide). Air samples can contain complex particulate matter, such as wood and cigarette smokes, plant debris (cellulose), and products of biomass burning. In some cases, the biomass may contribute a sizable fraction of the sample carbon. About 38% of the particulate carbon in SRM 1649a (an urban dust) is derived from biomass (see Certificate of Analysis and related publication [J. Res. Natl. Inst. Stand. Technol., 107:279-298, 2002] available at http://www.nist.gov/jres). For these reasons, a material more representative of the plant-derived components in air samples was sought.

Various plant-derived materials were examined to determine whether any would be useful as laboratory control samples. A well-characterized, stable material that chars also would be useful for proficiency testing, and it could potentially be used to produce a standard reference material. After a preliminary screening of candidate materials (e.g., agarose, alginic acid, starch, and cellulose), alginic acid was selected for further study. Alginic acid is a polysaccharide derived from sea kelp [76], it has adequate solubility in water, and it forms a significant amount of char during the analysis.

To prepare a solution, about 150 mg of alginic acid (Sigma, St. Louis, MO) was added to a test tube containing 10 mL of purified water (ultrafiltered, type I). The tube was shaken vigorously and allowed to sit overnight at room temperature. The following day, the tube was shaken again and then centrifuged to settle the suspended material. The clear supernatant was removed and syringe filtered. Aliquots of the alginic acid solution were applied to clean filter punches. The solution was analyzed over a seven-week period. Results of these analyses are plotted in Figure 4. No evidence of solution degradation was observed. A mean carbon loading of 13.98 $\mu g/cm^2$ (RSD = 3.06%, n = 22) was obtained for 10-µL aliquots of the solution. This translates to a carbon concentration of 2.06 µg /µL. About half of the carbon in alginic acid remained on the filter as char before oxygen was introduced, but the mean EC result (0.04 ±0.06 $\mu g/cm^2$) was not statistically different from that for the media blanks (0.06 ±0.03). Therefore, the pyrolysis correction was accurate.

Sets of diesel soot samples spiked with the alginic acid solution also were examined. Multiple punches (1.5 cm^2) were taken from a soot sample collected on an 8" x 10" filter. The punches were then analyzed before and after spiking with a 10-µL aliquot of the solution. Punches in a given set were taken from the same area of the filter to minimize variability, and the solution was applied in a consistent manner (dispersed evenly on one end of the punch where the laser penetrates it). Mean TC results for the unspiked and spiked samples are provided in Table 2. Results for three sample sets (A, B and C) are reported. For each set, the difference between the mean results for the unspiked and spiked samples is reported; this difference is the alginic acid carbon. Based on the mean (13.98 $\mu g/cm^2$) for 22 spiked blanks, recoveries of alginic acid carbon from the soot samples were 96%, 101% and 110% (sets A, B, and C, respectively). The pooled recovery for all spiked samples was 97%.

TABLE 2. RECOVERY OF ALGINIC ACID CARBON FROM DIESEL PARTICULATE SAMPLES SPIKED WITH 10-µL ALGINIC ACID SOLUTION.

Sample Set	Mean Carbon[a], micrograms/cm^2 (SD)			
	unspiked	spiked	difference[b]	Recovery[c] (%)
A	22.94 (1.49)	34.90 (0.66)	13.47	96
B	22.25 (0.28)	36.38 (0.65)	14.14	101
C	22.61 (0.33)	38.01 (0.80)	15.39	110
All	22.56 (0.84)	36.06 (1.32)	13.49	97

[a]Three unspiked samples per set. Seven spiked samples in sets A and B, and 3 in set C. [b]Spiked minus unspiked result. [c]Recovery based on mean result (13.98 µg/cm^2) for 22 analyses of blank punches spiked with 10-µL aliquot of alginic acid solution. Analyses done over a 7-week period.

EC results for the three sample sets are listed in Table 3. Spiked sample results for two sets (A and C) were slightly higher, while those for a third set (B) were slightly lower. Differences between the mean EC loadings on the unspiked and spiked samples were not statistically different. Thus, an accurate correction was again made for the char formed through pyrolysis of alginic acid. Additional tests on spiked samples are ongoing.

TABLE 3. EC RESULTS FOR SPIKED AND UNSPIKED DIESEL PARTICULATE SAMPLES.

Sample Set	Mean EC[a], micrograms/cm^2 (SD)		
	unspiked	spiked	difference[b]
A	4.24 (0.20)	4.36 (0.42)	0.12 (0.47)
B	3.88 (0.01)	3.78 (0.12)	-0.10 (0.12)
C	4.32 (0.14)	4.43 (0.12)	0.11 (0.18)

[a]Three unspiked samples per set. Seven spiked samples in sets A and B; three spiked samples in set C. [b]Spiked minus unspiked results.

i. Quality Assurance

Quality assurance (QA) procedures followed at NIOSH and NIOSH contract laboratories have included repeat analyses, analysis of OC standards, and analysis of media and field blanks. Results for repeat analyses of over 200 filter samples at a contract laboratory (DataChem Laboratories, Inc., Salt Lake City, UT) gave a pooled RSD (95% confidence) of about 4% for EC and TC, and 5% for OC [68]. The samples were collected in mines, and some contained other carbonaceous matter such as limestone. In the analysis of OC standards, recovery was typically within 6% of the expected value [68]. For example, the mean recovery for more than 400 sucrose standards analyzed at DataChem over a one-year period was 99.97 % ±6.07%. Nearly identical results (100.33 % ± 5.15%, n = 462) were obtained by Clayton Laboratory Services (Novi, MI). Different sets of field blanks (41 at DataChem and 129 at Clayton) analyzed by the two laboratories also gave comparable results [68]. Mean blank results (μg carbon per filter) were as follows: DataChem OC = 9.96 ± 7.05, Clayton OC = 12.80 ±5.76; DataChem EC = -0.54 ±1.89, Clayton EC = -0.08 ±2.14; DataChem TC = 9.26 ±7.30, Clayton TC = 12.70 ±6.18.

In lieu of an OC-EC reference material, a limited confirmation of results by a second laboratory is advisable. Our laboratory (NIOSH, Cincinnati, OH) has routinely performed repeat analyses on samples previously analyzed at a contract laboratory. As an added check, subsets of representative field samples also have been analyzed by a third laboratory. In the analysis of fifty samples (analyzed at DataChem, NIOSH, and Clayton) from mines, the pooled RSD (95% confidence) was about 6% for TC, 10% for EC, and 12% for OC [68]. These results are consistent with those found in a previous round robin [35].

EPA. The EPA recently conducted a special study [75] as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network (STN). Samples collected as part of this network were removed from refrigerated storage eight months after they were analyzed at Research Triangle Institute (RTI, Research Triangle Park, NC). The samples were then shipped to the EPA New England Regional Laboratory (NERL, Lexington, MA) for re-analysis. Good interlaboratory agreement was reported. The acceptance criteria for the archived samples were based on filter loading (μg/cm^2). The three acceptance criteria are the following: a difference ≤ 1 μg/cm^2 for loadings less than 5 μg/cm^2, a relative percent difference (RPD) ≤ 20% for loadings from 5 to 10 μg/cm^2, and an RPD ≤ 15% for loadings above 10 μg/cm^2. The OC, EC, and TC data had 85%, 96%, and 93% of the inter-laboratory results, respectively, within the acceptance criteria. The lower percentages for OC and TC are thought to reflect contamination of lightly loaded samples from adsorbed vapors and handling. An OC blank (passive) correction was applied, but it most likely was not representative of the entire sample set. Additional interlaboratory comparison results are discussed in a following section (see Section 3).

3. INTERLABORATORY COMPARISONS

a. NMAM 5040

When results of the initial method evaluation were published [34], an interlaboratory comparison was not possible because the thermal-optical instrument was available in only one laboratory. Interlaboratory comparisons are especially important in this type of analysis because variable results have been obtained by different OC-EC methods [35, 71 74], and a reference material is not yet available. After additional laboratories acquired thermal-optical instruments, a round robin comparison [35] was conducted. Matched sets of filter samples containing different types of complex carbonaceous aerosols were distributed to eleven laboratories. Six of the eleven analyzed the samples according to NMAM 5040, while five used purely thermal (i.e., no char correction) methods. Good interlaboratory agreement was obtained among the six laboratories that used NMAM 5040. In the analysis of samples containing diesel particulate matter, the variability (RSD) for the EC results ranged from 6% to 9%. Only low EC fractions were found in wood and cigarette smokes. Thus, these materials pose minimal interference in the analysis of diesel-source EC. In addition, only minor amounts of EC were found in two OC standards that char: about 1% and 0.1% for sucrose and the disodium salt of ethylenediaminetetraacetic acid (EDTA), respectively. Two aqueous solutions of OC standards were included in the comparison as a check on the validity of the char correction and accuracy of the TC results. Variability (RSD) of the TC results for the two standard solutions and five filter samples ranged from 3% to 6%.

Another interlaboratory comparison using NMAM 5040 was conducted more recently [77]. Seven environmental aerosol samples were analyzed in duplicate by eight laboratories. Four samples were collected in U.S. cities, and three were collected in Asia. Variability of the EC results ranged from 6% to 21% for six samples having EC loadings from 0.7 to 8.4 $\mu g/cm^2$. Four of the six had low EC loadings (0.7 $\mu g/cm^2$ to 1.4 $\mu g/cm^2$). The variability of the OC results ranged from 4% to 13% (OC loadings ranged from about 1 to 25 $\mu g/cm^2$). Results for TC were not reported, but the variability reported for the OC results should be representative of that for TC because the samples were mostly OC (75% to 92%).

b. Other Methods

Thermal methods. Different thermal methods have given consistent agreement for TC, but OC-EC results have been quite variable [35, 71 74]. The degree of variability depends on the sample type. In general, there is greater disagreement among methods when samples contain materials that char [35, 71, 72] (e.g., wood and cigarette smokes). Methods that employ a lower maximum temperature and/or do not correct for char obtain results that are positively biased relative to NMAM 5040 [35]. When a lower temperature (typically 550 °C) is used, less thermal breakdown of refractory organic components (and possibly carbonates) may occur. This, as well as lack of char correction, can positively bias the EC results. In the round robin study [35] discussed above, three laboratories employed four purely thermal methods that specified a maximum in nitrogen (not helium) of about 550 °C. Unlike the

NMAM 5040 results, these laboratories reported high EC contents for the two OC standards (about 52% for sucrose and 70% for EDTA). Similar findings (i.e., positive bias) for thermal methods having no char correction were obtained recently in another international round robin [72].

In contrast to round robin results obtained previously [35], relatively good agreement was seen in a recent comparison [78] between NMAM 5040 and a thermal method (ZH 1/120.44) used in Germany. The comparison was limited to two laboratories. Method ZH 1/120.44 specifies a 550 °C maximum in nitrogen. The other European laboratories that participated in the previous round robin [35] used variations of this method. In the European laboratories, nitrogen is used as the inert gas, and carbon determination is based on coulometric titration of carbon dioxide. For the comparison [78], samples were obtained in a mine where diesel equipment was being operated. The samples had a much higher EC content (about 50%) than did the round robin samples. No charring was noted in the thermograms, and only a minor amount of carbon was removed above 550 °C. Although differences in the OC-EC results were again seen, they were minor relative to those obtained in the round robin [35]. The mean EC fractions (EC:TC) found with methods ZH 1/120.44 and NMAM 5040 were 0.53 (σ = 0.19) and 0.46 (σ = 0.15), respectively. The relatively minor difference in the reported fractions was attributed to the different thermal programs employed.

IMPROVE method. Another thermal-optical method, called the IMPROVE (Interagency Monitoring of Protected Visual Environments) method [79], also was included in the NMAM 5040 round robin [35]. Relatively good agreement between NMAM 5040 and the IMPROVE method was obtained, although the IMPROVE EC was consistently a bit higher. The carbon analyzers used for the two methods are based on similar measurement principles, but they differ with respect to design and operation. For example, the optical correction in NMAM 5040 is based on filter transmittance, whereas that for the IMPROVE method is reflectance based. Different components are used to monitor these signals. The instrument (Sunset Laboratory, Inc., Forest Grove, OR) used for NMAM 5040 incorporates a pulsed diode laser (670 nm) and photodetector positioned on opposite sides of the filter. The instrument (Desert Research Institute, Reno [DRI], NV) for the IMPROVE method uses a quartz tube and fiber optic to measure helium neon laser light (632.8 nm, unmodulated) reflected from the filter surface. In addition to instrumental differences, NMAM 5040 specifies a higher maximum temperature (870 °C) in helium than the IMPROVE method (550 °C). As discussed in the preceding section, a higher temperature is used to better remove refractory OC components and carbonates. In the NMAM 5040 analysis, the transmittance of some samples continues to decrease as the temperature is stepped to 870 °C, which indicates charring is not complete at 550 °C. More exhaustive charring results in a lower EC result because the correction for it is larger, and volatile pyrolysis products can evolve to a greater extent. Although environmental samples contain only small amounts (if any) of carbonate, levels in some workplaces (e.g., mines, construction sites) can be relatively high. Collection of carbonate can be prevented (or minimized) through use of an impactor [62].

Two comparisons [73, 74] between the NMAM 5040 and IMPROVE methods were conducted recently. In one [73], the NMAM 5040 EC was typically less than half the IMPROVE EC, but a Sunset Laboratory instrument was not used. Instead, samples were analyzed on a prototype instrument by running two different thermal programs [73]. The results reported for NMAM 5040 (emulated on DRI instrument) may not be representative of those obtained

with a Sunset Laboratory instrument because, depending on the sample type, differences in instrument design can affect the results to varying degrees. Adjustment of the temperature program, according to another method's specifications, does not necessarily produce the same results as that method. For example, lower EC results [35] were obtained with a Sunset Laboratory instrument when a sucrose standard was analyzed according to the temperature program specified for a method used in Europe. No pyrolysis correction was made, and the total analysis time was shorter, yet the EC result was much lower (about 3 µg with the Sunset instrument and 11 µg with a different instrument).

When the NMAM 5040 thermal program was used on a DRI instrument, the filter transmittance reportedly exceeded its initial value before the addition of oxygen [73]. In a recent audit by CARB (California Air Resources Board), the same problem was seen with a DRI instrument, but not a Sunset Laboratory instrument (report [*2003 Performance Evaluation Evaluation Sample Audit of the CARB Lab*] available at http://www.epa.gov/ttnamti1/pmspec.html). Char loss was extensive when the NMAM 5040 program was used on a DRI instrument. Again, the filter transmittance exceeded its initial value in helium, but the split point was not assigned until after oxygen was introduced. These results contrast with those obtained by our laboratory and others, and such behavior was not seen in another comparison [74]; however, that comparison (and the CARB audit) was a direct comparison of the two methods (samples were analyzed with Sunset and DRI instruments). Only 2 of 52 samples analyzed by Sunset Laboratory showed an increase in transmittance before the addition of oxygen, and the OC-EC split was near the point where oxygen was added [74]. Both samples had low carbon loadings (OC = 4.0 µg/cm^2, EC = 0.6 µg/cm^2, OC = 3.3 µg/cm^2, EC = 0.5 µg/cm^2) and were thought to be wood-smoke dominated. As pyrolysis was evident, the increase in filter transmittance was attributed to char removal. Comparable EC results would have been obtained if the char had not been removed until after oxygen was added, because char is assigned to the OC fraction. In the NMAM 5040 analysis of organic compounds (e.g., sucrose), partial char loss in helium sometimes occurs. The varying degree of loss may relate to differences in filter purity.

4. OCCUPATIONAL EXPOSURE CRITERIA (U.S.)

In 1995, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed a Threshold Limit Value (TLV®) for diesel exhaust (see Notice of Intended Changes for 1995 1996). A TLV of 150 µg of submicrometer particulate matter per cubic meter of air was proposed. Four years later, a value of 50 µg/m^3 was proposed [80]. Because EC is a demonstrated exposure marker for diesel particulate exhaust and can be accurately quantified at low levels [81], the standard was recast in terms of an equivalent elemental carbon measurement in 2001 [81]. A TLV-TWA (time-weighted average) of 20 µg EC per cubic meter of air was recommended [82]. By comparison, the proposed TLV is high relative to an environmental standard supported by the California Office of Environmental Health Hazard Assessment (OEHHA). The California OEHHA has classified particulate emissions from diesel-fueled engines as a toxic air contaminant (TAC) and supports 5 µg/m^3 as the chronic inhalation reference exposure level (REL) [5]. Because EC is a fraction of the diesel particulate emissions, the difference between the two air standards is greater than four fold, and the magnitude of the difference is dependent on the EC mass fraction of the diesel particulate. For example, if EC constituted 40% of the diesel particulate mass, the proposed

TLV would be ten times higher than the OEHHA REL. The ACGIH withdrew diesel exhaust particulate, as EC, from the 2002 Notice of Intended Changes (NIC) and placed it under study [86].

An EC (or TC) standard, rather than submicrometer particulate mass, would simplify interpretation of the analytical results because the target analyte and exposure standard would be the same. This would eliminate the problem of extrapolation (to submicrometer mass), which is not straightforward and introduces unacceptable analytical error. As discussed previously, OC interferences are an issue when making TC measurements; variable EC content is a problem when measuring EC. If EC concentrations are high and samples are relatively free of OC contaminates, the TC concentration is a reasonable measure of the diesel particulate mass, and the EC:TC ratio is representative of the EC fraction of the mass. Unfortunately, this situation is uncommon outside of mines. In general industry, EC and OC levels are normally much lower. When EC levels are low, the EC:TC ratios are not reliable estimates of the EC fraction of diesel particulate matter because OC interferences can skew the ratios low and increase variability in the apparent ratio. In such cases, TC is an inaccurate measure of the diesel particulate concentration.

Exposures in the mining industry are of particular concern because diesel particulate concentrations in mines [62, 83, 84] sometimes exceed 2 mg/m^3, which is one thousand times higher than a typical environmental level. In its final rule [62] on metal and nonmetal mines, MSHA proposed an interim exposure standard of 400 µg TC per cubic meter of air. Five years after publication of the rule, a final standard of 150 µg TC per cubic meter was to apply. In response to a legal challenge, MSHA recently initiated limited new rulemaking [85] to revise certain provisions of the final rule. Among other amendments, MSHA agreed to propose a change of exposure surrogate from TC to EC. Comments on appropriate interim and final limits for EC were requested in the new rulemaking. MSHA exposure standards consider health risks and technical and economic feasibility, based on available engineering controls and their cost.

5. SUMMARY

NMAM 5040 is based on a thermal-optical analysis technique for particulate carbon. Its intended application is assessment of workplace exposure to particulate diesel exhaust, but thermal-optical analysis has been routinely applied to particulate carbon measurement in general. Both OC and EC (and TC as OC + EC) are determined by the method. For reasons discussed in this chapter, EC is a better exposure surrogate than TC. Over 30 epidemiological studies are consistent in finding a positive association between exposure to diesel exhaust and lung cancer, but quantitative exposure data are lacking. Accurate monitoring methods are necessary in quantifying the risks of exposure.

The thermal-optical instrument incorporates an optical feature that corrects for the char formed during the analysis of some materials. EC results of purely thermal methods show positive bias when samples contain materials that char. Although minimal charring has been observed with most diesel soot samples from mines, workplace (and environmental) air often contains components that char. Depending on the workplace and thermal protocol, these

components can be significant contributors to the measured EC. For this reason, an analytical protocol that maximizes removal of refractory OC components (and carbonates) and corrects for the char formed through thermal decomposition is important. In the NMAM 5040 analysis, the transmittance of some samples continues to decrease as the temperature is stepped to 870 °C in helium, which indicates charring is not always complete at the lower temperatures used in some methods. Partial char loss is sometimes observed (at 870 °C), but loss of original EC is uncommon.

Good interlaboratory agreement between OC-EC results has been obtained by laboratories using NMAM 5040. Because a certified reference material is not currently available, confirmation of results in a second laboratory using NMAM 5040 is advisable, particularly when samples char during the analysis because interlaboratory results for these are typically more variable. Organic materials that char are useful as quality control samples. Accurate pyrolysis correction was obtained in the NMAM 5040 analysis of an alginic acid solution spiked onto blank filters and diesel soot samples. Sucrose has traditionally been used as a check on the method's char correction, but alginic acid is more representative of complex, plant-derived components present in some air samples.

To ensure data quality, participation in proficiency testing among laboratories involved in major studies also is advised. At present, seven commercial laboratories (six in the United States and one in Canada) offer the NMAM 5040 analysis, and over 60 instruments are available globally for environmental and occupational monitoring. Method standardization is critical if results obtained by different laboratories are to be compared. Interlaboratory studies are useful in exposing differences among methods, but results of such comparisons must be interpreted with a clear understanding of each method's limitations (e.g., in dealing with interferences).

Additional research is necessary to address the potential health effects of diesel exhaust and other types of fine particle air pollution. Although the organic compounds associated with diesel particulate matter have potential health effects, those traditionally measured are not unique to diesel exhaust. Nevertheless, characterization of this fraction may be useful in assessment of exposure risks, particularly if compounds enriched in diesel relative to other particulate emissions can be used as indicators of mutagenic potency (e.g., specific nitro-PAH). This information also may reveal engine types or operating conditions that produce higher emission rates of genotoxic compounds.

Undoubtedly, much will be learned through additional research. As reasoned previously [34], regardless of whether the potential adverse health effects of diesel particles are due to the carbonaceous cores, adsorbed compounds, or a combination of both, monitoring and control of the particulate component are necessary if effects exist that are particle related. In most workplaces, diesel engines are the primary source of fine-particle EC. Other combustion sources may contribute to environmental levels of EC. These sources may be relevant from an emission control perspective, but if the potential toxicity of these particles is similar, their origin is not relevant from a health perspective.

6. FIGURES.

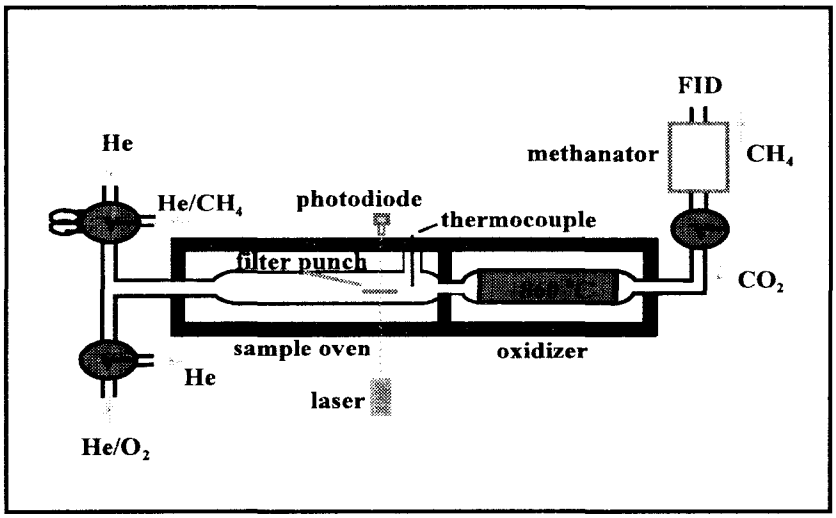

Figure 1. Schematic of thermal-optical instrument (*V* = valve) for determination of OC and EC in diesel particulate exhaust and other carbonaceous aerosols.

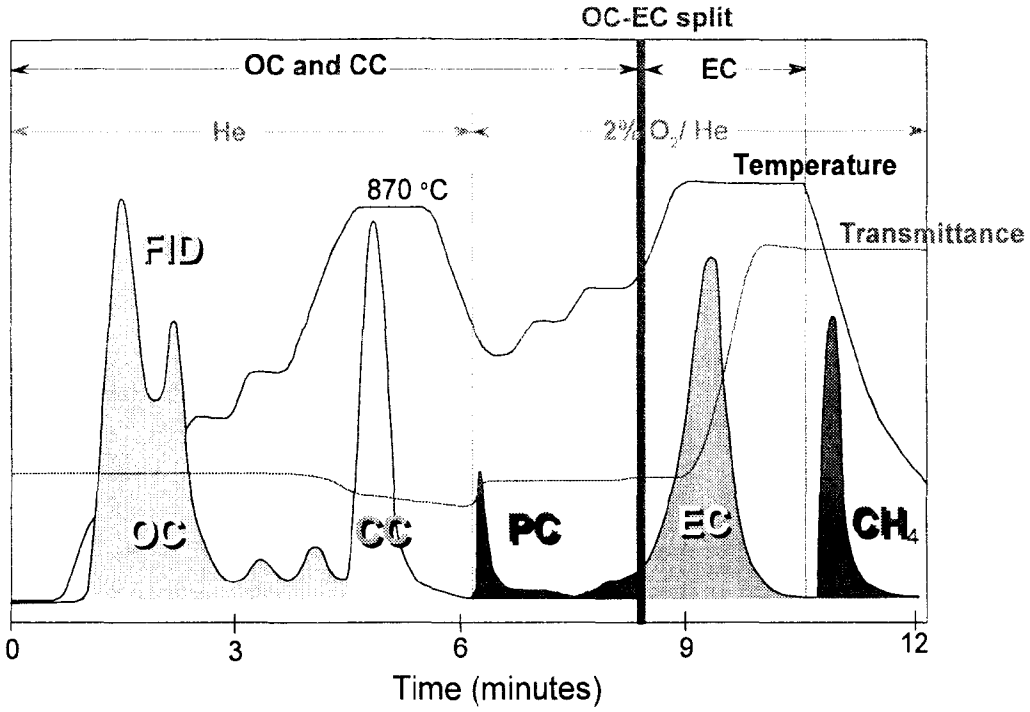

Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

Note: In the round robin study [35] discussed earlier, the actual maximum temperature in helium ranged from about 850 °C to 900 °C. Laboratories were asked to use the same maximum, but not all did. Comparable results were obtained because some differences in the thermal program do not affect the results significantly. For the purpose of standardization, use of the same maximum is recommended. An 870 °C maximum is near the middle of the range used by participants in the study.

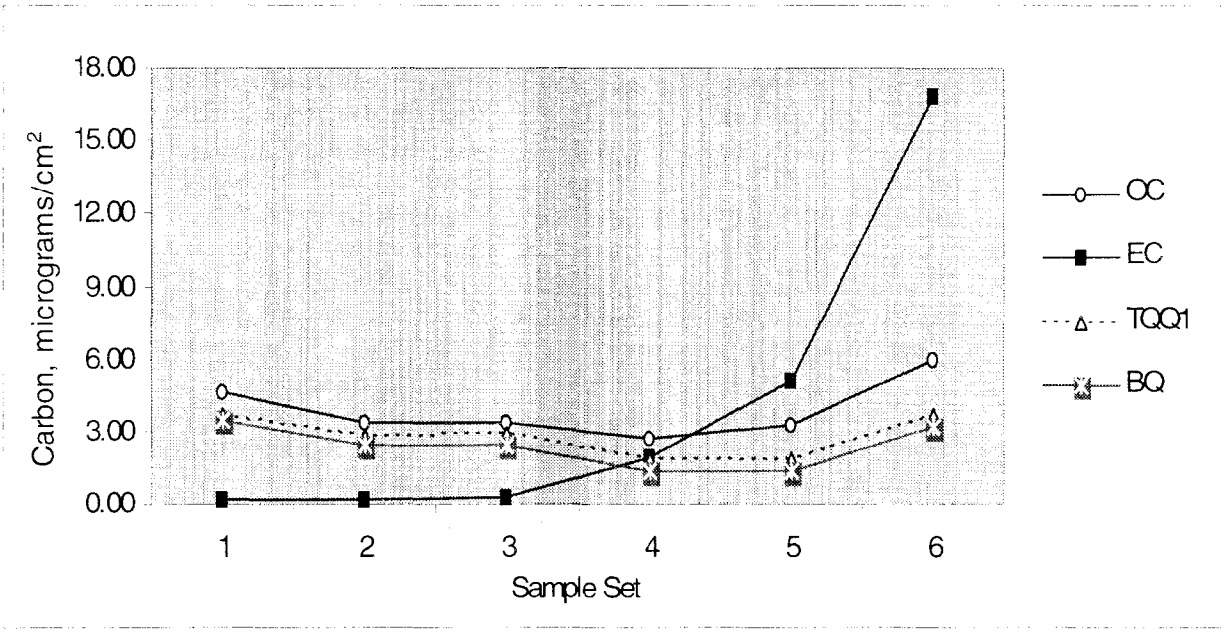

Figure 3. Results for six sets of air samples collected in two outdoor locations. OC and EC results are the means for the top quartz filters (QQ1) of quartz-filter pairs. TQQ1 is the mean carbon (total) result for quartz filters placed directly beneath Teflon. BQ is the mean carbon result for all bottom quartz filters (i.e., QQ2 and TQQ2). See text for additional details.

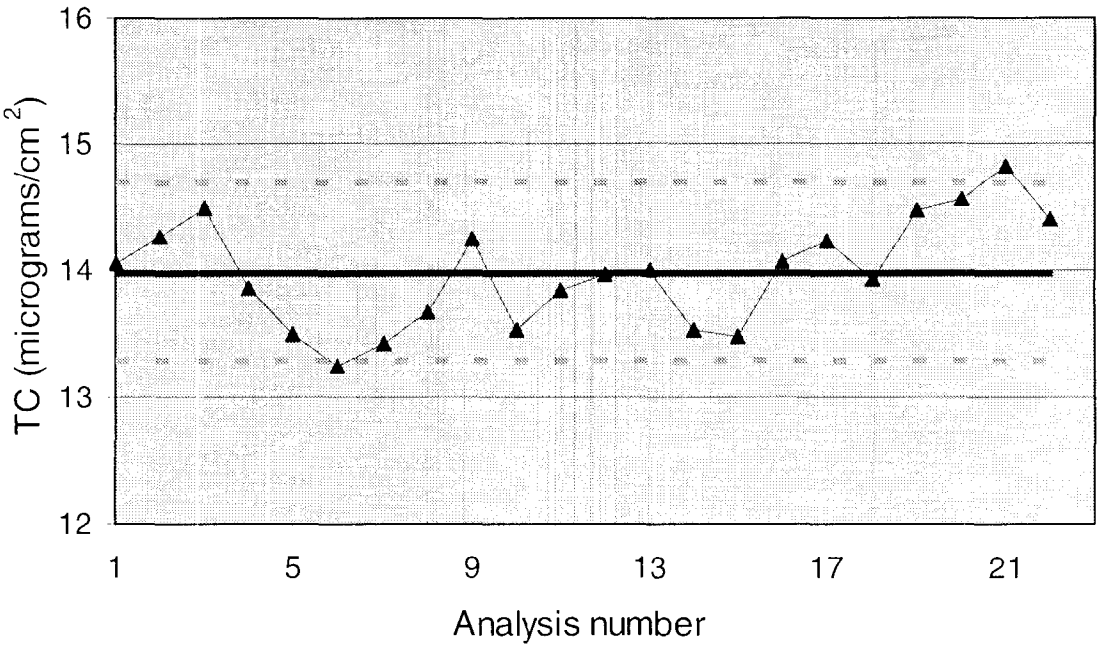

Figure 4. Results for clean punches (blanks) spiked with 10-µL aliquots of alginic acid solution. Analyses done over a 7-week period. The middle horizontal line is the mean result (13.98 µg/cm^2). The upper and lower dashed lines are ±5% of the mean.

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R. DETERMINATION OF AIRBORNE CRYSTALLINE SILICA

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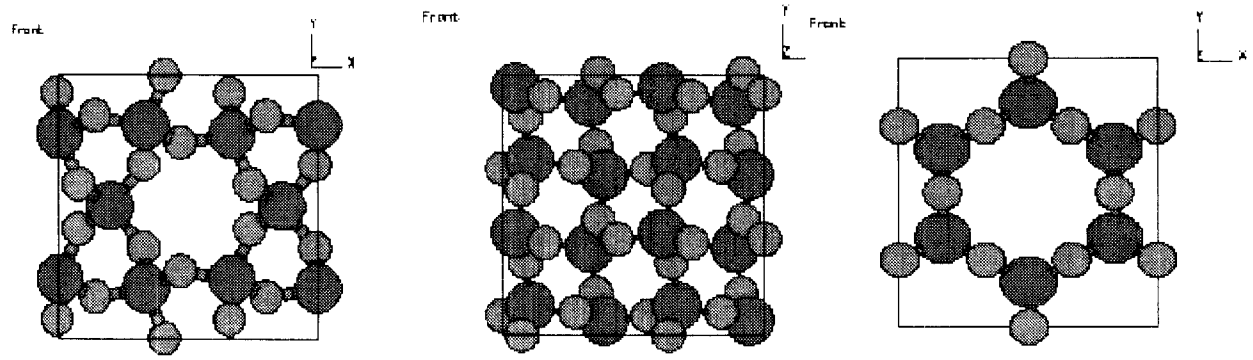
1. INTRODUCTION

A variety of air sampling and analysis methods for determining workers' exposures to crystalline silica have been published by the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), the Mine Safety and Health Administration (MSHA), the United Kingdom Health and Safety Executive (UK-HSE) and others. The following chapter provides information on the structure of silica, health effects, airborne exposure standards, sampling considerations and analytical considerations. The purpose is to provide information to the industrial hygienist, chemist, laboratory manager and the client of laboratory services to make an informed decision on which crystalline silica method should be used, and the quality assurance procedures that should be employed to obtain accurate results.

2. STRUCTURE, PROPERTIES AND OCCURRENCE OF SILICA

Silica is commonly found in the earth's crust and refers to the chemical compound silicon dioxide (SiO_2). Physical properties (such as specific gravity, refractive index and X-ray diffraction pattern) and toxicological properties depend on the chemical composition and the molecular structure. Silica occurs in both crystalline and non-crystalline forms. Crystalline forms are physical states in which the silicon dioxide molecules are arranged in a repetitive pattern that has unique spacing, lattice structure and angular relationship of the atoms. Crystalline silica forms (often referred to as polymorphs) include quartz, cristobalite, tridymite, keatite, coesite, stishovite and moganite [2,3,4]. Figure 1 shows the lattice arrangements of quartz, cristobalite and tridymite. Table 1 lists some physical properties of these polymorphs.



alpha Quartz alpha Cristobalite Tridymite

Figure 1. Polymorphs of crystalline silica [5].

TABLE 1. PHYSICAL PROPERTIES OF QUARTZ, CRISTOBALITE AND TRIDYMITE.

Silica Polymorph	Crystal Structure	Index of Refraction	Specific Gravity	Other Properties
Quartz	hexagonal	1.544	2.645 - 2.660	Mol.Wt. 60.08 m.p. °C 1610
Cristobalite	cubic or tetragonal	1.487	2.32	Mol.Wt. 60.08 m.p. °C 1723
Tridymite	rhombohedral	1.469	2.26	Mol.Wt. 60.08 m.p. °C 1703

In nature, quartz is the crystalline form most commonly encountered and is so abundant that the term quartz is often used in place of the general term crystalline silica [6, 7]. Quartz is abundant in most rocks and soils and is also present in sand, mortar, concrete, fluxes, abrasives, construction aggregate, porcelain, paints and brick [8]. In addition, quartz-containing dust may be generated in any process which involves movement of earth (e.g., mining, farming, construction), disturbance of silica-containing products such as masonry and concrete, or use of sand and other silica containing products (e.g., foundry processes). Consequently, workers are potentially exposed to quartz dust in many occupations and industries.

Cristobalite and tridymite can be found in volcanic rocks and soils. These polymorphs can also be produced in some industrial operations. For example, cristobalite transformations occur in foundry processes, calcining of diatomaceous earth, brick and ceramics manufacturing, and silicon carbide production [9-11]. Burning of agricultural waste or products such as rice hulls may also cause amorphous silica to become cristobalite [8,12].

The other crystalline polymorphs (i.e., keatite, coesite, stishovite, and moganite) are very rarely or never observed in nature and are formed only under very high pressures [2]. Since these polymorphs are generally formed in small quantities, they are therefore of limited industrial hygiene interest.

Non-crystalline, or amorphous, forms of silica exist when the silicon dioxide molecules are randomly arranged. Fly ash, silica fume and silica gel contain amorphous silica. Diatomaceous earth is 88% amorphous silica and is composed of the skeletons of small prehistoric aquatic plants related to algae [13]. Sometimes the compound may be hydrated, such as in opal.

Silica (both amorphous and crystalline) can transform. In unusual instances of extreme heat and very slow cooling conditions, amorphous silica can be transformed into crystalline silica as mentioned above. Similarly, various crystalline silica forms can transform into different crystalline forms when subjected to high heat or high heat and pressure. The presence of trace elements in the silica affects transformation rates. Heating rate is also important; on heating, cristobalite may form without first forming tridymite. Figure 2 illustrates some transitions between forms of silica upon heating and cooling.

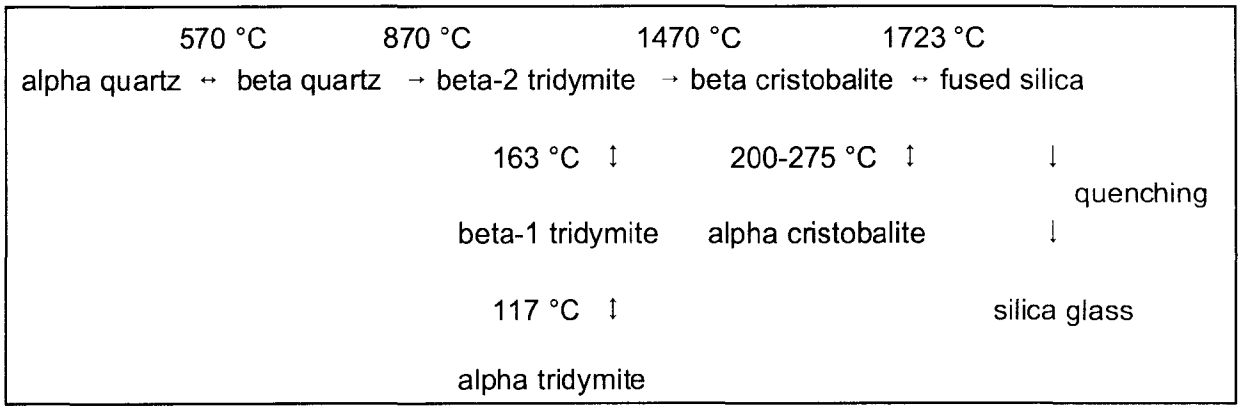


Figure 2. Silica transitions with temperature [8].

3. HEALTH EFFECTS AND EXPOSURE STANDARDS

At least 1.7 million U.S. workers are potentially exposed to crystalline silica, which can cause the debilitating and incurable, but entirely preventable, lung disease called silicosis. Reported mortality associated with silicosis has declined to 200 to 300 reported deaths each year during the period 1992-1995. However, silicosis remains under-reported, perhaps because of a long latency between exposure and disease. In addition, an unknown number of unreported or undiagnosed worker deaths occur each year from silicosis and other silica-related diseases such as pulmonary tuberculosis (TB), lung cancer, and scleroderma. Occupational exposure to respirable crystalline silica is associated with the development of silicosis, lung cancer, pulmonary tuberculosis and airways diseases. These exposures may also be related to the development of autoimmune disorders, chronic renal disease and other adverse health effects [14].

In 1974, NIOSH reviewed the available health effects data on occupational exposure to respirable crystalline silica and determined that the principal adverse health effect was silicosis [9]. On the basis of the evidence from the animal studies published by 1986, the International Agency for Research on Cancer (IARC) concluded that "sufficient evidence" existed for the carcinogenicity of respirable crystalline silica in experimental animals but only "limited evidence" existed for carcinogenicity in humans [15]. During the 1988 OSHA rule-making activity on air contaminants, NIOSH recommended an exposure limit of 0.05 mg/m^3 "as respirable free silica for all crystalline forms of silica" to protect workers from silicosis and cancer [16]. In addition, NIOSH testimony referred to the IARC [1987] review and recommended that OSHA label crystalline silica a potential occupational carcinogen [16]. IARC recently concluded that there is "sufficient evidence in humans for the carcinogenicity of inhaled crystalline silica in the form of quartz or cristobalite from occupational sources" (i.e., IARC category Group 1 carcinogen) [8]. The American Conference of Governmental Industrial Hygienists (ACGIH) has classified crystalline silica as a "suspected human carcinogen" (i.e., category A2 carcinogen) [17]. The National Toxicology Program reclassified respirable crystalline silica from "reasonably anticipated to be a carcinogen" to "known carcinogen" in the 9th Report on Carcinogens [18]. Furthermore, experimental research has shown that crystalline silica is not an inert dust. The toxicity of crystalline silica particles may be related to reactive sites on the surfaces of silica particles and the crystallinity index [19]. Table 2 lists the current U.S. and U.K. guidelines and limits for occupational exposure to crystalline silica.

TABLE 2. U.S. AND U.K. GUIDELINES AND LIMITS FOR OCCUPATIONAL EXPOSURE TO CRYSTALLINE SILICA.

Reference	Substance	Guideline or limit (mg/m^3)
NIOSH [9]	Crystalline silica:* quartz, cristobalite and tridymite as respirable dust	REL = 0.05 (for up to a 10-h workday during a 40-h workweek)
OSHA [29 CFR 1910.1000-Table Z-3]†	dust (respirable) containing quartz dust (respirable) containing cristobalite	8-h TWA PEL = 10 ÷ (% quartz + 2) PEL = half of the value calculated from the formula for dust-containing quartz
CFR [20]	dust (respirable) containing tridymite	PEL = half of the value calculated from the formula for dust-containing quartz
MSHA [30 CFR 56, 57, 70, 71]	dust (respirable) containing > 1% quartz in surface and underground metal and nonmetal mines	8-h TWA TLV = 10 ÷ (% quartz + 2)
CFR [20]	dust (respirable) containing > 1% cristobalite or tridymite in surface and underground metal and nonmetal mines	8-h TWA TLV = 5 ÷ (% SiO_2 + 2)
	dust (total) containing < 1% crystalline silica in surface and underground metal and nonmetal mines	8-h TWA TLV = 10 (for particulates listed in Appendix E, 1973 ACGIH TLVs only)
	dust (respirable) containing >5% crystalline silica in surface and underground coal mines	TWA RDS = 10 ÷ % SiO_2 (MRE equivalent)
	dust (respirable) containing ≤ 5% crystalline silica in surface and underground coal mines	TWA RDS = 2 (MRE equivalent)
ACGIH [17]	Respirable crystalline silica, quartz Respirable crystalline silica, cristobalite Respirable crystalline silica, tridymite	8-h TWA TLV = 0.05 8-h TWA TLV = 0.05 8-h TWA TLV = 0.05
UK-HSE [21, 22, 23]	Respirable crystalline silica, total (quartz + cristobalite)	8-h TWA MEL = 0.300

Adapted from Hearl [24].

*Identified by NIOSH as a potential occupational carcinogen [16].

†See this website for sample calculations of the OSHA PEL: http://www.osha-slc.gov/SLTC/silica_advisor/ mainpage.html. Other useful information is available on this website: http://www.osha-slc.gov/SLTC/ silicacrystalline/rosem/index.html. On this web page, click on "Frequently Asked Questions."

CFR = Code of Federal Regulations; REL = recommended exposure limit; PEL = permissible exposure limit; TWA = time-weighted average; RDS = respirable dust standard; MRE = Mining Research Establishment (United Kingdom); TLV = threshold limit value; MEL = maximum exposure limit.

Under the OSHA Hazard Communication Standard (HCS) materials containing 0.1% or more crystalline silica by weight must follow federal guidelines concerning hazard communication and worker training [6, 8, 16]. Although HCS does not require the analysis of materials for crystalline silica content, material suppliers or employers may want to have materials analyzed for crystalline silica to be exempt from HCS requirements. Unfortunately, laboratories may need to deal with clients that assume a low concentration of a commonly occurring mineral like crystalline silica can be measured reliably and accurately. Sample inhomogeneity, measurement sensitivity and specificity limitations when other minerals are present make it difficult if not impossible for a laboratory to provide the conclusive evidence that laboratory clients seek to avoid HCS requirements.

4. SAMPLING CONSIDERATIONS

Current methods for sampling airborne silica use a cyclone with a cassette to collect the respirable fraction of the aerosol. To minimize measurement bias and variability, these samplers should conform to the criteria of the International Organization for Standardization (ISO), the European Standardization Committee (CEN), and the American Conference of Governmental Industrial Hygienists (ACGIH) for collecting particles of the appropriate size [25, 26, 27]. Also, the cyclone should exhibit sufficient electrical conductivity to minimize the electrostatic effects on particle collection.

Cyclones typically used for crystalline silica measurements include the non-conductive Dorr-Oliver 10-mm nylon cyclone and the conductive Higgins-Dewell cyclone. These cyclones have been evaluated for their compliance with the ISO/CEN/ACGIH respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver cyclone and 2.2 L/min for the Higgins-Dewell cyclone provide minimum bias for a wide range of particle size distributions that is likely to occur in the workplace [28]. The Dorr-Oliver 10-mm cyclone is the approved sampler for MSHA (CFR 30 Parts 70.100-10.206 and 71.100-71.206) and is commonly used in the United States, while the Higgins-Dewell cyclone is used in the United Kingdom and is sold in the United States and Canada. (Though the sampling recommendations to adopt the ISO/CEN/ACGIH respirable sampling convention have been formally accepted by MSHA for coal mine dust sampling, MSHA currently requires the use of the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor to match an earlier sampling convention (British Medical Research Council [BMRC], 1961) [29].

Recently, the BGI GK2.69 cyclone [30] has become commerically available with a sampling rate equal to 4.2 L/min. The GK2.69 cyclone is expected to be at least as adequate as the nylon cyclone for conforming to the ISO/CEN/ACGIH respirable aerosol sampling convention; and it may be preferable for silica sampling since it is conductive, has well-defined dimensional characteristics and can be used at higher flow rates to achieve a lower detection limit. Given that current analysis methods do not have sufficient accuracy to monitor below current exposure standards, this sampler has promise for potentially lowering the levels of silica that can be measured and still meet the required measurement accuracy. The availability of a pre-selector such as the GK2.69 cyclone sampler, which is designed to conform to the respirable dust sampling criteria at a flow rate nearly two and a half times that of the nylon cyclone, offers the field industrial hygienist the ability to collect a quantifiable sample mass during tasks of short duration or of low dustiness, conditions which may not have yielded a quantifiable mass using the nylon cyclone. The hygienist must be mindful of such things as ambient conditions, analytical detection limit, working analytical range and required air volume when selecting the appropriate sampler.

Each type of cyclone exhibits its own unique particle collection characteristics and the three major methods of analysis (XRD, IR, and colorimetric) are subject to different particle size effects. Therefore, the use of a single cyclone type for each application is advised until evidence becomes available indicating that bias among cyclone types will not increase inter-laboratory variability. In practice, the Dorr-Oliver 10-mm nylon cyclone has been used since the 1960's and has been a basis for some epidemiological studies. While augmenting the list of recommended samplers with the Higgins-Dewell and the BGI GK2.69 cyclones would

allow better sensitivity in samples taken with them, interlaboratory precision would suffer due to the use of multiple sampling devices. At this time, silica sampling should be done with a 1.7 L/min Dorr-Oliver nylon cyclone to meet the ISO/CEN/ACGIH respirable sampling convention within the United States. A future change to the GK2.69 sampler is a possibility.

Both cyclones and filter cassettes should be leak-tested prior to sampling to avoid gross failure in the field [31,32]. The cyclones may be tested using a simple pressure- (or vacuum-) holding test. The filter cassette should also be checked for leakage while attached to the cyclone. Two approaches to testing the cassettes have been used. One approach used a micromanometer to measure pressure drop across a given cassette and compared it to the average pressure drop across well-sealed cassettes [33]. An alternative approach used a particle counter to measure the penetration of submicrometer ambient aerosol through the cassette, with the percentage of penetration serving as an indicator of leakage [31,34]. Evaluation of cassette leakage by several laboratories indicates that significant leakage can occur when cassettes are hand-assembled, when incorrect closing pressures are used on the cassettes and when cassettes are assembled with non-standard thicknesses of filter/backup pad combinations [34,35,36]. For press-fit cyclones, a press should be used to achieve a good seal, while screw-fit devices should have threads in good condition and be firmly screwed together.

5. ANALYTICAL CONSIDERATIONS

The measurement of airborne crystalline silica can be challenging. Sample preparation techniques may include complex procedures for reducing mineral interferences, redepositing the sample onto an analytical filter or using the collection filter for analysis (direct-on-filter measurement). Appropriate calibration of the analytical technique and the standard reference materials used for calibration are critical for accurate analyses. Identification of the analyte, whether quartz, cristobalite or tridymite, can be complicated by the presence of mineral interferences. There are several analytical methods to choose from, each having associated particle size effects. Thus, a high degree of attention is required throughout the analysis process. Discussion of crystalline silica measurement in bulk samples is beyond the scope of this chapter; however, a method for determining crystalline silica in bulk samples by infrared spectrometry is described elsewhere [37].

Prior to any sample preparation step, it is advisable to check the cassette received from the field for adherence of particles to the top or sides of the cassette. In an evaluation of Min-U-Sil 5 samples received in the American Industrial Hygiene Association (AIHA) Proficiency Analytical Testing (PAT) program for Rounds 146-148, it was observed that up to 20 % of the total sample was recovered by rinsing the top of the cassette prior to sample preparation [38].

Sample preparation may include procedures to reduce mineral interferences prior to analysis. A phosphoric acid digestion may be used if the presence of amorphous silica is suspected and alternate analytical peaks which are free of interferences do not provide sufficient sensitivity [39]. The phosphoric acid dissolves the amorphous silica, although some of the smaller crystalline silica particles may be lost [40]. Calcite, magnetite and hematite may be removed with dilute HCl. Kaolinite can be altered to an amorphous state through heating the sample within a specified temperature range. Some mineral interferences also may be dealt with during sample analysis via a thorough knowledge of the characteristic analytical peaks.

To ensure the accuracy of silica analysis, the sample deposit should be uniform across the filter. Since field samples are not always evenly distributed across the sampling filter, samples may be redeposited onto a different filter for analysis. The sample filter may be ashed (muffle furnace or low-temperature asher) or dissolved (tetrahydrofuran). The silica sample then is suspended in a solvent and redeposited onto an analytical filter by means of a filtration apparatus. Redeposition of the sample is difficult to perform at low sample loadings and requires the laboratory analyst to demonstrate good intralaboratory reproducibility. NIOSH and OSHA analytical methods use a 2-mL "buffer" of solvent in the filtration chimney prior to addition of the suspended sample in order to provide a cushion for more even deposition of the crystalline silica particles. No statistically significant difference in analytical results has been observed between ashing and chemical dissolution of the sample filter [40].

Direct-on-filter techniques are used by the United Kingdom, the European Union and Australia [41]. The sample collection filter is taken from the cassette and analyzed with no sample preparation. These techniques require less time and labor, avoid loss of analyte during sample preparation steps and are amenable to the predominant analytical methods [42]. Direct-on-filter methods should take into account deposition of the sample across the filter (deposition may be non-uniform) when choosing the area of the filter to measure and when comparing results to other methods. Aerosol deposits near the center of the filter are expected to be higher than deposits near edge of the filter. This potential source of error is generally minimized by using the same sampler and sampler conditions to prepare working calibration standards as was used for field sampling. Sample overloading is possible for a sample collected over a full work shift.

Calibration Standards: Calibration issues have proven to be critical in the accurate measurement of crystalline silica. Comparisons of various standard mineral reference materials used for calibration have shown varying degrees of agreement [43, 44, 45, 46]. In a statistical study of reference materials used by analytical laboratories participating in Round 133 of the PAT program, it was observed that use of multiple calibration standards contributed significantly to variability of the analytical results [40, 47]. To ensure accurate measurement of crystalline silica for analyses in the U.S., it is essential that only standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) (for which both particle size and phase purity have been established) be used to prepare calibration curves for quartz (1878 series, the current being 1878a) and cristobalite (1879 series, the current being 1879a). Efforts are being made to ensure continued availability of the NIST crystalline silica SRMs. No NIST SRM for tridymite is available, since this silica polymorph rarely exists in the workplace. However, a well-characterized sample of tridymite of the appropriate particle size is available from the U.S. Geological Survey and can be used as a reference standard. Tridymite reference material (Ref No. 210-75-0043) may be obtained from Dr. Stephen A. Wilson, U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225 (telephone: 303-236-2454; FAX 303-236-3200; e-mail: swilson@usgs.gov).

NIST is currently producing and certifying quartz and cristobalite deposited in known amounts (µg/filter) onto 25-mm PVC filters. For quartz, NIST SRM 1878a (quartz powder) deposited onto filters will be available in a "calibration set" of 6 concentration levels. NIST SRM 2950 quartz calibration set will contain 5 blank filters and 5 filters at each of the following target concentrations (µg quartz/filter): 10, 20, 50, 100, 250 and 500. In addition, NIST SRM 2951 will contain 5 blank filters and 5 filters at a target concentration of 5 µg quartz/filter and NIST

SRM 2958 will contain 5 blank filters and 5 filters at a target concentration of 1000 µg quartz/filter. For cristobalite, NIST SRM 1879a (cristobalite powder) deposited onto filters will be available in a "calibration set" of 6 concentration levels. NIST SRM 2960 cristobalite calibration set will contain 5 blank filters and 5 filters at each of the following target concentrations (µg cristobalite/filter): 5, 10, 20, 50, 100 and 250. In addition, NIST SRM 2967 will contain 5 blank filters and 5 filters at a target concentration of 500 µg cristobalite/filter. These filters can facilitate preparation of routine working standards at known concentration levels. These filters may also be useful in preparation of quality assurance samples.

Industrial hygiene laboratories use a variety of analytical techniques for the quantitative determination of quartz, cristobalite and tridymite [41,48]. The three most commonly used are X-ray diffraction spectrometry (XRD), infrared absorption spectrometry (IR) and colorimetric spectrophotometry. The sensitivities of these three techniques are influenced by the sample particle size. X-ray diffraction intensity varies considerably with particle size, smaller particles (0.2 to 2.0 µm) showing lower intensities [49]. Peak broadening and extinction effects are related to particle size; there is a decrease in intensity at larger particle diameters (>25 µm) due to extinction [50-52]. In addition, the X-ray diffraction intensity is affected by the fact that smaller particles contain a lower proportion of crystalline material because the amorphous surface layer makes up a higher proportion of the total. The infrared absorption response of both quartz and cristobalite is particle size dependent [53,54]. The response increases as particle size decreases to about 1.5 µm; below about 1.5, the response decreases due the presence of an amorphous surface layer. If a sample contains an appreciable portion of amorphous silica, neither XRD nor IR is entirely adequate, and both methods should be used for accurate quantification [55]. Colorimetric methods typically include a precisely timed heating step in which phosphoric acid is used to dissolve amorphous silica. The acid digestion may result in the loss of some of the smaller crystalline silica particles [40]. Since particle size and amorphous layer affect all three techniques, matching the particle size and phase purity of calibration standards with field samples is very important to minimize analytical bias. Because NIST SRM 1878 series (the current being SRM 1878a) consists of quartz with a distribution of particle sizes that is intended to be representative of respirable particles sampled, use a of respirable dust sampler (such as the Dorr-Oliver 10-mm nylon cyclone) should provide a collected dust sample which matches the calibration curve of the SRM [56].

TABLE 3. X-RAY DIFFRACTION SAMPLING AND ANALYTICAL METHODS FOR CRYSTALLINE SILICA.

	NMAM 7500	OSHA ID-142	MSHA P-2	MDHS 51 /2
Silica polymorph	quartz cristobalite tridymite	quartz cristobalite	quartz cristobalite	quartz
Sampler	10-mm nylon cyclone,1.7 L/min Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon Dorr-Oliver cyclone, 1.7 L/min	10-mm nylon Dorr-Oliver cyclone, 1.7 L/min	Higgins-Dewell cyclone, 1.9 L/min
Filter	37-mm 5-µm PVC membrane	37-mm 5-µm PVC membrane	37-mm 5-µm PVC membrane	25-mm 5-µm PVC membrane
Volume	400-1000 L total dust < 2 mg	408-816 L total dust < 3 mg	400-1000 L total dust < 3 mg	> 456 L total dust < 2 mg
Filter Preparation	RF plasma asher, muffle furnace or dissolve filter in THF	dissolve filter in THF	RF plasma asher	none
Redeposition	onto 0.45-µm silver membrane filter	onto 0.45-µm silver membrane filter	onto 0.45-µm silver membrane filter	none
Drift Correction	silver internal standard	silver internal standard	silver internal standard	external standard e.g.: aluminum plate
X-ray source	Cu Kα 40 kV, 35 mA	Cu Kα 40 kV, 40 mA	Cu Kα 50 kV, 35 mA	Cu Kα 45 kV, 45 mA
Calibration	suspensions of SiO_2 in 2-propanol (deposited on silver membrane filter)	suspensions of SiO_2 in 2-propanol (deposited on silver membrane filter)	suspensions of SiO_2 in 2-propanol (deposited on silver membrane filter)	sampling from a generated atmosphere of standard quartz dust
Proficiency Testing	PAT	PAT	PAT	WASP
Range (µg quartz)	20-2000	50-160 (validation range)	20-500	50-2000
LOD (µg quartz)	5 (estimated)	10	5	3
Precision*	CV = 8 % @ 50-200 µg	CV =10.6 % @ 50-160 µg	CV = 10 % @ 20-500 µg	CV = 5 % @ 50 µg

- Precision is noted in terms of CV (coefficient of variation) for all methods for convenience of comparison. CV is equivalent to s, (relative standard deviation). In some methods, precision is noted in terms of $\bar{s}_r$ (pooled relative standard deviation) which is equivalent to $\overline{CV}$.

NMAM=NIOSH Manual of Analytical Methods, OSHA=Occupational Safety and Health Administration, MSHA=Mine Safety and Health Administration, MDHS=Methods for Determination of Hazardous Substances, PVC=polyvinyl chloride, RF=radio frequency, THF=tetrahydrofuran, Cu=copper, kV=kilovolts, mA=milliamps, PAT=proficiency analytical testing, WASP=workplace analysis scheme for proficiency, LOD=limit of detection, CV = coefficient of variation.

XRD Methods. XRD methods include NIOSH Manual of Analytical Methods (NMAM) 7500, OSHA ID-142, MSHA P-2 and UK-HSE Methods for the Determination of Hazardous Substances (MDHS) 51 /2 [57-60]. Details of these methods are listed in Table 3. X-ray diffraction is capable of distinguishing between the different polymorphs of crystalline silica: quartz, cristobalite and tridymite.

The primary diffraction line for α-quartz is 26.66 °2θ (3.343 Å). Since silica often occurs in a matrix with other minerals, some of which exhibit spectra that overlap with the primary quartz diffraction peak, the use of alternate peaks for quantification may be necessary. A list of potential mineral interferences is given in OSHA ID-142, Appendix A [58]. The use of secondary, tertiary and even quaternary peaks may result in decreased sensitivity [61]. An X-ray diffraction scan to characterize the environmental matrix for a set of samples is required in NIOSH X-ray diffraction methods for each set of samples. A determination revealing the correct peak ratios for the three largest peaks can be taken as an indicator of lack of interferences; otherwise a phosphoric acid digestion may be required prior to analysis to reduce interferences [39]. A high level of analyst expertise is required to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase [62]. NIOSH XRD methods suggest that XRD analysts have some training (university or short course) in crystallography or mineralogy in order to have a background in crystal structure, diffraction patterns and mineral transformation. This is important for understanding the matrix in which the sample was taken.

For optimum XRD instrument performance, the X-ray source must be aligned and monitored routinely for stability. Counting statistics, which are crucial for precise measurement of peak intensity, can be improved by increasing the count time per increment, although this increases the total time per sample analysis. The scan rate of the detector should be no more than 1 °2θ min^{-1}. Error increases rapidly with increasing scan rate. A 1° divergence slit width is reasonable for measurement in the 20-80 °2θ range. For optimal intensity and resolution, the receiving slit width should be >0.2° and about the same as the X-ray beam width. Inherent properties of the sample, such as crystallinity, can also affect measured peak intensities. Parameters related to sample preparation include sample homogeneity, size distribution of the particles, size of the sample surface exposed to the X-ray beam, thickness of the sample deposition and choice of internal standards, if any. An internal standard, such as silver in NMAM 7500 and OSHA ID-142, serves to normalize the X-ray intensity measured and to provide information on matrix absorption effects. Sample spinning during analysis allows for the alignment of each crystal in the beam and thus reduces precision error by insuring that all crystals are measured. Monitoring X-ray tube emission is done via a permanently mounted standard (e.g.; NIST SRM 1976, a sintered alumina plate used as an instrument sensitivity standard for X-ray powder diffraction). In addition, line position and line shape can be monitored via silicon powder (NIST SRM 640c) or lanthanum hexaboride powder (NIST SRM 660a). Direct-on-filter methods depend on an external standard, such as an aluminum plate to correct for the gradual decline in X-ray tube emission [60].

TABLE 4. INFRARED SAMPLING AND ANALYTICAL METHODS FOR CRYSTALLINE SILICA.

	NMAM 7602	NMAM 7603	MSHA P-7	MDHS 37	MDHS 38
Matrix		coal mine dust	coal mine dust		
Sampler	10-mm nylon cyclone, 1.7 L/min Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon cyclone, 1.7 L/min Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon Dorr-Oliver cyclone, 2.0 L/min	Higgins-Dewell cyclone, 1.9 L/min	Higgins-Dewell cyclone, 1.9 L/min
Filter	37-mm 0.8 PVC or 5-µm MCE	37-mm 0.8 PVC or 5-µm MCE	37-mm 0.8-µm, 5-µm PVC pre-weighed	37-mm 0.8-µm, 5-µm PVC	37-mm 0.8-µm, 5-µm PVC
Volume	400-800 L total dust < 2mg	300-1000 L total dust < 2mg	not stated	>456 L total dust < 1mg	>456 L total dust < 0.7mg
Filter Prep	RF plasma asher or muffle furnace	RF plasma asher or muffle furnace	RF plasma asher	none	muffle furnace
Analytical Sample Prep	mix residue with KBr, press 13-mm pellet	redeposit on 0.45-µm acrylic copolymer filter	redeposit on 0.45-µm acrylic copolymer filter	none	mix residue with KBr, press 13-mm pellet
Standard	polystyrene film	polystyrene film	polystyrene film	polystyrene film	polystyrene film
Calibration	quartz diluted in KBr	suspensions of quartz in 2-propanol	suspensions of quartz in 2-propanol	sampling from a generated atmosphere of standard quartz dust	sampling from a generated atmosphere of standard quartz dust
Proficiency Testing	PAT	PAT	PAT	WASP	WASP
Range (µg quartz)	10-160	30-250	25-250	10-1000	5-700
LOD (µg quartz)	5 (estimated)	10 (estimated)	10	varies with particle size	varies with particle size
Precision*	CV < 15 % @ 30µg	CV = 9.8 % @ 100 - 500 µg	CV = 5-10 % @ 100 - 500 µg	CV = 5 % @ 50 µg	CV = 5 % @ 50 µg

- Precision is noted in terms of CV (coefficient of variation) for all methods for convenience of comparison. CV is equivalent to s_r (relative standard deviation). In some methods, precision is noted in terms of $\overline{s}_r$ (pooled relative standard deviation) which is equivalent to $\overline{CV}$.

NMAM=NIOSH Manual of Analytical Methods, MSHA=Mine Safety and Health Administration, MDHS=Methods for Determination of Hazardous Substances, PVC=polyvinyl chloride, MCE=methyl cellulose ester, RF=radio frequency, KBr=potassium bromide, PAT=proficiency analytical testing, WASP=workplace analysis scheme for proficiency, LOD=limit of detection, CV=coefficient of variation.

Infrared Methods. IR methods include NMAM 7602, NMAM 7603, MSHA P-7, MDHS 37 and MDHS 38 [63-67]. Details of these methods are listed in Table 4.

The different polymorphs of crystalline silica exhibit distinct absorption patterns with primary and secondary absorption lines [68]. Alpha-quartz exhibits a characteristic doublet at 798-790 and 779-780 cm^{-1} and secondary peaks at 694, 512, 460, 397 and 370 cm^{-1}. The 694 cm^{-1} peak may be used for quantification in cases where mineral interferences overlap with the primary doublet. Alpha-quartz may be quantified in the presence of amorphous silica by using the 694 cm^{-1} peak or, alternatively, a phosphoric acid digestion may be used prior to analysis. Cristobalite exhibits characteristic peaks at 798, 623, 490, 385, 297 and 274 cm^{-1}. The 623 cm^{-1} peak may be used for quantification in cases where mineral interferences overlap with the customarily used 798 cm^{-1} peak. Tridymite exhibits characteristic peaks at 793, 617 and 476 cm^{-1}. It may not be possible to quantify tridymite in the presence of alpha-quartz or cristobalite [69]. Matrix effects from interferences with other silicates (such as kaolinite) present analysis problems. There is a potential for bias when correcting for matrix absorption effects, with the bias increasing at low levels of quartz. In coal mining the assumption is made that alpha-quartz is the only polymorph present due to the geological processes involved in coal formation. The only mineral interference found in coal is kaolinite. MSHA P-7 gives a spectral correction procedure for eliminating IR interference from kaolinite [65]. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret crystal structure, matrix interferences and mineral transformation for the laboratory client. In addition, data bases of IR spectra for minerals and inorganic compounds can be valuable resources [e.g., 70].

Colorimetric Methods The colorimetric methods for crystalline silica [e.g., 71] are significantly less precise than either the X-ray or the infrared methods. The colorimetric analytical technique exhibits a nonlinear dependence on the mass of crystalline silica present [72]. There is a limited linear range and significant blank values (20 µg silica or higher) are common [39,72,73]. High intralaboratory variability (up to twice as high as XRD or IR) of the colorimetric methods has been noted in studies of Proficiency Analytical Testing (PAT) program results [40]. The colorimetric method is less precise than IR or XRD methods and has no advantage over these two techniques of analysis; therefore the colorimetric methods should no longer be used for routine measurement of exposure to crystalline silica.

Quality Assurance. Because of the complex nature of crystalline silica analysis, it is essential to have a quality assurance program which incorporates strict adherence to standardized procedures. The most important requirement should be following the analytical methods exactly as written. Any modifications made in the methods in daily laboratory practices should be accompanied by validation data demonstrating equivalency of the modified method. Other factors which are important in measurement accuracy and precision and should be tracked are sample preparation, calibration and proficiency testing.

In methods which redeposit the sample onto an analytical filter, redeposition techniques can be difficult, especially for low sample loadings, and require good intralaboratory precision. For methods involving redeposition of the sample, the entire analysis is dependent upon the uniform deposition of silica material onto the analytical filter for laboratory analysis. The analyst's ability to perform this step quantitatively and repeatably should be determined initially and periodically thereafter.

The most important calibration factor is the use of prescribed reference materials (i.e., NIST-certified SRMs for analyses in the U.S.). In addition, preparation of precise working standards at appropriate concentrations for calibration graphs is crucial. An optimal calibration approach is the preparation of multiple working standards from suspensions of SRMs, with care taken that the particles are deposited onto the analytical filter in an even thin layer. Five or more standards should be used to construct calibration curves. NIOSH methods require the inclusion of several low level calibration standards (20-50 µg). Calibration should be checked each day that samples are analyzed via measurement of laboratory QC samples. The NIST-certified "calibration sets" are intended to be a resource for the preparation of working standards and laboratory QC samples. In studies of PAT laboratory performance, it was found that laboratories that did not use five or more standards, did not include low level standards (<50 µg) or did not check calibration each day that samples were analyzed were found to have poor agreement with other laboratories participating in proficiency testing [47,74]. For direct-on-filter methods, working standards are prepared by air generation in a chamber [60]. It can be difficult to generate low-level standards (< 50 µg) with precision; it is advisable to use standardized equipment to ensure that deposition of standard materials across the filter matches the deposition of the field samples being analyzed.

Internal Quality Assurance data can be used to track the precision of analyses to demonstrate repeatability of measurements. Data from proficiency testing programs, such as AIHA's Proficiency Analytical Testing (PAT) Program (U.S.) and the Health and Safety Executive's Workplace Analysis Scheme for Proficiency (WASP) Program (U.K.), can be used by the laboratory to demonstrate reproducible results when compared to other laboratories participating in that program. Proficiency testing data should not be used for assessing performance of analytical methods [75].

6. FEASIBILITY OF SILICA ASSESSMENT AT VARIOUS CONCENTRATIONS

The efficacy of sampling and analytical methods for measuring concentrations of hazardous materials may be established using the NIOSH accuracy criterion, requiring better than 25% accuracy at concentrations within the working range of the method [76]. Accuracy, as a percentage of true concentration values, is defined in terms of an interval expected to contain 95% of (future) measurements. To account for method uncertainty, the upper 95%-confidence limit on the accuracy is measured and used in the criterion. Generally, the accuracy of a method is measured over a range of concentrations bracketing the permissible exposure limit (PEL). Use of a range of measurements means that accuracy is assured both at levels below the PEL for possible use in action level determinations and, more significantly, at the PEL itself, where method results must be legally defensible.

NIOSH has evaluated both an XRD silica method (NIOSH Method P&CAM 259, the forerunner to NIOSH Method 7500) and an IR silica method (MSHA Method P-7) in a collaborative test among several laboratories [77]. Experimental conditions and results are summarized in Tables 5 and 6. As indicated, both XRD and IR methods fulfill the NIOSH accuracy criterion over the range of filter loadings measured.

TABLE 5. INTRALABORATORY RESULTS FOR EVALUATION OF XRD SILICA METHOD.

Item	Filter Loading		
	69.4 µg/filter	98.4 µg/filter	204 µg/filter
Degrees of Freedom	12	11	12
RSD for sampling and analytical methods (%)*, †	8.8	6.3	8.1

Source: NIOSH, BOM [1983].

- RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

† Implications for XRD: Pooled filter levels and pump error (assumed to be <5%) indicate that the overall imprecision is as follows: Total RSD for sampling and analytical methods is 9.3 %. Therefore, the upper 95% confidence limit on the accuracy (35 degrees of freedom) is 21%.

TABLE 6. INTRALABORATORY RESULTS FOR EVALUATION OF IR SILICA METHOD.

Item	Filter Loading		
	67.2 µg/filter	99.7 µg/filter	161 µg/filter
Degrees of Freedom	10	12	11
RSD for sampling and analytical methods (%)*, †	5.8	7.8	7.4

Source: NIOSH, BOM [1983].

- RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

† Implications for IR: Pooled filter levels and pump error (assumed to be <5%) indicate that the overall imprecision is as follows: Total RSD for sampling and analytical methods is 7.1 %. Therefore, the upper 95% confidence limit on the accuracy (33 degrees of freedom) is 17%.

The airborne concentrations of silica to which these filter loadings correspond depend on the flow rate of the pre-sampler used. Currently the Occupational Safety and Health Administration (OSHA) uses the 10-mm Dorr-Oliver nylon cyclone at a sampling rate of 1.7 L/min. The concentrations relevant to the collaborative test conditions are listed in Tables 7 and 8 and assume an 8-hour sampling period . As indicated, the traditional nylon cyclone passes the accuracy criterion over a range of concentrations bracketing 100 µg/m^3 (the current OSHA PEL) (see nylon cyclone data in Tables 7 and 8). In addition, since the new BGI GK2.69 cyclone (discussed in Section 4 of this chapter) is expected to conform to the ISO/CEN/ACGIH respirable aerosol sampling convention, the NIOSH accuracy criterion was applied using the 4.2 L/min sampling rate of the GK2.69 cyclone. The GK2.69 cyclone evidently is accurate over a range of concentrations bracketing 50 µg /m^3 (0.5 times the current OSHA PEL) (see GK2.69 cyclone data in Tables 7 and 8).

TABLE 7. XRD METHOD EVALUATION: AIR CONCENTRATIONS (µg/cm^3) CORRESPONDING TO ACTUAL FILTER LOADINGS (µg/filter). [76]

Cyclone and sampling rate	Filter loading			Applicable exposure limit
	69.4 µg/filter	98.4 µg/filter	204 µg/filter	
Nylon cyclone, 1.7 L/min	85 µg/m^3	121 µg/m^3	251 µg/m^3	100 µg/m^3
GK2.69 cyclone, 4.2 L/min	34 µg/m^3	49 µg/m^3	102 µg/m^3	50 µg/m^3

*Eight-hour sampled masses are combined with results of NIOSH, BOM [1983].

TABLE 8. IR METHOD EVALUATION: AIR CONCENTRATIONS (µg/cm^3) CORRESPONDING TO ACTUAL FILTER LOADINGS (µg/filter). [76]

Cyclone and sampling rate	Filter loading			Applicable exposure limit
	67.4 µg/filter	99.7 µg/filter	161 µg/filter	
Nylon cyclone, 1,7 L/min	83 µg/m^3	123 µg/m^3	198 µg/m^3	100 µg/m^3
GK2.69 cyclone, 4.2 L/min	34 µg/m^3	50 µg/m^3	80 µg/m^3	50 µg/m^3

*Eight-hour sampled masses are combined with results of NIOSH, BOM [1983].

7. SUMMARY

Silica is commonly found in the earth's crust and occurs in both crystalline and non-crystalline forms. Exposure to crystalline silica causes silicosis, is associated with pulmonary tuberculosis, lung cancer, scleroderma and may be related to autoimmune disorders and chronic renal disease.

Current methods for sampling airborne crystalline silica use a cyclone/cassette to collect the respirable fraction of the aerosol. There are several cyclones available, each with specific particle collection characteristics. To support interlaboratory precision, a single sampler which meets the ISO/CEN/ACGIH respirable sampling convention should be used.

Accurate and sensitive measurement of crystalline silica is complex. A high degree of attention is required throughout the analysis. The sample cassette should be checked for any adherence of particles to the walls of the cassette. Mineral interferences may be removed prior to analysis or may be dealt with via analytical data and a thorough knowledge of the characteristic analytical peaks. For methods involving redeposition of the sample, the entire analysis is dependent upon the uniform deposition of the particles onto the analytical filter for laboratory analysis. Calibration of the technique is crucial; the most important factors being the use of prescribed SRMs, the preparation of standards at appropriate concentrations and the use of QC samples to monitor calibration. An internal quality assurance program which incorporates strict adherence to standardized procedures is essential for measurement accuracy and precision.

Table 2 summarizes NIOSH, OSHA, MSHA, ACGIH and UK-HSE crystalline silica guidelines and limits for occupational exposure to crystalline silica. Tables 3 and 4 summarize NIOSH, OSHA, MSHA and UK-HSE sampling and analytical methods for crystalline silica. Tables 5 to 8 summarize evaluations of an XRD and an IR method.

Research on crystalline silica sampling and analysis is ongoing at NIOSH and elsewhere in government, in academia and in the private sector. Thus, this guidance is subject to revision as sampling and analytical method improvements are published.

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ACETOIN 2558

$C_4H_8O_2$ MW: 88.11 CAS: 513-86-0 RTECS: EL8790000

METHOD: 2558, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: None
NIOSH: None
ACGIH: None

PROPERTIES: liquid, solid (dimer); d= 0.9972 g/mL @ 20 °C; BP= 148 °C; FP = 50°C; MP= 15°C; Miscible in water and alcohol

SYNONYMS: 3-Hydroxy-2-butanone, 2,3-butanolone, acetyl methyl carbinol, dimethylketol

SAMPLING

SAMPLER: Anasorb CMS Solid Sorbent Tubes (150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 10 L

SHIPMENT: Ship cold (5°C) and store in dark

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 10% of field samples

ACCURACY

RANGE STUDIED: Not Determined

BIAS: Not Determined

OVERALL PRECISION ($\hat{S}_{rT}$): Not Determined

ACCURACY: Not Determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Acetoin

DESORPTION: 1 mL of acetone/methanol (95:5) on rotary mixer for 1.5 hours

INJECTION VOLUME: 1µL

TEMPERATURE
-INJECTION: 225°C
-DETECTOR: 250°C
-COLUMN: 35°C (hold 3 min) to 200°C (6°C/min)

CARRIER GAS: He (2.8 mL/min)

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 1-µm film, Stabilwax-DA or equivalent

CALIBRATION: Standard solutions in acetoin in acetone/methanol (95:5) solvent

RANGE: 3 to 378 µg

ESTIMATED LOD: 1.0 µg

PRECISION ($\bar{S}_r$): 0.008

APPLICABILITY: The working range for acetoin was 0.6 to 75.6 mg/m^3 for a 5 L air sample.

INTERFERENCES: Any compounds with similar retention times to acetoin.

OTHER METHODS: None determined.

REAGENTS:

1. Acetoin, chromatographic grade.*
2. Acetone, pesticide grade.*
3. Methanol, pesticide grade.*
4. Helium, pre-purified and filtered.
5. Hydrogen, pre-purified and filtered.
6. Air, compressed, purified, and filtered.
7. Calibration stock solution: Add known amounts of acetoin to solvent in 10-mL volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Anasorb CMS solid sorbent tube (SKC, Inc. # 226-121).
2. Personal sampling pump, 0.01 to 0.2 L/min, connected with flexible tubing.
3. Gas chromatograph equipped with FID, data collection system, and capillary column with a deactivated glass inlet liner(page 2558-1).
4. Autosampler vials, 2-mL, glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipettes, 3-mL and 5-mL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Acetoin is a flammable and toxic compound. Acetone and methanol are flammable and pose a fire hazard. Work with all chemicals in a well ventilated laboratory safety hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tube immediately before sampling. Attach sampling tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 10 L.
4. Cap the samplers with plastic caps, pack in a manner to insure that the samplers are kept in the dark, and are shipped cold (5°C).

SAMPLE PREPARATION:

5. Place the front and back sorbent sections in separate amber vials. Place the glass wool plug preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of the acetone/methanol (95:5) solvent into each vial. Securely attach crimp caps to each vial.
7. Place each vial on a rotary mixer for 1.5 hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Weigh out a known amount of acetoin in a 10-mL volumetric flask and dilute to the mark with solvent. Prepare additional standards by serial dilution in additional 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg acetoin).
9. Determine the desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount (5 to 20 µL) of DE stock solution directly onto the front section of each Anasorb CMS with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and store overnight at ambient temperature.
   d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE vs µg acetoin recovered.

10. Analyze a minimum of 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 the conditions listed on page 2558-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    Note: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of acetoin 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 acetoin 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, like NMAM 2557 (Diacetyl), was developed in response to a request to identify and quantitate possible hazardous chemical causes of workplace lung disease occurring at a microwave popcorn packaging facility. Acetoin, an inhalation irritant and chemically reactive compound, was identified as a possible suspect chemical in the facility.

Due to the reactivity of acetoin (under certain environmental conditions acetoin can be converted to diacetyl and vice versa [2]), several special handling requirements were included in this method development. A deactivated glass inlet liner was used to retard the oxidation of acetoin to diacetyl and to prevent analyte decomposition in the injection port. The Stabilwax-DA capillary was used to reduce peak tailing and decomposition of oxygenated compounds during analysis. The reactivity of acetoin was further retarded by using amber glassware and storage of stock and samples at 5°C. Application of these analytical conditions resulted in an average DE recovery of 94.9% over a range of 57 to 378 µg. The results of the storage stability study indicated that acetoin was stable for 7 days at 5°C with a recovery of 93.5%. A slow increase in the amount of diacetyl formed during the study was noted, with a maximum of 16-18% recorded at 30 days.

It should also be noted that the acetoin monomer (liquid) will convert to a dimer (white solid) upon standing. However, when dissolved, acetoin will convert back to the monomer in solution. Because of the limited solubility of acetoin some sonication may be required to fully dissolve the required amounts in the solvent.

REFERENCES:

[1] Pendergrass SM [2001]. Acetoin Backup Data Report, October.
[2] Fix, GJ[1993]. Diacetyl: Formation, Reduction, and Control, Brewing Tech., July/August.

METHOD WRITTEN (REVISED) BY: Stephanie M. Pendergrass, NIOSH/DART

(1) $HOCH_2CH_2OCH_3$	MW: (1) 76.09	CAS: (1) 109-86-4	RTECS: (1) KL5775000
(2) $HOCH_2CH_2OCH_2CH_3$	(2) 90.12	(2) 110-80-5	(2) KK8050000
(3) $HOCH_2CH_2O(CH_2)_3CH_3$	(3) 118.17	(3) 111-76-2	(3) KJ8575000

METHOD: 1403, Issue 3 **EVALUATION: FULL** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

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

PROPERTIES: See Table 1

SYNONYMS: (1) 2-methoxyethanol: methyl cellosolve, ethylene glycol monomethyl ether, EGME
(2) 2-ethoxyethanol: cellosolve, ethylene glycol monoethyl ether, EGEE
(3) 2-butoxyethanol: butyl cellosolve, ethylene glycol monobutyl ether, EGBE

SAMPLING

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

FLOW RATE: 0.01 to 0.05 L/min

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

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: See Table 2.

BIAS: See Table 2.

OVERALL PRECISION ($\hat{S}_{rT}$): See Table 2.

ACCURACY: See Table 2.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol

DESORPTION: 1 mL methylene chloride/methanol (95:5) in an ultrasonic bath for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 225°C
-DETECTOR: 300°C
-COLUMN: 40°C (1 min) - 200°C (12°C/min)

CARRIER GAS: He, 2.5-3.0 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; crossbonded carbowax®-DA or equivalent

CALIBRATION: Solutions of analytes in desorption solvent

RANGE: (1) 2 to 387 µg (2) 2 to 373 µg (3) 3 to 361 µg

ESTIMATED LOD: (1) 0.8 µg/sample (2) 0.7 µg/sample (3) 1.0 µg/sample

PRECISION ($\bar{S}_r$): (1) 0.024 (2) 0.022 (3) 0.048

APPLICABILITY: The working range for 2-methoxyethanol was 0.095 to 204 ppm (0.33 to 64.5 mg/m^3) for a 6-L sample volume, for 2-ethoxyethanol was 0.053 to 99 ppm (0.20 to 373 mg/m^3) for a 1-L sample, and for 2-butoxyethanol was 0.3 to 36.8 ppm (1.5 to 180 mg/m^3) for a 2-L sample.

INTERFERENCES: Any compounds having similar retention times as the analytes of interest.

OTHER METHODS: This method is an improved update of NMAM 1403, issue 2 (15 August 1994) [1]. NMAM 1403 (15 August 1994) previously combined and replaced methods S76 [2], S79 [2], and S361 [3]. Other less sensitive methods include OSHA 79 [4] and OSHA 83 [5].

REAGENTS:

1. Methylene Chloride, HPLC chromatographic grade.*
2. Methanol, HPLC chromatographic grade.*
3. Desorption solvent: methylene chloride (HPLC chromatographic grade) containing 5% methanol.
4. 2-methoxyethanol, reagent grade.
5. 2-ethoxyethanol, reagent grade.
6. 2-butoxyethanol, reagent grade.
7. Helium, purified and filtered.
8. Hydrogen, filtered.
9. Air, compressed, purified, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated coconut shell charcoal (100 mg/50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and follows the back section. Tubes are commercially available from SKC, Inc.
2. Personal sampling pump, 0.01 to 0.05 L/min, connected with flexible tubing.
3. Gas chromatograph, FID, integrator, and capillary column (page 1403-1).
4. Autosampler vials, 11-mm glass with crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Methylene chloride is a carcinogen [6]. Methanol is very flammable.

SAMPLING:

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

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool preceding the front section into the vial containing the front sorbent section. Discard the remaining foam plugs.
6. Add 1.0 mL of the desorption solvent into each vial. Attach crimp caps to each vial.
7. Place the sample vials in an ultrasonic bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to 10-mL volumetric flasks and dilute to the mark with solvent.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of DE stock solution directly onto the front sorbent section of each charcoal tube with a microliter syringe.

c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs µg analyte recovered.

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

MEASUREMENT:

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

CALCULATIONS:

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

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

NOTE: mg/L = mg/m^3

EVALUATION OF METHOD:

Initial Method Development Effort (Issues 1 and 2)

Methods S79 (2-methoxyethanol), S361 (2-ethoxyethanol), and S76 (2-butoxyethanol) were issued on February 14, 1975 [2, 7], March 17, 1978 [3, 8, 9], and February 14, 1975 [2, 7], respectively, and validated using, respectively, 50-, 6-, and 10-L air samples of atmospheres generated by calibrated syringe drive. Storage stability of these alcohols was not determined.

Current Method Development Effort (Issue 3) [10]

Issue 3 is an update and improvement of NMAM 1403. Improvements in the method include the use of capillary column chromatography, lower LOD/LOQ values, a new 5 level desorption efficiency (DE) study at lower levels, and a storage stability study at 7, 14, and 30 days.

The average DE determined for 2-methoxyethanol was 97.8% (RSD = 1.0), for 2-ethoxythanol the DE was 100.2% (RSD = 1.2), and for 2-butoxyethanol the DE was 99.9% (RSD = 1.3). The average 30-day storage stability recovery at approximately 0.5x REL for 2-methoxyethanol was 103.8% (RSD = 1.4), for 2-ethoxyethanol was 105.0% (RSD = 1.6), and for 2-butoxyethanol was 82.6% (RSD = 1.4).

The precision and accuracy information listed in Table 2 was calculated by using the data from generated air samples [7, 8] and the analytical data from the current update [10].

REFERENCES:

[1] NIOSH [1994]. Alcohols IV: Method 1403, revised by George Williamson. In: Eller PM, ed. NIOSH Manual of Analytical Methods, 4th rev. ed. Cincinnati, OH: U.S. Department of Health Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[2] NIOSH [1977]. 2-Butoxyethanol: Method S76, and 2-Methoxyethanol: Method S79. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 77-157-B.

[3] NIOSH [1979]. 2-Ethoxyethanol: Method S361. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 79-141.

[4] OSHA [1990]. Method 79. Salt Lake City, UT: Occupational Safety and Health Administration: Organic Methods Evaluation Branch, OSHA Analytical Laboratory.

[5] OSHA [1990]. Occupational Safety and Health Administration: Method 83. Salt Lake City, UT: Organic Methods Evaluation Branch, OSHA Analytical Laboratory.

[6] NIOSH Recommendations for Occupational Safety and Health, U.S. Department of Health and Human Services, (NIOSH) Publ. 92-100 (January 1992).

[7] Documentation of the NIOSH Validation Tests, S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[8] Backup Data, S361, available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB288-629 from NTIS, Springfield, VA 22161.

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

[10] Pendergrass SM [1998]. Backup Data Report for Alcohols IV Method Development Effort, NIOSH/ARDB/ACS, January.

[11] NIOSH [1990]. User Check, DataChem Laboratories, NIOSH Sequence #6960-J,K (unpublished, August 15).

METHOD WRITTEN BY:

Issue 3

Stephanie M. Pendergrass, NIOSH/DART

Issue 1 & 2

George Williamson, NIOSH/ DPSE; methods originally validated under Contracts 99-74-75 and 210-76-0123.

TABLE 1. Exposure Limits and Physical Properties

Compound	OSHA (ppm)	NIOSH (ppm)	ACGIH (ppm)	mg/m^3 = 1ppm @ NTP	MW	BP (°C)	Density @ 20°C (g/mL)	VP @ 20°C, KPa (mm Hg)
2-methoxyethanol	25 (skin)	0.1 (skin)	5 (skin)	3.16	76.09	124	0.966	0.8 (6)
2-ethoxyethanol	200 (skin)	0.5 (skin)	5 (skin)	3.75	90.12	135	0.931	0.5 (4)
2-butoxyethanol	50 (skin)	5 (skin)	25 (skin)	4.91	118.17	171	0.902	0.11 (0.8)

TABLE 2. Method Evaluation

	Overall Method[a]					Analytical Method[b]				Storage Stability	
Compound	Range (mg/m^3)	Accuracy	Breakthrough @ 2 x OSHA PEL	Bias	Precision S_r,T	Range studied (µg/sample)	LOD (µg/sample)	Ave. DE	Measurement Precision S_r	Levels (µg/sample)	Recovery (%)
2-methoxyethanol	44-160	0.41	128 L[c]	NS[e]	0.072	2-387	0.8	97.8	0.024	120.5	103.7
2-ethoxyethanol	340-1460	0.11	> 10 L[d]	NS	0.056	2-373	0.7	100.2	0.022	118.0	101.7
2-butoxyethanol	124-490	0.14	> 44 L[c]	NS	0.071	3-361	1.3	99.9	0.024	90.0	82

a) Generated air sample data in References 7 and 8.
b) Data for analytical method in Reference 10.
c) Testing done in dry air.
d) Testing done in 90% relative humidity.
e) NS = not significant

ALCOHOLS COMBINED 1405

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

METHOD: 1405, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

COMPOUNDS:
(1) *n*-butyl alcohol
(2) *sec*-butyl alcohol
(3) isobutyl alcohol
(4) *n*-propyl alcohol
(5) allyl alcohol
(6) diacetone alcohol
(7) cyclohexanol
(8) isoamyl alcohol
(9) methyl isobutyl carbinol

SYNONYMS: See Table 3.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

	Compounds:	(1-3)	(4-9)
VOL-MIN:		2 L	1 L
-MAX:		10 L	10 L

SHIPMENT: Routine

SAMPLE STABILITY: See Evaluation of Method.

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied [1, 2].

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Compounds above

DESORPTION: 1 mL 5% 2-propanol in CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 220 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 35 °C (7 minutes), to 60 °C at 5 °C/minute, hold 5 minutes, up to 120 °C at 10 °C /minute, hold 3 minutes.

CARRIER GAS: He, 4 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 0.5 µm film polyethylene glycol, DB-wax or equivalent

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

RANGE: See EVALUATION OF METHOD.

ESTIMATED LOD: 1 µg each analyte per sample

PRECISION: See EVALUATION OF METHOD.

APPLICABILITY: This method may be used to determine two or more of the specified analytes simultaneously.

INTERFERENCES: High humidity reduces sampling capacity. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and updates Methods 1401 and 1402, NMAM, Fourth Edition, Issue 2. Estimated LOD for each analyte is approximately ten times lower than that of the old methods.

REAGENTS:

1. Carbon disulfide, chromatographic grade.*
2. 2-Propanol, chromatographic grade.*
3. Hexane, chromatographic grade.*
4. Heptane, chromatographic grade.*
5. Desorbing solution: Carbon disulfide with 5% (v/v) 2-propanol and 0.05% (v/v) hexane as an internal standard.
   NOTE: n-Undecane, 0.1 (v/v) or other suitable standard can be used.
6. Analyte(s).
7. Stock solution, 100 mg/mL. Prepare solutions of each analyte in heptane.
8. Nitrogen, purified.
9. Hydrogen, prepurified.
10. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass tube, 7-cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front - 100 mg; back - 50 mg) separated by a 2-mm urethane foam plug 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 1405-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 2 mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood. Propanol, hexane, and heptane are flammable. Analytes should be handled in a fume hood. Wear gloves, safety glasses, and appropriate protective clothing.

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards covering the range of samples.
   a. Add known amounts of analyte to DS in 2-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. µg analyte.
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus tree media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of stock solution directly onto front sorbent section with a microliter syringe.

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

10. Analyze three quality control bind 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 1405-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

Previous Evaluations [2]

This method, NIOSH 1405, combines and updates NIOSH Methods 1401 and 1402. Methods 1401 an 1402 were based on the 2nd edition NMAM Methods S66 (n-butyl alcohol), S53 (sec-butyl alcohol), S64 (isobutyl alcohol), S62 (n-propyl alcohol), S52 (allyl alcohol), S55 (diacetone alcohol), S54 (cyclohexanol), S58 (isoamyl aocohol), and S60 (methyl isobutyl carbinol) which were issued on January 17, 1975 [3] and validated using 10-L air samples of atmospheres generated by injection of the pure alcohol into dry air using a calibrated syringe drive [1]. No storage stability studies were performed. Overall precision and recoveries are shown Table 4, representing non-significant bias in each method.

Current Evaluation [4]

Methods for alcohols (n-butyl alcohol, sec-butyl alcohol, isobutyl alcohol, n-propyl alcohol, allyl alcohol, diacetone alcohol, cyclohexanol, isoamyl alcohol) were evaluated using analytes fortified on Anasorb CSC sorbent tubes (Lot #2000). Table 5 lists the desorption efficiency (DE) and precision for the compounds tested in the evaluation.

Storage stability studies were performed at two different concentration levels: one at approximately 10 µg each analyte/sample for the low level, and the other at approximately 150 µg each analyte/sample for the high level. The samples were stored for 7, 14, 21, and 30 days at 5 °C. The results are summarized in Table 5.

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METHOD WRITTEN BY:

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TABLE 1. PROPERTIES

Compound	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density (g/mL)	BP (°C)	VP @ 20°C, kPa (mm Hg)
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$; $C_4H_{10}O$	3.03	74.12	0.810 @ 20 °C	117	0.56 (4.2)
sec-Butyl alcohol	$CH_3CH(OH)CH_2CH_3$; $C_4H_{10}O$	3.03	74.12	0.808 @ 20 °C	99.5	1.7 (13)
Isobutyl alcohol	$(CH_3)_2CHCH_2OH$; $C_4H_{10}O$	3.03	74.12	0.806 @ 15 °C	108	1.2 (9)
n-Propyl alcohol	$CH_3CH_2CH_2OH$; C_3H_8O	2.46	60.09	0.805 @ 20 °C	97	2.0 (15)
Allyl alcohol	$CH_2=CHCH_2OH$; $C_3H_6O_2$	2.37	58.08	0.854	96-97	2.3 (17)
Diacetone alcohol	$(CH_3)_2C(OH)CH_2COCH_3$; $C_6H_{12}O_2$	4.75	116.16	0.931 @ 25 °C	167.9	0.1 (0.8)
Cyclohexanol	$C_6H_{12}O$	4.09	100.16	0.962	161; MP=24	0.13 (1.0)
Isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$; $C_5H_{12}O$	3.60	88.15	0.813 @ 15 °C	132	3.7 (28)
Methyl isobutyl carbinol	$(CH_3)_2CHCH_2CH(OH)CH_3$; $C_6H_{14}O$	4.18	102.18	0.802	132	0.4 (3)

TABLE 2. GENERAL INFORMATION

Compound	CAS #	RETECS #	Exposure Limits OSHA (ppm)	NIOSH (ppm)	ACGIH (ppm)
n-Butyl alcohol	71-36-3	EO1400000	100 TWA	C 50 (skin)	C 50 (skin)
sec-Butyl alcohol	78-92-2	EO1750000	150 TWA	100 TWA; 150 STEL	100 TWA
Isobutyl alcohol	78-83-1	NP9625000	100 TWA	50 TWA	50 TWA
n-Propyl alcohol	71-23-8	UH8225000	200 TWA	200 TWA; 250 STEL(skin)	200 TWA; 250 STEL (skin)
Allyl alcohol	107-18-6	BA5075000	2 TWA; (skin)	2 TWA; 4 STEL (skin) (Group 1 Pesticide)	2 TWA; 4 STEL (skin)
Diacetone alcohol	123-42-2	SA9100000	50 TWA	50 TWA	50 TWA
Cyclohexanol	108-93-0	GV7875000	50 TWA	50 TWA (skin)	50 TWA (skin)
Isoamyl alcohol	123-51-3	EL5425000	100 TWA	100 TWA; 125 STEL(skin)	100 TWA; 125 STEL
Methyl isobutyl carbinol	108-11-2	SA7350000	25 TWA; (skin)	25 TWA; 40 STEL (skin)	25 TWA; 40 STEL (skin)

TABLE 3. SYNONYMS

Compound	Synonyms
(1) n-butyl alcohol	1-butanol; n-butanol; propyl carbinol.
(2) sec-Butyl alcohol	2-butanol; methyl ethyl carbinol; 2-hydroxybutane.
(3) isobutyl alcohol	2-methyl-1-propanol; isopropyl carbinol; IBA.
(4) n-propyl alcohol	1-propanol; ethyl carbinol.
(5) allyl alcohol	2-propen-1-ol; 2-propenol; vinyl carbinol.
(6) diacetone alcohol	4-hydroxy-4-methyl-2-pentanone; 2-methyl-2-pentanol-4-one.
(7) cyclohexanol	hexalin; hydralin; hydroxycyclohenane; anol.
(8) isoamyl alcohol	3-methyl-1-butanol; isobutylcarbinol; isopentyl alcohol.
(9) methyl isobutyl carbinol	MIBC; 4-methyl-2-pentanol; methyl amyl alcohol.

TABLE 4. PREVIOUS METHOD EVALUATION

			Range Studied [1]				
Method	Overall Precision ($\hat{S}_{rT}$)	Recovery (%)	(mg/m3)	(µg / sample)	Breakthrough[a] @ 2X OSHA PEL	Avg. DE	Measurement Precision ($\hat{S}_r$)
S66	0.065	100.0	170 to 610	1,500 to 6,000	35 L	0.89	0.021
S53	0.066	107.2	270 to 850	2,200 to 9,000	15 L	0.92	0.028
S64	0.073	100.0	180 to 620	1,500 to 6,000	31 L	0.85	0.023
S62	0.075	103.5	225 to 835	2,500 to 10,000	19 L	0.89	0.016
S52	0.111	98.8	1.8 to 8.4	20 to 100	>48 L	0.90	0.023
S55	0.104	91.8	140 to 510	1,100 to 4,700	>48 L	0.78	0.054
S54	0.080	98.9	95 to 380	1,000 to 4,000	>48 L	0.99	0.015
S58	0.077	107.6	195 to 680	1,800 to 7,000	34 L	0.99	0.020
S60	0.080	101.8	45 to 175	500 to 2,000	>48 L	0.99	0.035

a) sampling done in dry air

TABLE 5. CURRENT METHOD EVALUATION

Compound	Range Studied (µg / sample)	Average DE	Measurement Precision ($\hat{S}_r$)	Storage Stability Levels	
				Low (day)	High (day)
n-Butyl Alcohol	8 to 3,040	0.91	0.025	<7	30
sec-Butyl alcohol	8 to 3,030	0.96	0.016	30	30
Isobutyl alcohol	8 to 3,020	0.94	0.015	30	30
n-Propyl alcohol	8 to 3,020	0.92	0.015	14	30
Allyl alcohol	9 to 152	0.80	0.026	<7	14
Diacetone alcohol	9 to 3,260	0.88	0.013	<7	7
Cyclohexanol	10 to 1,710	0.95	0.017	30	30
Isoamyl alcohol	8 to 1,450	0.92	0.017	14	30
Methyl isobutyl carbinol	8 to 1,430	0.96	0.018	30	30

ALIPHATIC ALDEHYDES 2018

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

METHOD: 2018 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

COMPOUNDS AND SYNONYMS: See Table 3

SAMPLING

SAMPLER: CARTRIDGE (containing silica gel coated with acidified 2,4-dinitrophenylhydrazine)

FLOW RATE: 0.1 to 1.5 L/min

VOL-MIN: 1 L @ 0.68 to 1.3 mg/m^3
-MAX: 15 L @ 7.0 to 15 mg/m^3

SHIPMENT: Ship cold (0 to 5 °C).

SAMPLE STABILITY: ≥30 days @ 5 °C [1]

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

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC; UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazones of aldehydes (Table 1)

EXTRACTION: Elution with 10 mL of carbonyl-free acetonitrile

INJECTION VOLUME: 20 µL

MOBILE PHASE: Acetonitrile:water (see Table 1 for percentages); 1.3 mL/min

COLUMN: Stainless steel, 3.9 x 150 mm, packed with 5-µm C-18, Symmetry™ or equivalent

DETECTOR: UV @ 360 nm

CALIBRATION: Standard solutions of aldehyde-DNPH derivatives in acetonitrile

RANGE: See Table 4 [1]

ESTIMATED LOD: See Table 4

PRECISION ($\hat{S}_r$): See Table 5 [1]

APPLICABILITY: Working ranges are approximately 0.05 to 15 mg/m^3 (approximately 0.02 to 4 ppm) for 15-L air samples for the four aldehydes. This method can be used for the determination of acetaldehyde and valeraldehyde for OSHA STEL and PEL exposures. Upper limits of the method for the Supelco sampler are 105, 183, 50, and 50 µg per sample for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde, respectively.

INTERFERENCES: Ozone has been observed to consume the 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent and to degrade the DNPH derivative of formaldehyde [2]. Thus, ozone may degrade other aldehyde-DNPH derivatives. An ozone scrubber may be attached to the inlet of the sampler to remove ozone from the air; this scrubber may contain granular potassium iodide to reduce ozone to oxygen. Ketones and other aldehydes can react with 2,4-DNPH; the derivatives produced, however, generally are separated chromatographically from the analyte of interest.

OTHER METHODS: ASTM method D5197-97 and EPA compendium method TO-11A are applicable to the same four aldehydes and employ air samplers containing DNPH-coated silica gel [3,4]. NIOSH methods 2538 [5] and 3507 [6] and OSHA method 68 [7] are other methods for determination of acetaldehyde in air. OSHA method 85 is applicable to valeraldehyde and employs DNPH on glass fiber filters [8].

REAGENTS:

1. Aldehyde-DNPH derivatives, ≥99% pure (available from Supelco, Inc., or Aldrich Chemical Co.).
2. Acetonitrile, high purity solvent for HPLC and pesticide analysis, low carbonyl content.*
3. Calibration stock solutions. Accurately weigh 10 mg of DNPH derivatives in separate 10-mL volumetric flasks. Add acetonitrile to the 10-mL mark of each flask. Store at 5 °C in airtight containers 30 days or less.
4. Acetaldehyde, 99% pure.*
5. Propionaldehyde, 97% pure.*
6. Valeraldehyde, 97% pure.*
7. Isovaleraldehyde, 97% pure.*
8. Water, deionized (DI water).
9. Acetaldehyde fortification stock solution, 2.40 mg/mL. Measure 155 µL of cold (0 °C) acetaldehyde with a cold (0 °C) 500-µL syringe. Dissolve in 35 mL of cold DI water in a 50-mL volumetric flask. Add DI water (~20 °C) to the 50-mL mark. Use within 15 min of preparation.**
10. Propionaldehyde fortification stock solution, 2.40 mg/mL. Dissolve 154 µL of 97% propionaldehyde in 35 mL of acetonitrile in a 50-mL flask. Add acetonitrile to the 50-mL mark.***
11. Valeraldehyde fortification stock solution, 2.40 mg/mL. Dissolve 154 µL of 97% valeraldehyde in acetonitrile in a 50-mL volumetric flask. Add acetonitrile to the 50-mL mark.***
12. Isovaleraldehyde fortification stock solution, 2.40 mg/mL. Dissolve 152 µL of 97% isovaleraldehyde in acetonitrile in a 50-mL volumetric flask. Add acetonitrile to the 50-mL mark.***

* See SPECIAL PRECAUTIONS

** Cool a 500-µL syringe by placing in the freezer compartment of a refrigerator for at least 45 minutes. Make sure there is no water in the needle which would freeze and clog the needle.

*** Aldehyde stock solutions should be used within 30 minutes of preparation or kept chilled in an ice bath.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 150 to 250-µm (60-100 mesh) silica gel coated with 1.0 mg of 2,4-dinitrophenylhydrazine which has been acidified. Pressure drop across sampler should be less than 28 inches of water (7 kPa) at 1.5 L/min. Samplers are commercially available [Supelco S10 LpDNPH cartridge, cat. No. 2-1014; a similar type of sampler is manufactured by Waters Corp. (Sep-Pak XPoSure Aldehyde Sampler, part No. WAT047205)].
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Vials, 20-mL, 4-mL, glass, PFTE-lined rubber septa in caps for airtight seals.
4. Liquid chromatograph with UV detector, recorder, integrator, and column. (See page 2018-1.)
5. Syringes, 100-µL, 500-µL, and 10-mL.
6. Volumetric flasks, 5-mL, 10-mL, and 50-mL.
7. Ozone scrubber (optional), available from Waters Corp., Milford, MA.
8. Aluminum foil, or black electrical tape (optional).

SPECIAL PRECAUTIONS: Acetaldehyde is a severe eye irritant, lachrymator, mutagen, confirmed animal carcinogen, human cancer suspect agent and possible sensitizer [9]. Contact of acetaldehyde with air may cause the formation of explosive peroxides, and contact of the peroxides with heat or flame may cause fires or explosions. Fire and explosion may result from contact of acetaldehyde with strong oxidizers. Acetaldehyde is an extreme fire hazard; flash point = -37.8 °C (closed cup). Allow excess acetaldehyde in the glass ampule to evaporate in a fume hood.
Propionaldehyde, valeraldehyde, and isovaleraldehyde are eye and skin irritants. Evidence for the potential carcinogenicity of propionaldehyde and valeraldehyde is inconclusive [9]. These three aldehydes are incompatible with strong oxidizers and are dangerous fire hazards (flash points = 17.8 °C, 12.2 °C and -1 °C, respectively). Bottles of these aldehydes should be flushed with nitrogen after use. Work with all aldehydes in a fume hood.
The DNPH reagent [11] and aliphatic aldehydes are light sensitive [10]. Also, DNPH is a suspect carcinogen. 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. If desirable, attach a representative ozone scrubber to the inlet of the sampler. However this method has not been evaluated with an ozone scrubber in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. The Waters sampler is bi-directional and can be connected at either end.
   NOTE: If sampling is to be performed in intense sunlight, protection of the DNPH-coated silica gel bed in the sampler from intense light would be suggested in order to prevent possible photodecomposition of the DNPH reagent [11] and the aldehyde derivatives. If desirable, wrap a portion of the sampler with aluminum foil or black electrical tape.
4. Sample 1 to 15 L of air at 0.1 to 1.5 L/min.
5. Place end caps onto the sampler and seal sampler in an envelope. Protect samples from heat.
6. Ship samples cold (0 to 5 °C). Ship blanks in a separate container.

SAMPLE PREPARATION:

7. a. Elute the aldehyde derivatives from the cartridge samplers with 10-mL quantities of acetonitrile. Collect effluent (ca. 9.5 mL) from each sampler in a separate 10-mL volumetric flask.
   b. Add acetonitrile to the 10-mL mark of the volumetric flask for each sample.
      NOTE: Carbonyl content of acetonitrile can be determined by passing 10 mL of the solvent through a cartridge of DNPH-coated silica gel and analyzing by HPLC. Contents of aldehydes of interest should be below the respective LODs.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Calculate the concentrations of the aldehyde-DNPH derivatives in the calibration stock solutions (about 1000 µg/mL). Calculate the equivalent concentrations of the free aldehydes in solution by multiplying the derivative concentrations by 0.197, 0.244, 0.324, and 0.324 (molecular weights of acetaldehyde, propionaldehyde, valeraldehyde and isovaleraldehyde divided by the molecular weights of the corresponding aldehyde-DNPH derivatives, respectively).
   b. Prepare a series of dilutions (working standards) from 0.01 to 10 or 20 µg/mL (ranges of equivalent concentrations of free aldehydes from values below the detection limits to values corresponding to upper limits of the analytical range). The working standards (standard solutions) are stable for more than a month when stored at 5 °C in the dark in airtight containers; however, it is suggested that fresh working standards be prepared weekly.
   c. Transfer 3-mL aliquots of working standards to 4-mL vials and analyze (steps 11, 13 and 14).
   d. Prepare calibration graphs, peak areas or heights vs. µg free aldehydes per sample.

9. Determine recoveries (R) of aldehydes from samplers in the calibration range (step 8). Prepare three sorbent beds at each of five concentration levels for each aldehyde plus three media blanks. Recovery is expected to be near 100% for acetaldehyde, propionaldehyde, and valeraldehyde and about 86% for isovaleraldehyde.
   a. Prepare series of dilutions of fresh fortification stock solutions in the range of 50 to 300 µg/mL in 20-mL vials (one dilution for each fortification level for each aldehyde). Cap vials tightly. Use acetaldehyde fortification solutions within 15 minutes of preparation or significant losses of acetaldehyde may occur. Use propionaldehyde, valeraldehyde and isovaleraldehyde fortification solutions within 30 minutes of preparation (a limit of 30 minutes is precautionary).
   b. Fortify beds of sorbent. Using a 100-µL syringe, measure 20 to 90 µL of the particular aldehyde solution. Penetrate the center of the frit at the inlet of the sampler with the needle of the syringe. Inject the solution into the center of the sorbent bed. It is recommended that each sampler be fortified with only one injection of 90 µL of less. Injection of an excessive volume of solution may lead to incomplete reaction of aldehyde with DNPH.
   c. Prepare the fortified samples (steps 7a and 7b).
   d. Transfer 3-mL aliquots of samples to 4-mL vials and analyze together with working standards (steps 11, 13 and 14).
   e. Prepare graph of peak height vs. concentration of aldehyde in µg/sample for each of the aldehydes.
   f. Calculate recovery (R) for each sample by dividing the quantity of aldehyde found in the sample by the quantity of aldehyde applied.
   g. Prepare graphs of R vs. µg of aldehyde found (recovered).
10. Fortify three quality control samples and three analyst samples with known quantities of free aldehyde and aldehyde-DNPH in separate experiments. Analyze these samples to ensure that the calibration and recovery graphs are in control.

MEASUREMENT:

11. Set the liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2018-1 and in Table 1.
12. Transfer an aliquot of the sample solution from step 7.b. to a 4-mL vial. Cap the vial.
13. Inject a 20-µL sample aliquot.
14. Measure peak height or peak area. If a sample peak is larger than the largest standard peak, dilute an aliquot of the remaining sample solution, reanalyze, and apply appropriate dilution factor in the calculations.
15. To ensure validity of the samples, identify those samples which contain more than 105, 183, 50 or 50 µg of acetaldehyde, propionaldehyde, valeraldehyde or isovaleraldehyde per sample, respectively. The capacity of the samplers may have been exceeded for these samples, and collection of smaller samples would be warranted.

CALCULATIONS:

16. Determine mass, µg, of aldehyde, W, found in the sample and the average media blank, B, from the appropriate calibration graph.
17. Calculate concentration, C, of the aldehyde in the air volume sampled, V (L).

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The backup data report for this method development contains the data on recovery and breakthrough studies for each of the aldehydes.[1]

This method was evaluated with Supelco S10 LpDNPH samplers and free (underivatized) acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde. Recoveries were determined after fortification of six samplers in each set with known quantities of free aldehyde (see Table 5). While acetaldehyde, propionaldehyde and valeraldehyde showed average recoveries greater than 90%, average recoveries of isovaleraldehyde in Table 5 were in the 80% range; the reason for these relatively low recoveries is unclear. For storage studies, six samplers in each set were fortified with 3.00-µg of free aldehyde and stored at 5 °C in the dark (see Table 6). Also, liquid standards (standard solutions of aldehyde-DNPH derivatives in acetonitrile) were stored at 5 °C in the dark in vials with airtight caps (see Table 6). Limits of detection and quantitation were determined by least squares calculations with series of six standard solutions of aldehyde-DNPH derivatives in acetonitrile (see Table 4).

This method also was evaluated for butyraldehyde-DNPH and free butryaldehyde on Supelco S10 LpDNPH samplers. Recoveries decreased from 98% to 79% when quantities applied increased from 1.5 µg to 20 µg. The negative slope caused difficulty or ambiguity in applying recovery factors to quantities found. This method is not recommended for butyraldehyde.

Crotonaldehyde and acrolein were also studied. The recoveries of crotonaldehyde (crotonaldehyde-DNPH) and acrolein (acrolein-DNPH) were found to be very low (less than 30%). This method is not recommended for either of these compounds [12].

In each breakthrough study, a pair of samplers in series was connected to an air pump. A glass U-tube (a Schwartz drying tube) preceded the front sampler. For dry air, an impinger of dried, indicating silica gel preceded the U-tube. For humid air, an impinger of water preceded the U-tube. Known quantities of free aldehyde in solution were placed into the U-tube, and the pump drew air through the system at 1 L/min.

Upper limits of the method for acetaldehyde and propionaldehyde were calculated as two-thirds of the smallest quantities of aldehyde placed into the U-tube which gave rise to 5% breakthrough. For these two aldehydes, breakthrough took place earlier in humid air than in dry air or laboratory air; this humidity effect was reversed in the case of formaldehyde [13].

However, quantities of valeraldehyde and isovaleraldehyde generally did not break through the front samplers, and excessive quantities of valeraldehyde and isovaleraldehyde remained on the front samplers without reaction with DNPH. Thus, upper limits of the method for valeraldehyde and isovaleraldehyde could not be determined from quantities of aldehyde which gave rise to 5% breakthrough. Upper limits of valeraldehyde and isovaleraldehyde were calculated as two-thirds of the largest quantities of aldehydes placed into the U-tube which gave rise to a mass balance or a near mass balance (see Backup Data Report [1]).

Since the sampler does not have a backup section for determination of breakthrough, the worker conducting sampling in the field may connect two samplers in series in the cases of acetaldehyde and propionaldehyde. The back pressure of the sampling train will be higher and a lower flow rate may be required. Use of backup samplers in the field for valeraldehyde and isovaleraldehyde would be meaningless because excessive quantities of these aldehydes are trapped on the front sampler without reaction with DNPH and breakthrough to backup samplers may never occur. Alternatively, sampling without a backup sampler may be conducted even when high concentrations of aldehydes and ketones are anticipated if the sampling period is minimal and the flow rate of the pump is low.

Although this method may be useful for determining aromatic aldehydes in the air, it would be very difficult or impossible to evaluate this method with free (underivatized) aromatic aldehydes. Aromatic aldehydes, such as benzaldehyde, undergo rapid oxidation in air to form the corresponding carboxylic acids, such as benzoic acid.

The capability to separate valeraldehyde-DNPH from isovaleraldehyde-DNPH by HPLC was investigated. Twenty microliters of a single acetonitrile solution containing valeraldehyde-DNPH at 2 µg/mL and isovaleraldehyde-DNPH at 1 µg/mL (equivalent concentrations of underivatized aldehydes) was injected into

the HPLC when the mobile phase consisted of 66:34 acetonitrile:water at 1.3 mL/min. Retention times of valeraldehyde-DNPH and isovaleraldehyde-DNPH were 7.82 and 7.32 min, respectively. Although two sharp peaks were observed, the separation was only partial.

This method can be used with SKC aldehyde samplers (DNPH-coated silica gel tubes, catalogue No. 226-119) for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde with modifications (see **APPENDIX**).

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METHOD DEVELOPED BY:

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

TABLE 1. PROPERTIES AND OTHER INFORMATION

Compound	Formula	CAS	RTECS	MW	Density @ 20 °C (g/mL)	BP (°C)	Mobile Phase Percentages of Acetonitrile and Water (v/v)
acetaldehyde	CH_3-CHO	75-07-0	AB1925000	44.05	0.788[a]	20.8	51:49
propionaldehyde	CH_3-CH_2-CHO	123-38-6	UE0350000	58.09	0.807	49	54:46
valeraldehyde	CH_3-$(CH_2)_3$-CHO	110-62-3	YV3600000	86.13	0.8095	102	66:34
isovaleraldehyde	CH_3-CH(CH_3)-CH_2-CHO	590-86-3	ES3450000	86.13	0.803[b]	90	66:34

[a] Density of acetaldehyde at 16 °C
[b] The temperature for this density of isovaleraldehyde was not specified but is assumed to be room temperature.

TABLE 2. EXPOSURE LIMITS AND CONVERSION FACTORS.

Compound	Exposure Limits			Conversion Factor
	OSHA REL (ppm)	NIOSH PEL (ppm)	ACGIH TLV (ppm)	ppm to mg/m^3 @ NTP
acetaldehyde	200	lowest feasible level	25 ppm (ceiling)	1 ppm = 1.80 mg/m^3
propionaldehyde	none	none	none	1 ppm = 2.38 mg/m^3
valeraldehyde	50	50	50	1 ppm = 3.52 mg/m^3
isovaleraldehyde	none	none	none	1 ppm = 3.52 mg/m^3

TABLE 3. ALIPHATIC ALDEHYDES AND SYNONYMS

Aldehyde	Synonyms
acetaldehyde	ethanal, acetic aldehyde, ethylaldehyde, acetylaldehyde
propionaldehyde	propanal, propylaldehyde, methylacetaldehyde, propaldehyde, propylic aldehyde
valeraldehyde	n-valeraldehyde, pentanal, valeral, valeric aldehyde, amyl aldehyde, valeric acid aldehyde, butyl formal
isovaleraldehyde	isovaleral, isopentaldehyde, isovaleric aldehyde, 3-methylbutanal, 3-methylbutyraldehyde, isoamyl aldehyde

TABLE 4. ANALYTICAL LIMITS OF THE METHOD

Compound	LOD (µg/sample)	LOQ (µg/sample)	Calibration Range (µg/sample)	Maximum Sampler Capacity[a] (µg/sample)
acetaldehyde	0.2	0.68	0.68 to >150	105
propionaldehyde	0.3	0.89	0.89 to >150	183
valeraldehyde	0.4	1.30	1.30 to >150	50
isovaleraldehyde	0.2	0.79	0.79 to >150	50

[a] The maximum sampler capacity is the upper limit of the method (explained in text). The numbers shown apply to the Supelco sampler, which contains 1 mg of DNPH. Predicted capacities of the Waters sampler are 90% of these values.

TABLE 5. AVERAGE RECOVERIES AND POOLED PRECISION OF MEASUREMENT [a]

Compound	Average Recovery at the Level Shown (n = 6)					Pooled RSD[b]
	1.50 µg	3.00 µg	6.00 µg	12.0 µg	20.0 µg	
acetaldehyde	106%	99%	108%	106%	100%	0.031
propionaldehyde	84%	94%	91%	92%	95%	0.028
valeraldehyde	91%	97%	94%	94%	98%	0.021
isovaleraldehyde	83%	84%	85%	88%	85%	0.030

[a] Average recoveries were determined after fortification of Supelco samplers with free aldehydes in solution with a syringe.

[b] RSDs at all five levels for acetaldehyde and isovaleraldehyde were homogeneous by Bartlett's test; thus, all five RSDs for acetaldehyde and isovaleraldehyde were poolable. Other pooled RSDs were based on three or four individual RSDs.

TABLE 6. STABILITIES OF DNPH DERIVATIVES ON SAMPLER AND IN SOLUTION

Compound	Storage Period[a] (days)	Average Recovery from Sampler (n = 6)	Concentration of Liquid Std. (µg/mL[b])	Stability Period for Liquid Std. (days)[d]
acetaldehyde	30	102%	1.25	≥36
propionaldehyde	32	104%	2.20	≥35
valeraldehyde	30	105%	2.20	≥35
isovaleraldehyde	3	90%[c]	2.20	≥35

[a] Samplers were stored at 5 °C in the dark.
[b] Each liquid standard consisted of aldehyde-DNPH derivative in acetonitrile solution, and each concentration presented is the equivalent concentration of underivatized aldehyde.
[c] The average recovery of 90% is not an indication of deterioration of isovaleraldehyde-DNPH; compare the recovery of 90% with recoveries for isovaleraldehyde in Table 5.
[d] Liquid standards were stored at 5 °C in the dark in airtight containers.

TABLE 7. 5% BREAKTHROUGH DATA AND STOICHIOMETRIC QUANTITIES.

Compound	Amount of aldehyde found to show 5% breakthrough at a flowrate of 1L/min (µg/sample)			Stoichiometric Quantity ofAldehyde[d] (µg/sample)
	(in Dry Air[a])	(in Lab Air[b])	(in Humid Air[c])	
acetaldehyde	178	173	158	222 µg
propionaldehyde	322	290	274	293 µg
valeraldehyde	>>500	>>507	>>473	435 µg
isovaleraldehyde	>>400	>>498	>400	435 µg

[a] Estimated relative humidity of dry air was 10% at room temperature.
[b] The relative humidity of the laboratory air was not measured.
[c] Estimated relative humidity of humid air was 85% at room temperature.
[d] The stoichiometric quantities shown are the theoretical maximum quantities of aldehydes which can react with 1 mg of DNPH on the silica gel bed in the Supelco sampler.

APPENDIX

The SKC sampler for aldehydes (DNPH-coated silica gel tube, catalogue No. 226-119) may be used for acetaldehyde, propionaldehyde, valeraldehyde and isovaleraldehyde with modifications of this method. These modifications include the following. (a) The maximum recommended air volume sampled probably should be less than 15 L for an air concentration near 10 mg/m^3 (indicated on page 2018-1) because of the upper limits of the method for the SKC, Inc. sampler are probably smaller than the upper limits in this method (105, 183, 50 and 50 µg per sample for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde, respectively). However, the maximum recommended air volumes for the SKC sampler are unknown. (b) The procedure for recovery of analyte from the sorbent would be modified; i.e., placement of sorbent sections into vials and addition of solvent and possible use of ultrasonic bath. (c) A volume of solvent much smaller than 10 mL can be used for recovery. However, the minimum volume used should be tested for adequate recoveries. (d) Consequences of using a much smaller volume of solvent for recovery include a lower LOD, a lower LOQ, the need for a different range of calibration standards, and the need for a different range of levels of fortification (section 8). (e) The maximum volume of solution for fortification of the front sorbent bed must be smaller than 90 µL and should be determined (section 8).

ANILINE and o-TOLUIDINE in urine 8317

(1) Aniline: C_6H_7N	MW: 93.13	CAS: 62-53-3	RTECS: BW6650000
(2) o-Toluidine: C_7H_9N	MW: 107.16	CAS: 95-53-4	RTECS: XU2975000

METHOD: 8317, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

BIOLOGICAL INDICATOR OF: exposure to (1) aniline and (2) o-toluidine

ACGIH BEI: none

SYNONYMS: (1) aniline: benzeneamine; aminobenzene; phenylamine
(2) o-toluidine: 2-aminotoluene

SAMPLING		MEASUREMENT	
SPECIMEN:	Urine	**TECHNIQUE:**	HPLC with electrochemical detection
VOLUME:	At least 4 mL of sample	**ANALYTE:**	Aniline and o-toluidine
PRESERVATIVE:	5 g citric acid	**TREATMENT:**	Base hydrolysis and liquid-liquid extraction
SHIPMENT:	Freeze urine; ship on dry ice in an insulated container	**INJECTION VOL.:**	50 µL
SAMPLE STABILITY:	Sample stable for over 6 months at -65 °C	**MOBILE PHASE:**	37:53 methanol-phosphate buffer (pH 3.3), containing ~67 mg/L sodium dodecyl sulfate.
CONTROLS:	Collect urine from non-occupationally exposed workers	**FLOW RATE:**	0.8 mL/min
		GUARD CELL:	1000 mV
		DETECTOR:	Dual electrode coulometric electrochemical monitored at 600 mV.
		COLUMN:	Highly endcapped C_{18}-RP column (Waters NovaPak), 300-mm x 4.6-mm, heated to 30 °C with 0.2 µm inline filter and guard column of same sorbent.
		CALIBRATION:	Analyte in mobile phase.
		QUALITY CONTROL:	Analyte in urine at 0, 4, 20, 100 ng/mL.
		RANGE:	1.4 to 1200 ng/mL
		ESTIMATED LOD:	Aniline 1.4 ng/mL o-Toluidine 0.6 ng/mL
		PRECISION ($\bar{S}_r$):	Aniline 0.17 [4] Acetanilide 0.16 @ 18 ng/mL o-Toluidine 0.20 n-Acetyltoluidine 0.17 @ 16 ng/mL; 0.10 @ 200 ng/mL

APPLICABILITY: This method, monitors the parent compounds and their acetyl metabolites to remove the ambiguity from the aminophenol's origin.

INTERFERENCES: No interferences were observed for aniline or o-toluidine

OTHER METHODS: El Bayoumy developed a biological monitoring method for aniline and o-toluidine in 1986 [3], in which each liter of sample spiked with internal standard was lyophilized, reconstituted, concentrated, liquid/liquid extracted 3 times, evaporated to dryness, reflux hydrolyzed for 2.5 hrs, liquid/liquid again extracted 3 times, evaporated to dryness, reacted with pentafluoropropionic acid, before being analyzed by GC-ECD.

REAGENTS:

1. Aniline and o-toluidine stock solution, 100 mg/L, is prepared by dissolving 100 mg o-toluidine and 139 mg of aniline hydrochloride in 1 L of 0.1 N Hcl.
2. Aniline and o-toluidine calibration solution, 1000 µg/L. Dilute 1.000 mL of the stock solution with water to 100 mL to produce a 1000 µg/L solution for spiking.
3. Aniline and o-toluidine calibration solution, 100 µg/L. Dilute 1.000 mL of the above 1000 µg/L calibration solution with water to 100 mL to produce a 100 µg/L solution. These standard solutions are stable at 4 °C for at least two weeks.
4. Mobile phase: Add 23.0 g of $NaH_2PO_4 \cdot H_2O$ and 6 mL of 8.5 % phosphoric acid to a 2-L volumetric flask. Bring to near volume with water, mix, and adjust pH to 3.3 ± 0.05 with 8.5 % phosphoric acid or 50% sodium hydroxide, then bring to 2L mark. Add 1226 mL of methanol and 200 ± 0.5 mg of sodium dodecyl sulfate to a 4-L HPLC resevoir and mix. Blend the aqueous buffer with the methanol solution to prepare the mobile phase. Total liquid volume will shrink when liquids are mixed.
5. Water, highly purified. >10 MΩ.
6. Methanol, HPLC grade.
7. Sodium dihydrogen phosphate monohydrate, $NaH_2PO_4 \cdot H_2O$.
8. Sodium dodecyl sulfate.
9. Aniline hydrochloride.*
10. o-toluidine.*
11. Phosphoric acid 85%.*
12. Butyl chloride, HPLC grade.*
13. Sodium hydroxide, reagent grade pellets.*
14. Hydrochloric acid 0.1 N, Fisher certified.*
15. Citric acid, anhydrous, reagents grade.
16. Urine from non-occupationally exposed persons, who have no exposure to tobacco smoke.*

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Bottles, polypropylene, screw-top, 8-oz, 250-mL.
2. Bottles, polypropylene, screw-top, 2-oz, 60-mL.
3. HPLC system consisting of the following components in series; 5-L reservoir, in-line degasser filter, pump, pulse dampener, electrochemical guard cell (1.0 V), auto injector, in-line 0.2 µm in-line filter, a guard column, a 300 mm X 4.6 mm analytical column in an oven set at 30 °C, dual electrode coloumetric electrochemical detector connected to a data acquisition system, and a liquid waste container. The column packing material is highly end-capped 3 µm C_{18}-RP particles (Waters NovaPak or equivalent). The detector has two electrodes, one of which is used to remove potential interferences oxidizing below 400 mV and the other for analyte detection at 600 mV.
4. pH meter.
5. Vortex mixer.
6. Rotatory mixer.
7. Centrifuge tubes, 15-mL with teflon lined caps, disposable.
8. Reagent dispenser, 8-mL.
9. Auto-injector vials.
10. Water bath at 80 °C.
11. Dispensing pipette, 2-mL and 5-mL, disposable.
12. Micropipette, 1000-µL
13. Pasteur transfer pipettes.
14. Volumetric pipettes *, 1-, 2-, 3-, 4-, 5-, and 10-mL.
15. Syringes, 3-cc plastic disposable.
16. Syringe filters, Anotop^{TM} 10, 0.2 µm pore size.
17. Volumetric flasks *, convenient sizes for preparing standard solutions.
18. Scintillation vials, 10-mL polypropylene.

* Wash all permanent glassware with 0.1 N NaOH, 0.1 N HCl, water, and then methanol before use.

SPECIAL PRECAUTIONS: Urine samples may contain a number of bacterial and viral agents, including hepatitis B virus, and should be handled using Biosafety Level 2 practices, containment equipment, and facilities. [CDC & NIH, *Biosafety in Microbiological and Biomedical Laboratories*, 3rd ed., HHS Publication No. (CDC) 93-8395 (1993)]. Methanol and butyl chloride are NFPA level 3 fire hazards. Concentrated phosphoric acid and sodium hydroxide are a NFPA level 3 health and level 2 reactivity hazards, besides being corrosive. o-Toluidine is a bladder carcinogen, and may cause damage to the blood or kidneys. Aniline may be fatal if swallowed, inhaled, or absorbed through the skin. Aniline causes irritation to skin, eyes, and respiratory tract, and may cause cyanosis.

SAMPLING:

1. Timing of Collection: In humans, aniline is rapidly metabolized and excreted in the urine [1]. Rat data suggest that o-toluidine likewise is rapidly metabolized and excreted [2]. Thus, biological monitoring using pre and post shift urine samples is recommended in order to capture the metabolites quickly after exposure.
2. Collect urine in one or more 250-mL polypropylene bottles. Measure the total volume and transfer approximately 50 mL to a 60-mL polypropylene bottle containing 5.0 g of citric acid preservative. Label the bottle with the code unique to that specimen. Freeze immediately on dry ice.
3. Ship in a packing container that is designed for dry ice storage and transport. Store at -65 °C.

SAMPLE PREPARATION:

4. With each batch of 20 field urine samples, also process 2 quality control samples, 2 water blanks, and 2 field samples analyzed in a previous batch, a total of 26 samples per batch.
5. Assemble 26 conical centrifuge tubes in a racks.
6. Add 1.00 ± 0.05 g of NaOH pellets, cap, and label tubes.
7. Thaw samples to room temperature. To minimize analyte loss, keep caps tightly sealed and minimize time between steps 7-14.
   NOTE: Frozen urine samples are inhomogeneous. Insure that the samples are completely thawed and well mixed before removing aliquot.
8. Add 4.0 mL of sample to each tube and recap tightly.
9. Heat for 2 hr ± 5 minutes at 80 °C in a water bath.
10. Cool to room temperature, add 8.0 mL of butyl chloride to tubes and recap.
11. Tumble tubes for 10 minutes at 50 rpm, and centrifuge for 5 minutes at 3000 rpm.
12. Transfer 5.0 mL of the upper butyl chloride layer to a second set of labeled centrifuge tubes.
13. Add 1.0 mL of 0.1 N HCl to tubes containing butyl chloride solution.
14. Tumble tubes for 10 minutes at 50 rpm, and centrifuge for 5 minutes at 3000 rpm.
15. Remove lower aqueous layer with a Pasteur pipette, and transfer to a 3 cc syringe barrel fitted with a 10-mm 0.2 µm filter.
16. Insert syringe plunger and inject the aqueous extract through the filter into a HPLC auto-injector vial and seal.
17. Order the samples and standard solutions in the auto-injector carrousel in a fixed pattern of two standard solutions bracketing every two sample extracts, e.g. standard, unknown, unknown, standard, unknown ....., standard. Within the fixed order randomize the standards and samples separately.
18. Analyze samples by HPLC (Steps 29 to 32).

CALIBRATION AND QUALITY CONTROL:

19. Label ten 50-mL volumetric flasks with the concentrations listed in the second column of the table below. Using the table below, prepare the standard solutions listed by diluting the indicated volume of stock standard solution to 50 mL with mobile phase.

	Calibration Solution	Volume of Stock Standard Solution (mL)		Volume of Mobile Phase
	(µg/L)	1000 µg/L	100 µg/L	(mL)
1.	100	5.0		45.0
2.	80	4.0		46.0
3.	60	3.0		47.0
4.	40	2.0		48.0
5.	20	1.0		49.0
6.	10		5.0	45.0
7.	8		4.0	46.0
8.	6		3.0	47.0
9.	4		2.0	48.0
10.	2		1.0	49.0

The calibration solutions are stable a 4 °C for at least 2 weeks. It is recommended to, prepare half of the calibration solutions fresh with each set of samples. Alternate the use of duplicate primary stock standard solutions so that every other set of calibration solutions is made from the alternate stock standard solutions.

20. Analyze these 10 calibration solutions with each batch of samples, so that every 2 field samples are bracketed with calibration solutions.
21. Because the calibration results are non-linear at low concentrations a quadratic curve should be prepared using data from the calibration solutions. Make the nominal mass of amine in pg injected the independent X variable and its peak height response the dependent variable of the calibration curve.

$$Y = aX^2 + bX + c$$

where a, b, and c are regression coefficients

22. Also, prepare quality control samples by collecting 1 L of fresh urine from unexposed non-smoking individuals, who are not taking medication.
23. To one liter of this fresh urine add 100 g of citric acid.
24. Add 25, 5, and 1 mL of stock 1000-µg/L standard solution to three 250-mL volumetric flasks, and dilute to the mark with the acidified urine. The nominal concentrations of these samples, i.e. 100, 20, and 4 µg/L, respectively, must be corrected for the average concentration of o-toluidine and aniline in the unfortified urine.
25. After each standard solution is added to urine, the fortified and unfortified urine is aliquoted into 10-mL polypropylene scintillation vials and stored at -65 °C.
26. Analyze these quality control samples with each batch and maintain quality control charts.
27. Also, analyze at least one replicate sample from a previous batch with each new batch to assess precision with variable matrices.
28. Blind field splits are also recommended as a check on method precision.

MEASUREMENT:

29. Set the chromatograph according to manufacturer's recommendations and to the conditions given on page 1. Inject 50 µL of final solution in step 16.

30. Measure peak heights of aniline and o-toluidine in the calibration solutions and in the samples.
31. Peak purity can be confirmed, if necessary, by re-analyzing the extract and three calibration solutions, once with Electrode 2 set at 520 mV and once at 600 mV. The response ratios of the unknown at these two voltages should match the response ratio of the calibration solutions within ± 3 standard deviations.
32. If the sample gives a peak for aniline and o-toluidine with a peak height out of the calibration range, re-analyze the extract using a 5 µL injection. If the 5 µL injection still gives a peak out of the calibration range, reduce the detector gain.

CALCULATIONS:

33. Calculate the concentration, C(pg/µL), of aniline or o-toluidine in the unknown from the peak heights and the calibration curve for aniline or o-toluidine, respectively (C, µg/L).

$$C = -b + \frac{\sqrt{b^2 - 4a(c - Y)}}{2a} \cdot \frac{1}{D} \cdot \frac{E}{F} \cdot \frac{G}{H}, pg / \mu L$$

a, b, c, and Y are defined in step 21
D = µL of injection volume
E = initial volume of urine
F = volume of 0.1 M HCl back extractant
G = initial volume of butyl chloride
H = transferred volume of butyl chloride

This equation does not account for a change in detector gain.

GUIDES TO INTERPRETATION:

This method was applied to 171 urine specimens from a chemical plant worker population with a known excess of bladder cancer. The median levels of o-toluidine were: exposed preshift = 11 µg/L; exposed postshift = 65 µg/L; nonexposed preshift = 0.7 µg/L; and nonexposed postshift = 2.6 µg/L. The median levels of aniline were: exposed preshift = 11 µg/L; exposed postshift = 23 µg/L; nonexposed preshift = 2.0 µg/L; and nonexposed postshift = 3.2 µg/L. [4-8]

The Karam El-Bayoumy et al. study [3] reported the total mass of aniline and o-toluidine excreted by urine of 19 occupationally exposed subjects, and they found that the workers excreted from 0.02 to 8.8 µg of aniline and 0.3 to 12.9 µg of o-toluidine during a 24-hour period.

EVALUATION OF METHOD:

The American Conference of Governmental Industrial Hygienists has recommended a biological exposure index (BEI) for aniline of 50 mg of 4-aminophenol per milligram of creatinine, measured in end-of-shift urine specimens. 4-Aminophenol is the ring hydroxylated metabolite of aniline [1]. Before a BEI for o-toluidine can be established, a relationship between exposure to *o*-toluidine and excretion of the metabolite must be established. Rat studies suggest that o-toluidine is also substantially metabolized by a ring hydroxylation pathway, but no one has demonstrated the presence of the metabolite in the urine of humans exposed to *o*-toluidine [2]. Other xenobiotics, I.e.. acetoaminophen, reach the same metabolic fate of 4-aminophenol as does aniline. This method, monitors the parent compounds and their acetyl metabolites to remove the ambiguity from the aminophenol's origin.

The method was characterized during a field study that included 45 batches of samples. Each batch contained QC samples of aniline with nominal levels of aniline spiked at 6.9 ng/mL, 18 ng/mL, and 77 ng/mL and with nominal levels of o-toluidine spiked at 4.2 ng/mL, 20 ng/mL, and 102 ng/mL. QCs samlpes were also made using acetanilide and N-acetyl-o-toluidine spiked to an equivalent free amine concentration of 19 ng/mL

and 16 ng/mL, aniline and o-toluidine. The precision and recovery data reported on page 8317-1 was an average of these levels, and reported below in a more detailed results table. In addition, blind field splits were also used to characterize the precision of the method.

RECOVERY [4]	aniline	109 % @ 6.9 ng/mL
	aniline	97 % @ 18 ng/mL
	aniline	93 % @ 77 ng/mL
	acetanilide	96 % @ 19 ng/mL
	o-toluidine	101 % @ 4.2 ng/mL
	o-toluidine	93 % @ 20 ng/mL
	o-toluidine	86 % @ 102 ng/mL
	N-acetyltoluidine	83 % @ 16 ng/mL
PRECISION ($\bar{S}_r$) [4]	aniline	0.26 @ 6.9 ng/mL
	aniline	0.14 @ 18 ng/mL
	aniline	0.12 @ 77 ng/mL
	acetanilide	0.16 @ 19 ng/mL
	o-toluidine	0.32 @ 4.2 ng/mL
	o-toluidine	0.17 @ 20 ng/mL
	o-toluidine	0.14 @ 102 ng/mL
	N-acetyltoluidine	0.17 @ 16 ng/mL

Duplicate blind splits	
Pairs of duplicates	43
Range (ng/mL)	10 - 350
Average Relative Standard Deviation	23 %

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METHOD DEVELOPED BY:

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$CH_3CH_2CH_2Br$	MW: 123.00	CAS: 106-94-5	RTECS:TX4110000
$(CH_3)_2CHBr$	123.00	75-26-3	TX4111000

METHOD: 2552, ISSUE 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: None
NIOSH: None
ACGIH: None

PROPERTIES: **1-BP:** liquid; d= 1.354 g/mL @ 20 °C; BP= 71 °C; MP = -110 °C; FP= 25 °C.
2-BP: liquid; d= 1.310 g/mL @ 20 °C; BP= 59 °C; MP= -89 °C; FP= 19 °C.

NAMES & SYNONYMS: 1-Bromopropane: Propyl bromide, 1-BP.
2-Bromopropane: Isopropyl bromide, 2-BP.

SAMPLING

SAMPLER: Solid Sorbent Tube [1]
(Anasorb CSC, 100/50 mg)
Alternative sampler
(Anasorb CMS, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.1L
-MAX: 12 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 days at 5°C

BLANKS: 10% of field samples

ACCURACY

RANGE STUDIED: Not determined.

BIAS: Not determined.

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined.

ACCURACY: Not determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1-Bromopropane and 2-Bromopropane

DESORPTION: 1-mL CS_2 for 30 minutes with agitation.

INJECTION VOLUME: 1-µL

TEMPERATURE:
-INJECTION: 200°C
-DETECTOR: 250°C
-COLUMN: 35°C (3 min) to 150°C (8°C/min)

CARRIER GAS: Helium

COLUMN: Capillary, fused silica,30-m x 0.32-mm ID; 1.8-µm film phenyl/methyl polysiloxane, Rtx-502.2 or equivalent

CALIBRATION: Standard solutions of analytes in CS_2.

RANGE: 1-BP: 3.0 to 406.0 µg per sample [1]
2-BP: 4.5 to 393.0 µg per sample [1]

ESTIMATED LOD: 1-BP: 1.0 µg per sample [1]
2-BP: 1.0 µg per sample [1]

PRECISION ($\bar{S}_r$): 1-BP: 0.015 [1]
2-BP: 0.022 [1]

APPLICABILITY: Method can be applied to any process where bromopropanes are volatilized. The method was field tested in an industrial setting where 1-bromopropane was used in the application of adhesive to foam strips [2].

INTERFERENCES: Any compounds with similar retention times.

OTHER METHODS: None.

REAGENTS:

1. 1-Bromopropane, GC grade.
2. 2-Bromopropane, GC grade.
3. Carbon disulfide, GC grade.
4. Helium, prepurified and filtered.
5. Hydrogen, prepurified and filtered.
6. Air, compressed, purified, filtered.
7. Calibration stock solution: Add known amounts of analytes to carbon disulfide in 10-mL volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of Anasorb® CSC or equivalent (100/50 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section.
2. Alternative sampler: glass tube, 7 cm long, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of Anasorb® CMS or equivalent (150/75 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section.
3. Personal sampling pump, 0.01 to 0.2 L/min, connected with flexible tubing.
4. Gas chromatograph equipped with FID, integrator and capillary column (see page 2552-1).
5. Autosampler vials, 2-mL, glass, with PTFE-lined crimp caps.
6. Syringes, 10-µL, 25-µL, and 1-mL.
7. Pipettes, 3-mL and 5-mL.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic, explosive, and a fire hazard (FP= -30°C). Work with carbon disulfide in a well ventilated hood.

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Break the ends of sampling tube immediately before sampling. Attach sampling tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 12 L.
4. Cap the samplers with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of carbon disulfide into each vial. Attach crimp caps to each vial.
7. Allow to stand for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in a 10-mL volumetric flask and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of Anasorb CSC or Anasorb CMS used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of DE stock solution (5 to 25 µL) directly onto the front sorbent section of each tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE vs µg analyte recovered.
10. Analyze a minimum of 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 1025-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Desorption efficiency was checked for 1- and 2-bromopropane by spiking known amounts (in CS_2) on 2 different sorbents, Anasorb CSC and Anasorb CMS. The effect of volatility on sample recovery was also determined for each analyte spiked on Anasorb CSC and Anasorb CMS sorbent tubes using GelAir portable pumps to pull air through each tube at 0.2 L/min for 60 minutes (total volume was 12 L). Storage stability was determined for each analyte after 7, 14, and 30 days.

The average DE determined for 1-bromopropane from Anasorb CSC was 96.8% (RSD = 0.015) and for 2-bromopropane was 101.0% (RSD = 0.020). When air was pulled through spiked sorbent tubes to determine the effects of volatility on sample recovery, the average DE determined for 1-bromopropane was 103.7% (RSD = 0.013) and for 2-bromopropane was 99.7% (RSD = 0.026).

The average 30-day storage stability recovery for 1-bromopropane on Anasorb CSC was 106.9% (RSD = 0.009) and for 2-bromopropane was 98.2% (RSD = 0.013). The 30 day storage recovery using Anasorb CMS was 106% (RSD = 0.014) for 1-Bromopropane and 100.6% for 2-Bromopropane.

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

BUTOXYACETIC ACID IN URINE 8316

$C_6H_{12}O_3$ MW: 132.16 CAS: 2516-93-0 RTECS: None

METHOD: 8316, Issue 1	EVALUATION: PARTIAL	Issue 1: 15 March 2003

BIOLOGICAL INDICATOR OF: Exposure to 2-butoxyethanol (CAS # 111-76-2, RTECS # KJ8575000)
2-butoxyethyl acetate (CAS # 112-07-2, RTECS # KJ8925000).

SYNONYMS:

2-butoxyethanol: Ethylene glycol monobutyl ether, Monobutyl glycol ether, Butyl Cellosolve®, Butyl oxitol, Dowanol® EB, EGBE, Ektasolve EB®, Jeffersol EB

2-butoxyethyl acetate: Ethylene glycol monobutyl ether acetate, Butyl Cellosolve® acetate, Butyl glycol acetate, EGBEA, Ektasolve EB® acetate,

SAMPLING

SPECIMEN: Urine

VOLUME: 20 mL of sample

PRESERVATIVE: None

SHIPMENT: Frozen; on dry ice

SAMPLE STABILITY: At least 9 months at -70 °C

CONTROLS: Urine specimens from non-exposed persons, number determined by design of study.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD Ni-63

ANALYTE: Pentafluorobenzyl butoxyacetate, PFB-BAA

INJECTION VOLUME: 5 µL

TEMPERATURE
-INJECTION: 150 °C
-DETECTOR: 177 °C
-COLUMN: 70 °C for 2 min, 50 °C/min to 120 °C, 2 °C/min to 170 °C

CARRIER GAS: Helium, 10 mL/min

COLUMN: Capillary, fused silica, 5 m x 0.53-mm ID, deactivated and uncoated, followed by 30 m x 0.53-mm ID fused silica capillary with a 2.65-µm film of polydimethyl siloxane, HP-1 or equivalent.

CALIBRATION: Standard solutions of PFB-BAA in toluene/2-propanol

QUALITY CONTROL: Standard solutions of butoxyacetic acid (BAA) in urine

RANGE: 10 to 450 µmol/L in urine

ESTIMATED LOD: 10 µmol/L in urine

PRECISION ($\hat{S}_r$): 0.13

ACCURACY: Not determined

APPLICABILITY: Urinary butoxyacetic acid (BAA) is a biomarker of exposure to 2-butoxyethanol and 2-butoxyethyl acetate. Both 2-butoxyethanol and 2-butoxyethyl acetate are metabolized to butoxyacetic acid (BAA) and *N*-butoxyacetylglutamine, which are excreted in urine [1]. Since BAA produces the adverse hematogic effects attributed to exposures to 2-butoxyethanol and 2-butoxyethyl acetate, urinary BAA serves also as a biomarker to these particular exposure-related adverse health effects [2].

INTERFERENCES: No analytical interferences found. Consumption of ethanol is predicted to inhibit metabolism of 2-butoxyethanol to BAA [2], and thus may effect the accuracy of biomonitoring.

OTHER METHODS: This method is based on those of Smallwood *et al.* [3] and Johanson [4]. Grosenken *et al.* [5] published a method using lyophilization, derivatization with pentafluorobenzyl (PFB) bromide, then GC. The method of Rettenmeier *et al.* [1] determined both free BAA and its conjugate with glutamine using extraction and derivatization with 4-nitrobenzyl bromide, then HPLC. Sakai *et al.* [6] used acid hydrolysis, extraction, derivatization with trimethylsilyldiazomethane, then GC to determine free plus conjugated BAA.

REAGENTS:

1. Tetrabutylammonium hydrogen sulfate ($C_{16}H_{36}N{\cdot}HSO_4$).
2. Potassium dihydrogen phosphate.
3. Potassium hydroxide.
4. Phosphoric acid, 85%.*
5. Water, deionized.
6. $C_{16}H_{36}N{\cdot}HSO_4$ in phosphate buffer: 0.2 M KH_2PO_4 and 0.1 M $C_{16}H_{36}N{\cdot}HSO_4$ in deionized water, made pH 6 with 85% H_3PO_4 or 10 M KOH.
7. Methylene chloride.*
8. PFB bromide, 2,3,4,5,6-pentafluorobenzyl bromide.*
9. 2-Propanol.*
10. Toluene.*
11. Isopropanol-toluene mixture, 1:1 (v/v).
12. PFB-BAA, pentafluorobenzyl ester of butoxyacetic acid, MW 312.24 amu. Synthesized according to Groeseneken [5], purified by RP-HPLC, and analyzed to one major peak by GC/MS. Density 1.359 g/mL GC-MS (EI) fragmentation pattern; 240, 181, 131, 87, 73, 51amu.
13. PFB-BAA stock standard solution, 680 µmol/L. Dissolve 21 ± 0.1 mg of PFB-BAA in 100 mL of 1:1 isopropanol-toluene using an amber 100-mL volumetric flask. Store at 0 to 5 °C.
14. BAA, Butoxyacetic acid, >99%.
15 Urine from unexposed volunteers, stored at -20 to -15 °C for a maximum of 2 weeks.
16. BAA-in-urine stock solution, 4000 µmol/L. Dissolve 53 ± 1 mg of BAA in 100 mL of urine. Dilute with urine from unexposed volunteers for preparation of the quality control samples.
17 Argon with 5% methane.
18 Helium.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Gas chromatograph with ^{63}Ni electron capture detector, temperature programming, splitless injection port with purge, and autoinjector. The detector makeup gas was 5% methane in argon at 60 mL/min.
2. Polypropylene bottles, 30- and 250-mL with screw caps.
3. Graduated cylinders, 100- and 250-mL.
4. Shipping container, polystyrene foam, with dry ice.
5. Culture tubes, 16-mm x 100-mm, with teflon-lined screw caps, disposable.
6. Disposable serological pipettes, 0.2-mL in 0.001-mL increments, and 2-mL in 0.1-mL increments. Micropipette, 10-µL.
7. Aluminum foil.
8. Tube rotator.
9. Centrifuge, 3000 rpm.
10. Evaporator, nitrogen purge-type, with 30 °C heating bath.
11. Vortex mixer.
12. Ultrasonic water bath, room temperature.
13. Autoinjector vials, amber with crimp caps.
14. Balance, five-decimal-place analytical.
15. Volumetric flasks, amber, 10- and 100-mL.

SPECIAL PRECAUTIONS: See material safety data sheets. Urine samples may contain a number of bacterial and viral agents, including hepatitis B virus, and should be handled using Biosafety Level 2 practices, containment equipment and facilities [CDC & NIH, *Biosafety in Microbiological and Biomedical Laboratories*, 3rd ed., HHS Publication No. (CDC) 93-8395 (1993)]. Pentafluorobenzyl bromide is volatile compound, a powerful lacrimator, and a suspected carcinogen. Methylene chloride, isopropanol, and toluene are NFPA level 3 fire hazards. Phosphoric acid is highly corrosive.

SAMPLING:

1. Collect a spot urine sample in one or several 250-mL polypropylene bottles. Measure and record the volume of the whole voiding and transfer approximately 20 mL to a 30-mL polypropylene bottle. Label the bottle with the code unique to that specimen. Freeze immediately with dry ice.
2. Ship in a polystyrene-foam shipping container kept frozen with dry ice.
3. Store the samples at -76 °C until time of analysis.

SAMPLE PREPARATION:

4. Thaw the urine sample to room temperature. Remove a portion for creatinine analysis [8].
5. Transfer 0.200 mL of the sample to a culture tube.
6. Add 1.80 mL of tetrabutylammonium hydrogen sulfate in phosphate buffer, 2.00 mL of methylene chloride, and then 10 µL of pentafluorobenzyl bromide. Cap the tube.
7. Wrap the tube with aluminum foil to prevent exposure to light, and tumble with the rotator for 20 hr at 30 rev/min. Timing is critical, because analyte recovery reaches a maximum at 20 hr then decreases.
8. At 20 hours, centrifuge culture tubes for 5 min at 3000 rpm.
9. Transfer 1.5 mL of the methylene chloride (lower layer)to a clean culture tube. Evaporate to dryness under nitrogen at 30 °C.
10. Add 1.00 mL of 1:1 isopropanol-toluene to the residue, vortex for 1 min, then sonicate for 1 min.
11. Transfer the solution to an autoinjector vial, cap, and seal.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the GC for each batch of samples.
    a. Prepare 9 working standards by diluting the PFB-BAA stock solution with 1:1 toluene/propanol to 9 equally-spaced concentrations between 0.8 and 68 µmol/L (equivalent to urinary levels of 5.3 to 453 µmol/L).
    b. Analyze these standards with the unknowns in step 17 in random order but after every third unknown in the batch.
    c. Prepare a calibration graph of peak area versus analyte concentration, using, if necessary, quadratic regression to fit the data.
13. Prepare and analyze a minimum of 4 BAA-in-urine quality-control samples per batch.
    a. Prepare control samples at 0, 20, 90, and 400 µmol/L by diluting aliquots of BAA-in-urine stock solution with urine from unexposed individuals.
    b. Analyze quality control samples and five samples of the unspiked urine with the unknowns.
    c. Correct the nominal values for the control samples for the background level of BAA in the blank urine.
    d. Calculate the recoveries and plot them on a control chart for the method.
14. Re-analyze two field samples from the previous batch with each batch.
    a. If possible, select field samples with levels at both ends of the analytical range, but above the detection limit.
    b. Calculate the percent difference for each duplicate and plot it on a control chart for the method.
15. Analyze at least one sample of pure water with each batch as a check for background interferences.

MEASUREMENT:

16. Set the gas chromatograph system according to the manufacturer's recommendations and the conditions given on page 8316-1.
17. Inject 5 µL of sample from step 11 or standard from step 12.
    Note: With the chromatographic system used for method development, the PFB-BAA peak had an efficiency of 124,000 plates, an asymmetry factor of 1.4, and a retention time of 31.7 min. The intensity and precision of the detector's response to PFB-BAA were sensitive to temperature, with an optimal precision obtained at 177 °C.
18. Measure peak area.

CALCULATIONS:

19. Calculate from the calibration curve the concentration of PFB-BAA (C_c, µmol/L) in the final solution.
20. Calculate the concentration of BAA (C_u, µmol/L) in the urine sample from the equation below.

$$Cu = 6.67 \cdot Cc, \mu mol / L$$

where 6.67 is the dilution for the sample preparation steps.

21. Adjust the result for the creatinine level and report in micromoles per mole creatinine or in milligrams per gram creatinine, using the conversion 1 µmol/mol equals 1.17 mg/g.

GUIDES FOR INTERPRETATION:

A urinary BAA level of 51 mmol/mol creatinine (60 mg/g creatinine) corresponds to the NIOSH recommended exposure level for a 10-hr work shift of 5-ppm TWA for 2-butoxyethanol and 2-butoxyethyl acetate, assuming no dermal exposure to the liquid. Biological monitoring for exposure is recommended, because 1) dermal absorption may be a major route of exposure, 2) workload can significantly influence inhalation exposure, and 3) butoxyacetic acid itself exerts hematologic toxicity [2].

BAA levels up to 282 µmol/mol creatinine (330 mg/g creatinine) have been measured in occupationally exposed persons [7]. Levels as high as 0.5 µmol/mol creatinine (0.6 mg/g creatinine) have been found in urine of people not occupationally exposed to 2-butoxyethanol or 2-butoxyethyl acetate [6]. 2-Butoxyethanol is commonly found in household products, such as paints and cleaners.

EVALUATION OF METHOD:

A detection limit of 10 µmol/L was estimated using results from 11 urine samples spiked with BAA over the range 0.27 to 32 µmol/L. Recovery averaged 93% (range 53% to 146%) for 20 quality-control samples containing BAA at concentrations 12 to 3000 µmol/L. Precision was estimated at 13% relative standard deviation from duplicate analysis of 12 field samples from workers exposed to 2-butoxyethanol.

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METHOD DEVELOPED BY:

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CAPTAN AND THIOPHANATE-METHYL 9202
in Handrinse

Thiophanate-Methyl:	$C_{12}H_{14}N_4O_4S_2$	MW: 342.40	CAS: 23564-05-8	RTECS: BA3675000
Captan:	$C_9H_8Cl_3NO_2S$	300.59	133-06-2	GW5075000

METHOD: 9202, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

	Captan	Thiophanate-methyl
OSHA:	N/A	N/A
NIOSH:	N/A	N/A
ACGIH:	N/A	N/A

PROPERTIES:
Thiophanate-methyl: Colorless prisms, mp 181.5-182.5°C, soluble in acetone, methanol, chloroform, acetonitrile, insoluble in water.
Captan: Odorless crystals, mp 178°C, soluble in chloroform, practically insoluble in H_2O.

NAMES & SYNONYMS:
Thiophanate-Methyl: Topsin-M; [1,2-phenylenebis(iminocarbonothioyl)]bisdimethyl ester carbamic acid
Captan: N-(trichloromethyl)thio-4-cyclohexene-1,2-dicarboximide; Captec

SAMPLING

SAMPLER: POLYETHYLENE BAG
12" x 18", polyethylene bag containing 150 mL isopropanol

SHIPMENT: transfer wash to 250-mL wide-mouth glass jars with PTFE-lined caps. Ship cold.

SAMPLE STABILITY: at least 28 days at 4° 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: HPLC, UV detector

ANALYTE: Captan and Thiophanate-methyl

INJECTION VOLUME: 5 µL

MOBILE PHASE: A=2% n-propanol in water, 0.02 M TEA-PO_4 adjusted to pH 7.0 +/- 0.1 using phosphoric acid;
B=2% n-propanol in acetonitrile.
Gradient increasing from 20% B to 70% B over 20 min., decreasing to 20% B (2 min.) hold at 20% B (5 min.)

COLUMN: Reversed Phase C-18, 4µ, 250 x 2.00 mm (or equivalent).

DETECTOR: UV @ 200 nm

CALIBRATION: Solutions prepared in isopropanol

RANGE: Table 1

ESTIMATED LOD: Table 1

PRECISION ($\hat{S}_r$): Table 1

APPLICABILITY: This method was developed for the analysis of captan and thiophanate-methyl in an isopropanol hand rinse solution from orchard workers. In addition, this method may also be used to analyze other fungicides and pesticides that may be present in the field as long as they are sufficiently separated from the analytes by the analytical conditions of the method and soluble in isopropanol. (Figure 1.) Outside of the investigation into possible analytical interferences, extensive research was not completed on other pesticides and fungicides.

INTERFERENCES: The potential interferences include other organic compounds, in particular other agricultural chemicals that have the same retention time on a C18 column. Confirmation of the target fungicide can be checked by using an amino or phenyl LC column. Possible interferences include: ziram, myclobutanil, mancozeb, imidacloprid, and phosmet.

OTHER METHODS: This method was developed in conjunction with NMAM 5606, Thiophanate-methyl in air and NMAM 9205, Captan and Thiophanate-methyl on dermal patches.

REAGENTS:

1. Isopropanol, HPLC pesticide grade.*
2. Acetonitrile, HPLC grade.*
3. Triethylamine (TEA).*
4. Deionized water.
5. Thiophanate-methyl* stock solution, 10 mg/mL. Prepare in acetonitrile.
6. Captan* stock solution, 5 mg/mL. Prepare in acetonitrile.
7. TEA-PO_4 Preservative. Dissolve 1.4 mL of TEA in 90 mL of deionized water in a 100 mL volumetric flask. Add phosphoric acid to lower pH to 7.0 +/- 0.1 as indicated by a calibrated pH meter. Bring volume to 100 mL with water. Keep tightly capped and refrigerated. Solution stable for 12 months.
8. Mobile phase A. Combine 20 mL of n-propanol and 2.8 mL triethylamine in a 1 L volumetric flask and bring to volume using deionized water. Adjust pH to 7.0 (+/- 0.1) with phosphoric acid using a pH meter. Final concentrations: 2% n-propanol, 0.02 M TEA-PO_4. Degas prior to use.
9. Mobile phase B. Transfer 20 mL of n-propanol to a 1 L volumetric flask and adjust to volume with acetonitrile. Degas prior to use.
10. Ortho-phosphoric acid* >85% by weight, ACS grade or better.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 8" x 12" Scienceware™ Reusable Heavyweight Polyethylene Bags, 4 mm wall thickness (Bel-Art No. H13178-0812).
2. Container: 250 mL screw-top container with PTFE liner.
3. High Performance Liquid Chromatograph (HPLC) with UV detector.
4. Autosampler or injection valve capable of 5 µL injections.
5. Analytical column: Phenomenex® Synergi™ 4µ Hydro-RP 80A (250 x 2.00 mm) or equivalent.
6. Vials, 2-mL with PTFE-lined caps.
7. Syringes, 50-µL, 1-mL, and 5-mL.
8. Volumetric flasks, 5-mL, 100-mL, and 1-L.
9. PTFE syringe filter, 4-mm, 0.45-µm pore.
10. pH meter.
11. Graduated cylinders, 50-mL.
12. Pipettes, glass, disposable, 2-mL.
13. Bagged refrigerant.

SPECIAL PRECAUTIONS: Thiophanate-methyl: Avoid inhaling vapors or dust; avoid skin contact. Wear gloves and suitable clothing when handling pure material. Solvents: Avoid skin contact and open flame. Use in a hood. Phosphoric acid: Avoid skin contact. Captan: Use in hood. Avoid contact with skin, eyes, and clothing and ingestion or inhalation. Eye protection should be worn.

SAMPLING:

1. Pour 150 mL of isopropanol into the polyethylene bag.
2. Insert hand into bag. Wrap the top of the bag securely around the forearm, several inches above the wrist.
   NOTE: Allergies to alcohol are extremely rare. Before conducting the handwash, check to see if the person has ever had a reaction to alcohols, or is taking medications that could react with the alcohol. Some skin conditions, such as cuts, abrasions, and eczema can be irritated by contact with alcohols. If the person's hand seems "dried-out" after the handwash, hand lotion can be applied.
3. Shake hand in alcohol with constant back and forth motion for 30 seconds. Remove hand from bag and dry with paper towel.
4. Transfer solution to glass jar, cap securely.
5. Label and pack for shipment.
6. For field blank, add 150 mL isopropanol to a clean bag, shake for 30 seconds, then transfer the solvent to a glass jar for shipment.

SAMPLE PREPARATION:

7. Prepare analyst spike samples, solutions of isopropanol spiked with varying concentrations of the analytes of interest used for quality assurance, when field samples are received and store them together. Analyze with the field samples, blanks, and the liquid standards. Include unused 150 mL isopropanol wash of a polyethylene sampling bag as a media blank.
8. Remove a 1 mL aliquot from the sample container and filter with a 4mm 0.45 µm syringe filter.

CALIBRATION AND QUALITY CONTROL:

9. Determine retention times for analytes using the column and chromatographic conditions as shown on pages 9202-1 & 9202-2. The approximate retention time of thiophanate-methyl is 11 minutes and captan is 19 minutes. (See Figure 1.)
10. Calibrate daily with at least six working standards containing each of the two analytes and covering the analytical range for thiophanate-methyl and captan.

MEASUREMENT:

11. Set LC conditions according to manufacturer's recommendations. Set the wavelength for detection at 200 nm and the flow rate at 0.200 mL/min.
12. Inject a 5 µL sample aliquot with autosampler.
    NOTE: If the peak area of a sample is greater than the area of the highest standard, dilute with isopropanol and reanalyze.
13. Measure peak area of the analyte.

CALCULATIONS:

14. Perform a separate regression analysis of peak area vs. concentration of standard for each of the analytes. Determine the concentration, C (µg/mL), of the analyte in each sample from the calibration graph.
15. Calculate the mass of each analyte, M (µg), in the submitted sample volume, V(mL). Use a volume of 150 mL for the volume of the sample.

$$M = C \cdot V, \mu g / sample$$

EVALUATION OF METHOD:

This method was evaluated with a recovery study at room temperature over the range of 8949-60270 µg/sample for thiophanate-methyl and 13140-44070 µg/sample for captan using spiked laboratory samples with respective average recoveries in the range of 91.1-100% and 93.7-95.3%. [1] A recovery study at 4°C was also performed over the range of 8940-60420 µg/sample for thiophanate-methyl and 13130-43930 µg/sample for captan using spiked laboratory samples with respective average recoveries in the range of 101-111% and 102-105%. The storage study at room temperature was completed at 33990 µg/sample for thiophanate-methyl and 26200 µg/sample for captan with respective recovery averages of 102-107% and 102-127% over the 28 days of the study. The storage study at 4°C was completed at 34130 µg/sample for thiophanate-methyl, and 25520 µg/sample for captan with respective recovery averages of 110-121% and 102-112% over the 27 days of the study.

Originally, carbendazim was included in the investigation since it is a breakdown product of thiophanate-methyl. Attempts to quantitatively measure carbendazim suffered from reproducibility problems prompting carbendazim's removal from this method as an analyte that can be quantified. This method may be used to qualitatively determine carbendazim. Under method conditions, its approximate retention time is 6 minutes.

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Table 1.

Analyte	Range (µg/sample)	Estimated LOD (µg/sample)	Precision ($\bar{S}_r$)
Captan	410 - 44070	123	0.0326
Thiophanate-methyl	198 - 60270	60	0.0181

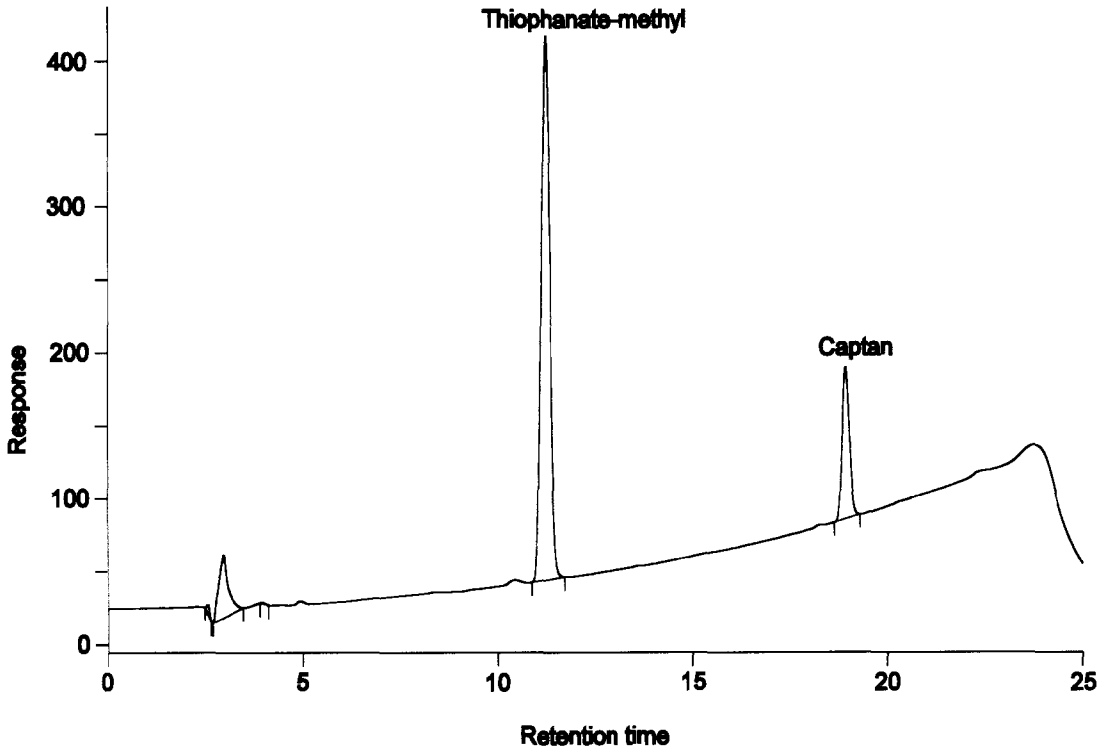

Figure 1. A typical chromatogram from the analysis of a hand rinse storage sample. The concentrations of the analytes shown here are: thiophanate-methyl - 226 µg/mL and captan - 175 µg/mL.

CAPTAN and THIOPHANATE-METHYL on Dermal Patch

9205

Thiophanate-Methyl:	$C_{12}H_{14}N_4O_4S_2$	MW: 342.40	CAS: 23564-05-8	RTECS: BA3675000
Captan:	$C_9H_8Cl_3NO_2S$	300.59	133-06-2	GW5075000

METHOD: 9205, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

	Captan	Thiophanate-methyl
OSHA:	N/A	N/A
NIOSH:	N/A	N/A
ACGIH:	N/A	N/A

PROPERTIES:
Thiophanate-methyl: Colorless prisms, mp 181.5-182.5°C, soluble in acetone, methanol, chloroform, acetonitrile, insoluble in water.
Captan: Odorless crystals, mp 178°C, soluble in chloroform, practically insoluble in H_2O

NAMES & SYNONYMS:
Thiophanate-Methyl: Topsin-M, [1,2-phenylenebis(iminocarbonothioyl)]bisdimethyl ester carbamic acid
Captan: N-(trichloromethyl)thio-4-cyclohexene-1,2-dicarboximide, Captec

SAMPLING

SAMPLER:	DERMAL PATCH (Cleanroom wipe, 4" x 4")
PASSIVE EXPOSURE:	place patch in card holder with 7.6-cm diameter circle cut in one side. Affix to worker's clothing or skin.
SHIPMENT:	transfer patch to 50-mL centrifuge tubes with caps. Ship cold.
SAMPLE STABILITY:	At least 28 days at 4°C.
BLANKS:	2 to 10 field blanks per set.

ACCURACY

RANGE STUDIED:	Not determined
BIAS:	Not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	Not determined
ACCURACY:	Not determined

MEASUREMENT

TECHNIQUE:	HPLC, UV detector
ANALYTE:	Captan, Thiophanate-methyl
EXTRACTION:	30 mL 40% isopropanol:60% acetonitrile (V/V) w/ TEA-PO_4 preservative.
INJECTION VOLUME:	5 µL
MOBILE PHASE:	A=2% n-propanol in water, 0.02 M TEA-PO_4, pH adjusted to 7.0 +/- 0.1 using phosphoric acid B=2% n-propanol in acetonitrile. Gradient from 20% B to 70% B (20 min.), decreasing to 20% B (2 min.), hold at 20% B (5 min.)
COLUMN:	reversed phase C-18, 4µm, 250 x 2.00 mm or equivalent.
DETECTOR:	UV @200 nm
CALIBRATION:	Solutions prepared in extract solvent
RANGE:	Table 1
ESTIMATED LOD:	Table 1
PRECISION ($\hat{S}_r$):	Table 1

APPLICABILITY: This method was developed for the analysis of the two analytes listed above on a dermal patch sampler from orchard workers. (See Figure 1.) In addition, this method may be used to analyze other fungicides and pesticides that may be present as long as they are separated from the two analytes by the analytical conditions of the method. It may be necessary to make adjustments to the gradient conditions of the method to obtain the required separation.

INTERFERENCES: The potential interferences include other organic compounds, in particular other pesticides or fungicides that have the same retention time on a C18 column. Positive identification may be confirmed by dual column chromatography using an appropriate alternative LC column. Possible interferences include: ziram, myclobutanil, mancozeb, imidacloprid, and phosmet.

OTHER METHODS: This method was developed in conjunction with method NMAM 5606, Thiophanate-methyl in air, and NMAM 9202, Captan and Thiophanate-methyl in handrnise.

REAGENTS:

1. Isopropanol, HPLC pesticide grade.*
2. Acetonitrile, HPLC grade.*
3. Triethylamine (TEA).*
4. Ortho-phosphoric acid >85% by weight, ACS grade or better.*
5. Deionized water.
6. Extraction solution: 40% isopropanol/60% acetonitrile w/2 mL TEA-PO_4 preservative for every liter of extraction solution prepared.
7. Thiophanate-methyl * stock solution, 10 mg/mL. Prepare in acetonitrile.
8. Captan* (Chem Service) stock solution, 5 mg/mL. Prepare in acetonitrile.
9. TEA-PO_4 Preservative. Dissolve 1.4 mL of TEA in 90 mL of deionized water in a 100 mL volumetric flask. Add phosphoric acid to lower pH to 7.0(± 0.1) as indicated by a calibrated pH meter. Bring volume to 100 mL with water. Keep tightly capped and refrigerated. Solution stable for 12 months.
10. Mobile phase A. Combine 20 mL of n-propanol and 2.8 mL TEA in a 1 L volumetric flask and bring to volume using deionized water. Adjust pH to 7.0 (+/- 0.1) with phosphoric acid using a pH meter. Final concentrations: 2% n-propanol, 0.02 *M* TEA-PO_4. Degas prior to use.
11. Mobile phase B. Add 20 mL of n-propanol to acetonitrile in a 1 L volumetric flask and bring to volume. Degas prior to use.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Dermal Patch: Texwipe™ AlphaWipe® polyester cleanroom wipe (4" x 4") in holder. The wipe is available commercially.
2. Patch Holder: White, 2-side chipboard, 0.08 SBS with a 7.6 cm diameter circle cut in one side (Wellman Container Corp, Fairfield, Ohio).
3. High Performance Liquid Chromatograph (HPLC).
4. Autosampler capable of 5 µL injections.
5. Analytical column: Phenomenex® Synergi™ 4µ Hydro-RP 80A (250 mm x 2.00 mm) or equivalent.
6. UV detector at 200 nm.
7. Vials, 2 mL, PTFE-lined caps.
8. Centrifuge tubes, polypropylene, 50 mL.
9. Syringes, 50-µL, 1-mL, and 5-mL.
10. Volumetric flasks, 5-mL, 100-mL, and 1-L.
11. PTFE syringe filter, 4-mm, 0.45-µm pore.
12. Large vial/tube rotator.
13. pH meter.
14. Graduated cylinders, 50-mL.
15. Pipettes, glass, disposable, 2-mL.
16. Forceps.
17. Bagged refrigerant.

SPECIAL PRECAUTIONS: Thiophanate-methyl: Avoid inhaling vapors or dust; avoid skin contact. Wear gloves and suitable clothing when handling pure material. Solvents: Avoid skin contact and open flame. Use in a hood. Phosphoric acid: Avoid skin contact. Captan: Use in hood. Avoid contact with skin, eyes, and clothing and ingestion or inhalation. Eye protection should be worn.

SAMPLING:

1. Secure the patch material in the patch holder with staples at two opposite corners. Attach the patch and holder to the appropriate location of the skin or clothing and sample for designated time period.
2. At the end of the sampling time, remove the patch from holder using clean forceps and transfer to a 50-mL centrifuge tube.
3. Label and pack the tube securely for shipment. These are shipped cold with other samples.
4. Samples should be stored under refrigeration until needed for analysis.

SAMPLE PREPARATION:

5. Add 30 mL of extraction solvent to each centrifuge tube and recap.
6. Mix by rotating the tubes end-over-end for at least one hour.
7. Filter an extract aliquot into a 2-mL autosampler vial through a 4-mm, 0.45 µm pore, PTFE filter.

CALIBRATION AND QUALITY CONTROL:

8. Determine retention times for analytes using the column and chromatographic conditions as outlined on pages 9205-1 and 9205-2. The approximate retention time of thiophanate-methyl is 14 minutes and captan is 21 minutes. (See Figure 1.)
9. Calibrate daily with at least six working standards containing each of the two analytes and covering the analytical range (Table 1) for thiophanate-methyl and captan.
10. Prepare QC samples by placing a new patch in a 50 mL tube and spiking with known amounts of the two analytes. Allow the samples to set open until the solvent has evaporated. Cap the tube and prepare for analysis in the same manner as the field samples in steps 5-7.

MEASUREMENT:

11. Set LC according to manufacturer's recommendations. Set the wavelength for detection at 200 nm and flow rate at 0.200 mL/min.
12. Inject 5 µL aliquot of the sample extract with autosampler.
    NOTE: If peak area of a sample is greater than the area of the highest standard, dilute with extracting solvent and reanalyze.
13. Measure peak area of the analyte.

CALCULATIONS:

14. Perform a separate regression analysis of the peak areas vs. quantity of standard for each of the two analytes. Determine the concentration,µg/mL, (corrected for DE) of the analyte in each sample patch (C_P) and in the media blank (B_b) from the calibration graph.
15. Calculate the mass of each analyte, M (µg), on a sample patch by adjusting for the volume , V (mL) of extraction solvent.

$$M = (C_P V_P - B_b V_b), \mu g$$

EVALUATION OF METHOD:

This method was evaluated with a recovery study at room temperature over the range of 306.0 - 6120 µg/sample for thiophanate-methyl and 300.4 - 6220 µg/sample for captan using spiked laboratory samples with respective average recoveries in the range of 89.1-95.5% and 89.6-96.0%. [1] The storage study at 4°C was completed at 6000 µg/sample for thiophanate-methyl, and 1500 µg/sample for captan with respective recovery averages of 86.2-92.2%, and 87.6-95.7% over the 28 days of the study.

Carbendazim, which is a decomposition product of thiophanate-methyl, may also be found in the chromatogram along with the other two analytes. An attempt was made to quantitatively analyze carbendazim as a part of this method. However, reproducibility problems for carbendazim in the presence of thiophanate-methyl has necessitated that the analysis be only qualitative for carbendazim. The reproducibility problem was more pronounced when the ratio of thiophanate-methyl to carbendazim was greater than about eight to one. Additionally, this problem is compounded when other materials, such as benomyl, which also decomposes to produce carbendazim, are present in the sample. Because this method is unable to distinguish the decomposition source of the carbendazim, it can only provide qualitative data for carbendazim. Under the method conditions, its approximate retention time is 9 minutes.

Field samples have been analyzed by this method. Because the field samples contained other organic compounds and/or interferences, it was necessary to make adjustments to the analysis parameters. For example, it was necessary to insert a longer column rinse at the end of the solvent gradient to elute higher molecular weight compounds and/or other material from the column. It was also necessary to change the end of the gradient solvent run to have a greater organic phase ratio to help rinse the column of these materials.

Based on the needs of the laboratory and the complexity of the samples to be analyzed, it may be necessary to make other changes to the analysis parameters to get the best resolution of the compounds in the samples.

REFERENCES:

[1] Jaycox LB, Andrews RN [2002]. Backup data report for Captan and Thiophanate-methyl on Dermal Patch method development, Cincinnati, OH: National Institute for Occupational Safety and Health, DART/NIOSH (unpublished, June).
[2] NIOSH [1998]. Method 9201: Chlorinated organonitrogen herbicides (dermal patch). In: Cassinelli ME, O'Connor PF, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed., 2nd supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publ 98-119.

METHOD WRITTEN BY: Larry B. Jaycox, Ph.D. and Ronnee N. Andrews, NIOSH/DART

Table 1.

Analyte	Range	Estimated LOD	Precision ($\hat{S}_r$)
Captan	67.5-6220 µg/sample	20.2 µg/sample	0.0256
Thiophanate-methyl	62.0-6120 µg/sample	18.6 µg/sample	0.0229

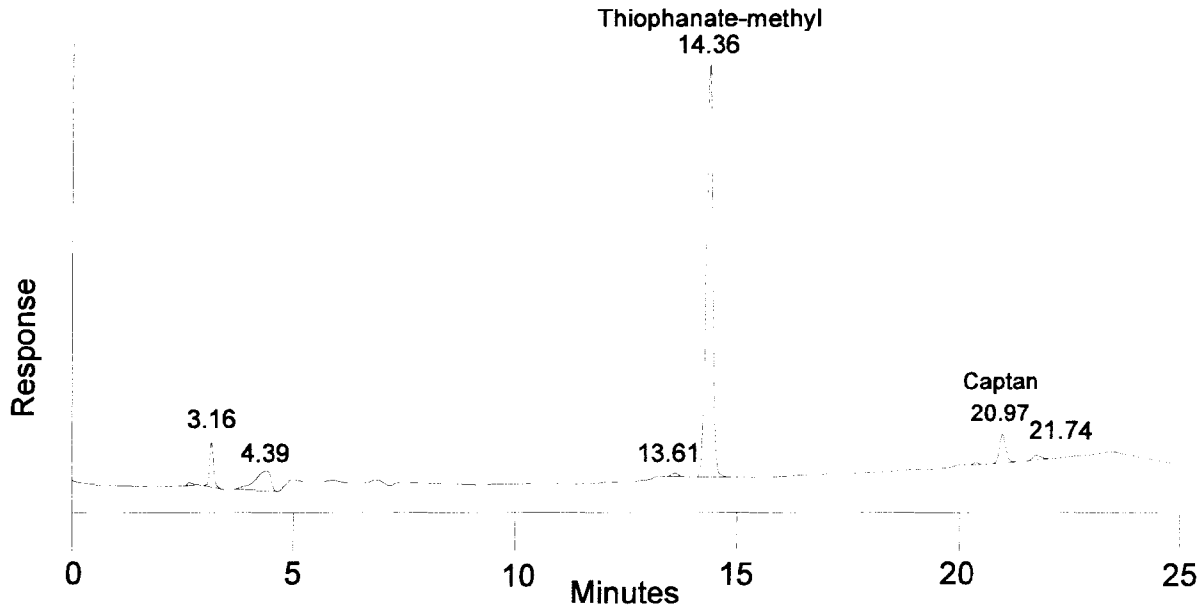

Figure 1 This chromatogram shows results from a spiked patch sample that was extracted and analyzed by this method. The analyte quantities were: thiophanate-methyl - 200 µg/sample and captan- 50 µg/sample.

CELLULOSE INSULATION 7404

$(C_6H_{10}O_5)_n$ MW: 00.00 CAS: 9004-34-6 RTECS: FJ5691460

METHOD: 7404, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

PROPERTIES: solid

SYNONYMS: cellulosic fiber loose fill thermal insulation. Cocoon.

SAMPLING

SAMPLER: FILTER (0.45- to 1.2-um polycarbonate membrane, 25-mm; conductive cowl on cassette)

FLOW RATE: 1 L/min

VOL-MIN: N/A
-MAX:

SHIPMENT: Routine (pack to reduce shock)

SAMPLE STABILITY: Stable

BLANKS: 2 or 10% field blanks per set

ACCURACY

RANGE STUDIED: Not determined

BIAS: Not determined

OVERALL PRECISION: Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, SCANNING ELECTRON (SEM)

ANALYTE: Fibers, (manual count)

SAMPLE PREPARATION: Colloidal graphite paint/carbon disk planchet.

EQUIPMENT: Scanning electron microscope

CALIBRATION: SEM performance standard

RANGE: Not determined

ESTIMATED LOD: 1 confirmed cellulose fiber above 95% of expected mean blank value

PRECISION: Not determined

APPLICABILITY: This method is useful for the quantitative determination of airborne cellulose fibers during isulation installation [1].

INTERFERENCES: Non-fibrous cellulose. Very large cellulose fibers and cellulose fibers with convoluted shapes might interfere with fibers characterization. Other fiber types are typically rare and then only in trace amounts.

OTHER METHODS: The counting rules in this method were derived from Method 7400.

REAGENTS:

1. Colloidal Graphite.*

* (See SPECIAL PRECAUTIONS.)

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three- piece cassette with ca. 50-mm electrically conductive extension cowl and poly-carbonate filter, 0.45- to 1.2-um pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. This is needed when field blanks contain fibers.
   NOTE 2: The electrically conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling.
2. Personal sampling pump, battery or line-powered vacuum, of sufficient capacity to meet flow rate requirements (see step 4), with flexible connecting tubing.
3. Microscope, scanning electron, operated at 15Kv with viewing screen having an inscribed or overlain calibrated scale.
4. Tape, shrink- or adhesive-.
5. Tweezers.
6. 25-mm carbon disk planchets.
7. Colloidal graphite paint.
8. Grounding wire, 22-gauge, multi strand.
9. Sputter coater.

SPECIAL PRECAUTIONS: Colloidal graphite contains isopropanol, which is flammable. Take precautions not to ignite it. Use only in well ventilated area.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fasten the (uncapped) open-face cassette to the worker's lapel. The open face should be oriented downward. Wrap joint between extender and monitor body with tape to keep the joint clean and prevent contamination when disassembled. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.
3. Submit at least 2 field blanks (or 10% of total samples, whichever is greater) for each set of samples. Remove top covers from field blank cassettes and store top covers and cassettes in a clean area (e.g., a closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 1L/min.
   NOTE: If the cellulose insulation is being applied dry, sample for a shorter period time than if the application is wet. Obtain two personal samples per worker. Sample at same flow rate but for different durations. A minimum duration of 1 minute is appropriate for very dusty environments. The longer duration should be determined by the overall dustiness, size of the area being insulated and other factors as well.
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 minimize jostling or damage.
   NOTE: Do not use untreated polystyrene foam in the shipping container because electrotatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

7. Mount the entire 25-mm filter directly on a carbon disk planchet by painting the planchet with a colloidal graphite paint and immediately laying the filter, glossy(sample) side up, on the planchet. The sample number is scratched into the back of the planchet prior to mounting the filter.
8. The planchet is then placed in a labeled petri dish and permitted to dry completely.
9. When dry, place sample in a sputter coater and deposit, following manufacturer's instructions, a heavy metal conductive coating on the sample.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturer's instructions. At least once daily use an SEM performance standard, such as the NIST traceable U1011. Record in log book the results of the examination of this standard.
11. If more rigorous magnification calibration is needed, use a diffraction grating replica.
    a. Insert a mounted diffraction grating replica into the sample chamber.
    b. Obtain a secondary electron image of the replica and measure the distance (mm) between the same relative position (e.g., between left edges) of two widely-separated lines on the grating replica.
    c. Measure the distance separated lines on the grating replica. Count the number of spaces between the lines.
    d. Calculate the true magnification(M)

$$M = \frac{(X)(G)}{Y}$$

where: X = total distance (mm) between the two grating lines;
G = calibration constant of the grating replica (lines/mm)
Y = number of grating replica spaces counted.

MEASUREMENT:

12. Use secondary electron detector(at ~15KeV) and scan the filter at low magnification (~100X). Observe the particulate loading. If the filter is not evenly loaded, it should not be analyzed (see note 4 below)
13. Adjust magnification to ~1200X and find the center of the filter using the X-Y manipulators. Fields are examined at regular intervals from the center of the filter along a traverse in one direction.
14. Determine the area of the viewing field at this magnification using the inscribed or overlain calibrated scale.
15. Count fibers in each field; distinguish, based upon morphology, between cellulose and other fiber types and make note of the relative proportion of fibrous to non-fibrous material in the field.
16. Counting rules: (Modified A rules, NIOSH Method 7400).[2]
    a. Count any fiber longer than 5 µm (see note 2 below for exceptions)
        i. Count only fibers longer than 5 µm. Measure and record length of fibers.
        ii. 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 viewing field:
        i. Use the X-Y manipulators as needed, to follow and measure the entire length of any fibers that meet the criteria of rule a above. Return to original viewing field before moving to the next field.
        ii. Reject and do not count all other fibers.
    c. Count enough viewing fields to yield at least 100 cellulose fibers. Count a minimum of 40 fields.

d. When selecting fields, ensure that fields do not contain fibers counted and measured from a previous field.

NOTE 1: When analyzing a viewing field, continuously scan a range of focal planes by moving the focus knob to observe and measure fibers which have do not lie flat on the filter.

NOTE 2: This method allows for differentiation of fibers based on morphology. Cellulose fibers are easily distinguished from asbestos and glass fibers by morphology [3]. Do not count any fibers that have parallel sides.

NOTE 3: Do not approach closer than 3 viewing fields from the edge of the filter.

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 (during dry application), 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. In extreme cases, much of the sample may be adhering to the cassette itself [4].

CALCULATIONS:

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

$$E = \frac{\frac{F}{n_f} - \frac{B}{n_b}}{A_f}, fibers / mm^2$$

18. Calculate and report the concentration, C (fib/mL), of cellulose 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):

$$C = \frac{(E)(A_c)}{(V)(10^3)}, fibers / mL$$

19. Calculate and report the fiber length ranges(minimum and maximum) as well as the average length.

EVALUATION OF METHOD:

This method draws on both Methods 7400 for counting procedures and 7402 for instrumentation and setup. The major difference is the counting rules have been adapted from the A rules to allow for the counting and sizing of all cellulose fibers having a 3:1 or greater aspect ratio and a length of at least 5 microns. There are no diameter limits as cellulose fibers are truly 3 dimensional. This is illustrated in the figures below. The complex shapes and constantly varying diameters make even an approximate diameter determination impossible.

Sampling and analysis of both wet and dry cellulose insulation application has shown that there is much more uniform fiber deposition across the filter when the wet process is used. There is also much less fiber lost to the cassette walls.

REFERENCES:

[1] NIOSH [2001]. Hazard evaluation and technical assistance report: Cellulose Insulation Applicators: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, NIOSH HETA Report No. 2000-0332-22827

[2] NIOSH [1994]. Asbestos and Other Fibers by PCM: Method 7400. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] McCrone W and Delly J [1973]. "The Particle Atlas," Ann Arbor, MI: Ann Arbor Science.

[4] Baron P, Deye G [1990]. "Electrostatic Effects in Asbestos Sampling," Parts I and II Amer. Ind. Hyg. Assoc. J., *51*, 51-69.

METHOD WRITTEN BY:

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FIGURES:

The figures below are examples of cellulose insulation fibers and accompanying non-fibrous cellulose.

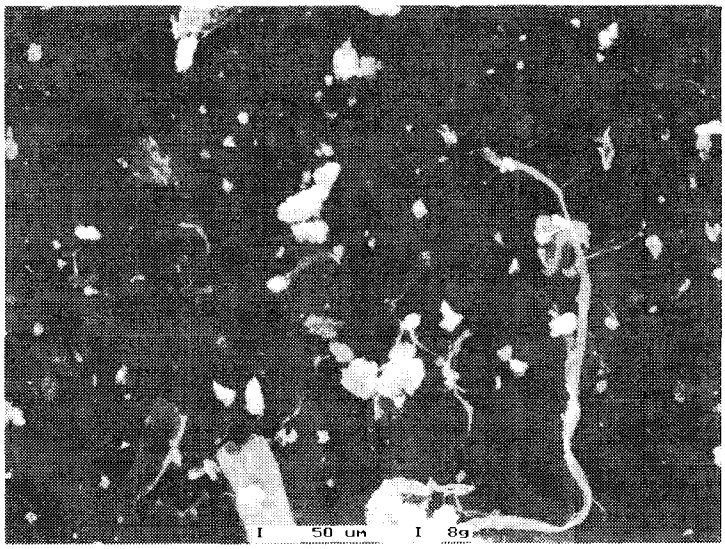

FIGURE 1. Figure shows many of the shapes and sizes of both fibrous and non-fibrous cellulose insulation.

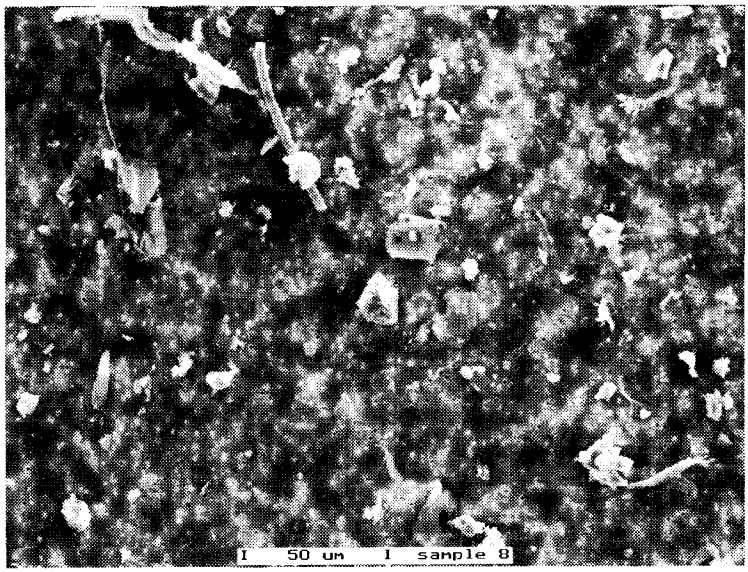

FIGURE 2. Figure shows the variety of shapes and sizes, as in Figure 1, as well as a glass fiber left over from the previous attic insulation.

p-CHLOROBENZOTRIFLUORIDE 1026

$C_7H_4ClF_3$ MW: 180.56 CAS: 98-56-6 RTECS: XS9145000

METHOD: 1026, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: Not Established
NIOSH: Not Established
ACGIH: Not Established
(1 ppm = 7.41 mg/m³)

PROPERTIES: liquid; d 1.353 g/mL @ 20 °C; BP 139°C; VP 5.3 mm Hg @ 20 °C

SYNONYMS: 4-Chlorobenzotrifluoride, 1-Chloro-4 (trifluoromethyl) benzene, 4-Chloro-α,α,α-trifluorotoluene, PCBTF

SAMPLING

SAMPLER: Coconut Shell Charcoal (CSC) (100/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.1 L
-MAX: 10.0 L (25 ppm)

SHIPMENT: Routine

SAMPLE STABILITY: 7 days @ 25°C; 30 days @ 5 °C

BLANKS: 10% of field samples

ACCURACY

RANGE STUDIED: Not Determined

BIAS: Not Determined

OVERALL PRECISION ($\hat{S}_{rT}$): Not Determined

ACCURACY: Not Determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: p-Chlorobenzotrifluoride

DESORPTION: 1 mL of carbon disulfide/methanol (99:1)

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 40°C (1 min) to 150°C (10°C/min)

CARRIER GAS: Helium; 2.8 mL/min

COLUMN: capillary, fused silica, 30-m x 0.32 mm ID; 1 µm film 100% crossbonded dimethyl polysiloxane

CALIBRATION: Solutions of p-CBTF in solvent

RANGE: 1.8 µg to 676 µg [1]

ESTIMATED LOD: 0.6 µg [1]

PRECISION ($\hat{S}_r$): 0.0131 [1]

APPLICABILITY: The working range for p-chlorobenzotrifluoride was 0.024 to 9.15 ppm (0.178 to 67.8 mg/m³) for a 10-L air sample. [1]

INTERFERENCES: Any compounds having similar retention times may co-elute with the analyte of interest.

OTHER METHODS: None determined.

REAGENTS:

1. p-Chlorobenzotrifluoride, 98%.
2. Carbon disulfide, low benzene grade*.
3. Methanol, HPLC grade*.
4. Helium, purified.
5. Air, prefiltered and purified.
6. Hydrogen, purified.
7. Calibration stock: Dilute 5 µL of p-CBTF in 10 mL solvent. Prepare remaining standards by serial dilutions.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm ID, 4-mm ID, flame-sealed ends, containing two sections of activated 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. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, FID, integrator, and Rtx-1, or equivalent, fused silica capillary column.
4. Autosampler vials, glass, 1.8 mL, with PTFE-lined caps.
5. Syringes, 10-µL to 1-mL.
6. Volumetric flasks, 10-mL and 250-mL.
7. Pipets, various sizes.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable. Methanol is moderately toxic and flammable. Perform all work in a chemical hood and wear appropriate protective equipment. p-CBTF is an irritant compound.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sample tube in line.
2. Break open the ends of the sample tube immediately prior to sampling. Attach sample tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 10 L.
4. Cap both ends of the sample tubes and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the initial glass wool plug and front sorbent section of the sample tube in an autosampler vial. Place the back sorbent section of the sample tube in a separate autosampler vial. Discard the polyurethane foam separator and the remaining glass wool plug.
6. Add 1.0 mL of carbon disulfide/methanol (99:1) solvent to each vial and cap securely.
7. Allow to stand for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working calibration standards from below the LOD to 10 times the LOQ. If necessary additional standards may be added to extend the calibration curve.
   a. Add known amounts of calibration stock solution to carbon disulfide/methanol (99:1) in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. Prepare calibration graph (peak area vs. µg p-CBTF).
9. Determine the desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.

b. Inject a known amount of analyte stock solution directly onto the front sorbent section of each charcoal tube.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 10 and 11).
e. Prepare a graph of DE vs. µg p-CBTF recovered.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1026-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with carbon disulfide/methanol (99:1), reanalyze and apply the appropriate dilution factor in the calculations.
11. Measure peak areas.

CALCULATIONS:

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

$$C = \frac{(Wf + Wb - Bf - Bb),}{V} mg / m^3$$

EVALUATION OF METHOD:

This method development was based upon a health hazard evaluation request where p-chlorobenzo-trifluoride was being used as a cleaning solvent for automobile parts. After an evaluation of various solid sorbent tubes and solvent/solvent mixtures, coconut shell charcoal tubes and carbon disulfide/methanol (99:1) solvent were selected for use in this method development. The desorption efficiency (DE) was determined for p-chlorobenzotrifluoride at 4 levels ranging from 27.1 µg to 541.2 µg. The average DE determined for p-chlorobenzotrifluoride was 100.6%. The LOD was determined to be 0.6 µg/sample. The analytical method precision, as determined from the pooled relative standard deviation (S_r), was determined to be 0.0131. Para-chlorobenzotrifluoride was determined to have acceptable storage stability (102.6%) for 30 days [1] at a level 0.1 times the recommended exposure level suggested by the manufacturer. [2]

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METHOD WRITTEN BY:

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CHROMIUM, HEXAVALENT
by Ion Chromatography

7605

Cr(VI) MW: 52.00 (Cr); 99.99 (CrO_3) CAS: 18540-29-9 RTECS: GB6262000

METHOD: 7605, Issue 1 **EVALUATION: FULL** **Issue 1: 15 March 2003**

OSHA : 0.1 mg/m³ (as CrO_3)
NIOSH: 0.001 mg/m³/10 h; carcinogen
ACGIH: 0.050 mg/m³ (as Cr, soluble); some insoluble chromates are human carcinogens

PROPERTIES: oxidizing agent

SYNONYMS: Vary depending upon the compound; chromate commonly used, "chrome six."

SAMPLING

SAMPLER: FILTER (5.0-µm PVC membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 1 L @ 0.05 mg/m³
-MAX: 400 L

SHIPMENT: Routine. Can be shipped cold when deemed necessary.

SAMPLE STABILITY: Stable for 2 weeks at room temperature. Stable for 4 weeks if stored in refrigerator.

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.05 to 120 µg Cr(VI) [1,2]

BIAS: -1.6% [2]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07

ACCURACY: ± 17.4% (0.6 - 960 µg/m³) [1]

MEASUREMENT

TECHNIQUE: Ion chromatography with post-column derivatization and UV detection.

ANALYTE: CrO_4^{-2}-diphenylcarbazide (DPC) complex

EXTRACTION: 5 mL 2% NaOH- 3% Na_2CO_3. Dilute to 25 mL after heating.

INJECTION VOLUME: 100 µL

COLUMN: Dionex NG1 Guard, HPIC- AS7 Separator or equivalent

MOBILE PHASE: 250 mM $(NH_4)_2SO_4$ /100 mM NH_4OH

FLOW RATE: 1.0 mL/min; 0.7 mL/min post column

POST-COLUMN REAGENT: 2.0 mM DPC + 10% MeOH +1N H_2SO_4

DETECTOR: 540 nm

CALIBRATION: Standard solutions of $K_2Cr_2O_7$ in NaOH-Na_2CO_3 buffer

RANGE: 0.05 to 20 µg per sample

ESTIMATED LOD: 0.02 µg per sample [3]

PRECISION ($\hat{S}_r$): 0.015 @ 0.5 to 5 µg/sample [3]

APPLICABILITY: The working range is 0.00025 to 0.1 mg/m³ for a 200-L air sample. This method can be used for the determination of Cr(VI) using 2% NaOH - 3% Na_2CO_3 for extraction.

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

OTHER METHODS: Method 7703 is a field portable method for Cr(VI). OSHA Method W4001 is for the measurement of Cr(VI) in wipe samples [4]. OSHA Method ID-215 is for measurement of Cr(VI) and employs precipitation to reduce Cr(III) oxidation. [5]. A similar air method is ISO 16740 [6]. EPA Method 218.6 is for water matrices [7]. Method 7604 is also specific for hexavalent chromium, using ion chromatography, but has a higher detection limit than 7605.

REAGENTS:

1. Sulfuric acid, conc. (98% w/w).*
2. Ammonium hydroxide, conc. (28%).*
3. Ammonium sulfate monohydrate, reagent grade.
4. Sodium carbonate, anhydrous.
5. Sodium hydroxide, reagent grade.*
6. Methanol, HPLC grade.*
7. 1,5-Diphenylcarbazide, reagent grade.
8. Potassium dichromate or potassium chromate.* Dry at 100 °C and store in a desiccator.
9. Post-Column Derivatizing Reagent: Diphenylcarbazide solution. Dissolve 500 mg 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. While stirring, add 500 mL water containing 28 mL of conc. sulfuric acid. Dilute to a final volume of one liter with water. This reagent is stable for 4 - 5 days. Prepare in one-liter quantities as needed.
10. Cr(VI) standard, 1000 µg/mL. Dissolve 2.829 g potassium dichromate in deionized water to make one liter, or use commercially available solution.
    NOTE: 3.731 g K_2CrO_4 can also be used.
11. Calibration stock solution, 1.0 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:1000 with deionized water.
12. Filter extraction solution, 2% NaOH-3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make one liter of solution.
13. Eluent (mobile phase); 250 mM ammonium sulfate/200 mM ammonium hydroxide. Dissolve 33 g ammonium sulfate in approximately 500 mL distilled water and add 6.5 mL conc. ammonium hydroxide. Dilute to one liter with distilled water and mix.
14. Nitrogen, pre-purified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder.
   NOTE: Some PVC filters promote reduction of Cr(VI). Check each lot of filters for recovery of Cr(VI) standard.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Vials, scintillation, 20-mL glass, PTFE-lined screw cap.**
4. Forceps, nonmetallic.
5. Gloves, polypropylene or latex.
6. Liquid chromatography apparatus consisting of autosampler; pump; NG1 (Dionex Corp.) or equivalent guard column; HPIC-AS7, 4 x 250-mm (Dionex Corp.) separator column (or equivalent); post-column reagent delivery system, 2.2-m PEEK™ tubing mixing/reaction loop with 1 m in a water bath at 32 °C ± 3 °C; and UV detector.
7. Filtration apparatus, PTFE luer-lock filter (Gelman IC Acrodisc or equivalent)/syringe.
8. Beakers, borosilicate, 50-mL.**
9. Watch glass.**
10. Volumetric flasks, 25-, 100-, and 1000-mL.**
11. Oven at 107°C, not to exceed 115°C.
    NOTE: Hot plate can be used. An ultrasonic bath can be used instead of oven or hot plate.
12. Micropipettes, 10-µL to 0.5-mL.
13. Pipettes, TD 5-mL.**
14. Bagged refrigerant.

** Clean all glassware with 1:1 HNO_3:H_2O and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Many chromate compounds are suspected human carcinogens [8]. All sample preparation should be performed in a hood. Concentrated acids and bases are toxic and corrosive. When working with concentrated acids and bases, wear protective clothing. Ammonium hydroxide is a respiratory irritant. Methanol is flammable and toxic.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 1 to 400 L. Do not exceed 1 mg total dust loading on the filter.

3. Filters can be left in the cassettes for shipping to the lab, but to minimize sample contamination during shipping, remove the filter from the cassette within one hour of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with gloved hands and nonmetallic forceps. Discard the backup pad. As a precaution, it is recommended to ship the samples with bagged refrigerant.

SAMPLE PREPARATION:

4. Don a clean pair of disposable plastic gloves (to prevent sample contamination). Using forceps, transfer the PVC filter to a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH/3% Na_2CO_3. Start media blanks at this point.
   NOTE 1: If significant amounts of Cr[III] are expected to be present in the samples, either (a) degas the sodium hydroxide/sodium carbonate extraction solution by bubbling nitrogen through it for 5 min. before proceeding, or (b) use a precipitation reagent [1].
   NOTE 2: If only soluble chromates are of interest, use ammonium sulfate buffer in place of carbonate extraction solution [9, 10].
5. Cover the beaker with a watchglass and heat it to near the boiling point (100°C to 115°C) in an oven with occasional swirling for 45 min. Do not boil the solution. Longer heating times (up to 90 minutes) may be necessary for some samples (e.g., paint spray). Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost due to reaction with the PVC filter and/or co-collected aerosol constituents. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.
   NOTE: A hot plate, heater block, or ultrasonic bath can also be used for this step [9, 11].
   a. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask. Bring to volume with distilled water.
      NOTE: If the solution is cloudy, filter an aliquot through a PTFE luer lock filter attached to a syringe.
   b. Transfer an aliquot of the solution to the appropriate vial for the chromatograph's autosampler and analyze (steps 9 through 13).

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards. Transfer 5 mL of extraction solution to each of a series of 25-mL volumetric flasks. Pipet known volumes (0 to 5 mL) of calibration stock solution (1.0 µg/mL) into the volumetric flasks. For higher standards, pipet 10 - 20 µL of the 1000 µg/mL concentrated stock and bring the volume to 25 mL with distilled water. These working standards contain 0 to 20 µg Cr(VI) per sample.
7. Analyze the working standards together with blanks and samples (steps 9 through 13).
8. Prepare a calibration graph [instrument response vs. µg Cr(VI)].

MEASUREMENT:

9. Set wavelength on the detector to 540 nm.
10. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 7605-1. With a mobile phase flow rate of 1.0 mL/min., a post-column reagent flow rate of 0.7 mL/min., and a 2.2-m post-column tube, the derivative retention time should be approximately 3.7 - 4.7 minutes.
    NOTE: If the instrument response for the samples is higher than the standards, dilute using a 1:5 dilution of extraction solution:water to maintain a constant ionic strength; repeat the analysis; and multiply the measured concentration by the appropriate dilution factor. Alternatively, inject a smaller volume and multiply by the appropriate factor.
11. After the analysis is complete, flush the entire system with ASTM Type II water for at least one hour at 1.0 mL/min. with all columns on line. Remove the columns and continue flushing for an additional two hours. Flush the autosampler with several injections of water. Leaving the columns in line while the system is idle is not recommended.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method was evaluated in the laboratory with spiked filters and a certified reference material containing a known loading of Cr(VI). This certified reference material (CRM) is European Commission, Institute for Reference Materials and Measurements EC/IRMM) CRM 545, Cr(VI) and Cr(total) in welding dust loaded on a glass fiber filter [12]. This method was evaluated for extraction efficiency over the concentration range of 0.15 - 5 µg/sample testing two brands of filters, SILICAL® and GLA-5000™[3]. In these experiments, test atmospheres were not generated; instead, Cr(VI) as the dichromate was fortified on the face of the sample filters, then 240 L of air with 35% relative humidity was pulled through at 1 L/min. A 30-day storage study using both types of filters was conducted at 1.5 µg/sample (30x LOQ) at ambient room temperature and 4 °C. The average recovery of the stored samples was 94.8%. The estimation of the limit of detection and limit of quantitation (LOD/LOQ),were determined analyzing a series of liquid standards . The LOD and LOQ, 0.02 µg/sample and 0.07 µg/sample respectively were calculated by Burkart's method [13].

To fully evaluate this method, a field-study was conducted in which side-by-side samples were taken to measure exposures to Cr(VI) during spray-painting and electroplating operations. These samples were analyzed subsequently by 4 different methods (NIOSH Method 7605, 7703, 7300 and OSHA ID-215) [1]. NIOSH method 7300 was used to measure total chromium. The results from the other 3 methods correlated very well showing no statistical difference among the 3 methods. Recoveries of 98.4 ($\pm$ 3.4) % were obtained for CRM 545 (n = 6) [2].

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CHROMIUM, HEXAVALENT, by Field-Portable Spectrophotometry

7703

Cr[VI] MW: 52.00 (Cr) 99.99 (CrO_3) CAS: 18540-29-9 RTECS: GB6262000

METHOD: 7703, Issue 1 **EVALUATION: FULL** **Issue 1: 15 March 2003**

OSHA: C 0.1 mg/m³ (as CrO_3)
NIOSH: 0.001 mg/m³/10 h (carcinogen)
ACGIH: 0.050 mg/m³ (water-soluble compounds); 0.010 mg/m³ (insoluble compounds)

PROPERTIES: oxidizing agent

SYNONYMS: vary depending on the compound; chromate commonly used

SAMPLING

SAMPLER: FILTER (5.0-µm PVC membrane [1,2]; 0.8-µm MCE or 1.0-µm PTFE acceptable for field analysis [3]).

FLOW RATE: 1 to 4 L/min

VOL-MIN: 10 L (2 L/min for 5 min)
-MAX: 1200 L (2 L/min for 600 min)

SHIPMENT: refrigerant pack at 4 ± 2 °C (optional)

SAMPLE STABILITY: analyze within 24 hours; if applicable, keep samples at 4 ± 2 °C.

BLANKS: One per twenty field samples, minimum of 2 per set.

ACCURACY

RANGE STUDIED: 0.045 to 1146 µg/m³ (~20 to ~200-L samples) [3, 4]

BIAS: -1.00% [3]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.080

ACCURACY: ± 15.7%

MEASUREMENT

TECHNIQUE: FIELD-PORTABLE VISIBLE SPECTROPHOTOMETRY

ANALYTE: Cr[VI] - diphenylcarbazone complex

EXTRACTION: 10 mL 0.05 M $(NH_4)_2SO_4$ / 0.05 M NH_4OH (pH = 8 ± 0.5), ultrasonic extraction 30 min

Cr[VI] ISOLATION: Strong anion exchange solid phase extraction

ELUTION SOLUTION: 0.5 M $(NH_4)_2SO_4$ / 0.1 M NH_4OH

WAVELENGTH: 540 nm, 1-cm path length

CALIBRATION: standard solutions of K_2CrO_4 in 0.5 M $(NH_4)_2SO_4$ / 0.1 M NH_4OH

RANGE: 1 to 400 µg per sample

ESTIMATED LOD: 0.08 µg Cr[VI] per sample [3]

PRECISION ($\hat{s}_r$): 0.035 @ 3 to 400 µg per sample [3]

APPLICABILITY: The working range is (at least) 0.05 to 1000 µg/m³ for a 200 to 500-L air sample. This method may be used for the determination of soluble forms of Cr[VI]. Insoluble Cr[VI] requires modification of the method using ultrasonic extraction with carbonate buffer.

INTERFERENCES: Interferences from reducing agents such as Fe^{2+} are minimized to the extent possible by the alkaline ultrasonic and solid phase extraction procedures. Interferences from other metal cations are eliminated by solid phase extraction [5]. Some reduction can occur on the filter during sampling, and is usually due to the presence of Fe^{2+}, organic material, and/or acidic conditions [6]. Reduction of Cr[VI] can occur over time on any filter type, and is especially problematic on MCE filters [7]. However, the use of MCE and PTFE filters has been found to be acceptable for field use, where performance has been found to be equivalent to that of PVC filters [3]. During ultrasonic extraction, oxidation of Cr[III] in solution to Cr[VI] is prevented by the use of an ammonium buffer [8].

OTHER METHODS: This method is designed to be used in the field, but can also be utilized in the fixed-site laboratory. It is an alternative to laboratory methods such as NIOSH method 7605 or OSHA method ID-215 (hot plate digestion and ion chromatography). NIOSH method 7600 is a similar procedure, but no separation step is used. A field method not involving a Cr[VI] isolation step, MDHS method 61, has been promulgated by the British Health and Safety Executive [9].

REAGENTS:

1. Ammonium sulfate, reagent grade.
2. Ammonium hydroxide, reagent grade.
3. Water, distilled or deionized.
4. Hydrochloric acid (37%), reagent grade.
5. Acetonitrile, reagent grade.*
6. 1,5-Diphenylcarbizide (DPC), reagent grade.
7. Methanol, reagent grade.
8. Extraction solution (extraction buffer): 0.05 M $(NH_4)_2SO_4$ / 0.05 M NH_4OH, 1 L, aqueous in distilled or deionized water.
   NOTE: Modification of method by using carbonate buffer (e.g., sodium carbonate) is required for extraction of insoluble Cr[VI].
9. Elution solution (elution buffer): 0.5 M $(NH_4)_2SO_4$ / 0.1 M NH_4OH, 250 mL, in distilled or deionized water.
10. Cr(VI) standard (as potassium chromate),* 1000 µg/mL.
11. Calibration stock solution, 100 µg/mL: Dilute 1000 µg/mL Cr(VI) standard 1:10 with extraction buffer. (Solution is stable for a month.)
12. Diphenylcarbazide complexation solution (20 mM): Measure 0.48 g DPC powder and place in a 100-mL volumetric flask. Add ~80 mL of acetonitrile and dissolve the DPC. Bring up to the mark with additional acetonitrile and mix thoroughly.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Samplers: 5-µm pore size polyvinylchloride (PVC), 0.8-µm pore size mixed cellulose ester (MCE), or 1.0-µm polytetrafluoroethylene (PTFE) filters, 37-mm diameter, with backup pads, in polystyrene cassette filter holder, 2- or 3-piece.
   NOTE: MCE filters, and some PVC filters, promote reduction of Cr[VI] on a timescale of a few days. However, either filter type is acceptable for field use if the samples are to be analyzed within 24 h of collection.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ultrasonic bath (sonicator), 100 W minimum power.
4. Solid phase extraction manifold, 12- or 24-port.
5. Portable vacuum pump with pressure metering valve.
6. Portable visible spectrophotometer, sample path length 1 cm with Quartz cuvette(s).
7. Strong anion exchange solid phase extraction (SPE) cartridges, 10-mL, disposable; loaded with 500 or 1000 mg quaternary amine bonded silica, capacity ~1 meq/g.
8. Pipettors, mechanical, assorted volumes (e.g., 1 to 10 mL) with disposable tips.
9. Micropipettors, mechanical, assorted volumes (e.g., 10 to 100 µL) with disposable tips.
10. Centrifuge tubes, plastic, 15-mL, with screw caps.
11. Scintillation vials, 20-mL, glass, with PTFE-lined screw caps.
12. Assorted beakers (and possibly Erlenmeyer flasks), various volumes.
13. Volumetric flasks, 25-, 100-, 250-, and 1000-mL.
14. Forceps, PTFE-coated.
15. Glass or plastic rods.
16. Disposable gloves, plastic or latex.
17. Laboratory wipes.
18. Portable power generator (if necessary).
    NOTE: If no power supply is available at the field site, electric power can be provided by means of a portable, gasoline (or other) generator.

SPECIAL PRECAUTIONS: Hexavalent chromium is a human respiratory carcinogen [10]. Efforts must be made to prevent aerosolizing chromate-containing compounds and solutions. All sample preparation should be carried out in a well-ventilated area (vacuum hood preferable); forced ventilation should be used if no hood is available. Acetonitrile solutions are flammable must be handled carefully, i.e., wearing of impermeable gloves, and avoidance of vapors. To the extent possible, solutions should be prepared in the laboratory before taking them to the field.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range of 1 to 4 L/min for a sample size of 100 to 1000 L. Do not exceed 2 mg of particulate loading on the filter. Label the filter cassette.
3. Don a fresh pair of disposable plastic or latex gloves (to prevent sample contamination).
4. With PTFE-coated forceps, remove filters from cassettes after of completion of sampling, and place in separate plastic 15-mL centrifuge tubes for subsequent sample preparation. Discard cellulose backup pads and gloves.

SAMPLE PREPARATION:

5. Add 10 mL of extraction solution (weak buffer) to each 15-mL centrifuge tube containing the filter sample. Ensure that the filter is covered by the extraction solution. If necessary, push the filter down with a clean glass or plastic rod to immerse the entire filter. Cap and label the tubes.
6. Place sample tubes in the ultrasonic bath (sonicator). The water level in the bath should be higher than the liquid level in the centrifuge tube. Sonicate for 30 minutes.
   NOTE: Numerous centrifuge tubes containing sample filters can be subjected to sonication at one time, depending upon the size of the ultrasonic bath. Ensure that the bath is warm (but $\leq$ 40°C).
7. Set up the solid phase extraction manifold.
   a. Place disposable solid phase extraction (SPE) cartridges in each port, and place scintillation vials beneath the cartridges. Label the cartridges.
   b. Attach the vacuum pump to the SPE manifold.
   c. To condition SPE cartridges, pipet 3 mL of methanol into each cartridge, and evacuate. Then pipet 3 mL of extraction solution into each cartridge, and evacuate. Repeat.
8. Extract Cr[VI] from sample solution.
   a. Pipet 3 to 5 mL of each ultrasonicated sample solution from the centrifuge tubes into the disposable SPE cartridge. Dispose of the pipet tip.
   b. Adjust the vacuum to obtain an extraction rate of about one drop per second (approximately 8" Hg; no more than 10" Hg). Manually tighten cartridges by twisting, if necessary, to slow down the rate of liquid dripping.
      NOTE 1: For samples in the which the expected Cr[VI] concentration is high, smaller aliquots (1 to 2 mL) should be dispensed into the SPE cartridges to prevent breakthrough. High concentration of Cr[VI] can be assessed visually by its orange color.
      NOTE 2: For samples having low Cr[VI] concentration, additional 3 to 5 mL aliquots of ultrasonicated sample solution can be loaded onto SPE cartridges (step 8.a.). In this manner, the cartridge can be used to preconcentrate Cr[VI].
   c. When it appears the solution has passed through all the cartridges, increase the vacuum to ensure that all solution passes through the cartridges. This step selectively binds Cr[VI] to the stationary phase of each cartridge.
   d. To remove residue of Cr[III] and other potential interferences, turn the vacuum down (by turning counterclockwise) to 0" Hg. Add 1 mL distilled or deionized water to each cartridge, adjust vacuum to 1 drop per second (~8" Hg), then reduce to 0" when completed.
   e. Remove the scintillation vials beneath the cartridges and discard.
      NOTE: This solution contains unwanted fractions that should contain no Cr[VI].
9. Place clean, labeled scintillation vials beneath correct cartridges in the SPE manifold.
   a. Add 9 mL of the elution solution (elution buffer) to each cartridge to elute Cr[VI], and repeat steps 8.b. through 8.d.
   b. Remove the scintillation vials, and cap them. Dispose of the used SPE cartridges.
      NOTE: The scintillation vials now contain extracted and isolated Cr[VI], which is ready for subsequent analysis.
10. Uncap each scintillation vial containing extracted and isolated Cr[VI], and add 100 µL Hcl.
11. Add 2 mL DPC complexation solution, recap vials, and mix thoroughly. Allow to stand for at least 5 min for complete color development.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least 6 working standards over the range of 0 to 2 µg/mL of Cr[VI] per standard.
    a. To 10-mL volumetric flasks containing ~5 mL of elution solution (strong buffer), pipet known volumes (20 to 300 µL) of Cr[VI] calibration stock solution (100 µg/mL) to produce concentrations of 0.1, 0.2, 0.5, 1.0, and 2.0 µg/mL. Add 100 µL of HCl and 2 mL of diphenylcarbazide (DPC) complexation solution to each. Dilute to the mark with elution solution and mix thoroughly.
       NOTE: A minimum of two of the concentration levels (e.g., 0.1 and 1.0 µg/mL) should be run at least in triplicate.
    b. Prepare a blank by pipetting 100 µL of HCl and 2 mL of DPC complexation solution into 10-mL volumetric flask containing ~5 mL of the elution solution (elution buffer); dilute to the mark with elution solution and mix thoroughly.
    c. Analyze the calibration solutions and the blank (steps 15 to 20).
13. Analyze at least two field blanks, one field blank per twenty samples (steps 10, 11 and 15 to 20). Also analyze at least three of the calibration solutions in triplicate.
14. Prepare a calibration graph of absorbance vs. Cr[VI] concentration.
    NOTE: As an alternative to steps 12 to 14, the standard addition approach can be used [11].

MEASUREMENT:

15. Turn on the spectrophotometer, and allow for an appropriate warm-up period.
16. Set the spectrophotometer to 540 nm. Set portable spectrophotometer parameters according to the manufacturers instructions and the conditions on page 7703-1.
17. Rinse the quartz cuvette three times with distilled or deionized water, then rinse with blank solution.
18. Measure the blank. Adjust the spectrometer to zero absorbance.
19. Uncap the scintillation vial containing the sample solution to be analyzed.
    a. Condition the cuvette by filling with the solution to be analyzed, and discard the solution.
    b. Refill the cuvette with the sample solution to be analyzed.
    c. Place the cuvette in the spectrophotometer.
       NOTE: Wipe any extra moisture or liquid off the sides of the cuvette with a dry laboratory wipe, and take care to handle the cuvette only by the frosted sides.
20. Analyze samples, standards, and blanks. Record the absorbance.
    NOTE: If the absorbance value is greater than 2 absorbance units, dilute the solution to be analyzed with elution solution (strong buffer) and reanalyze.

CALCULATIONS:

21. From the calibration graph, determine the mass of Cr[VI] in each sample, W (µg), and in the average field blank, B (µg).
    NOTE: If standard addition method was used, make appropriate adjustments from the calibration graph obtained [11].
22. Calculate the concentration, C (mg/m^3), of Cr[VI] in the air volume sampled, V (L):

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

NOTE: If samples were diluted during sample preparation, be sure to account for the dilution factor in the calculation.

EVALUATION OF METHOD:

This method was evaluated in the laboratory with spiked filters [3-5] and a certified reference material containing a known loading of Cr(VI) [4]. This certified reference material (CRM) is European Commission, Institute for Reference Materials and Measurements (EC/IRMM) CRM 545, Cr(VI) and Cr(total) in welding dust loaded on a glass fiber filter [12]. The method has also been evaluated in the field, where samples collected during aircraft maintenance operations were analyzed on-site [3, 4]. The accuracy was estimated using the protocol summarized in a NIOSH technical report [13].
Alternative filter types can also be used, e.g., PTFE, binder-free glass fiber filters, or quartz fiber filters. Filter materials should be tested before use to ensure Cr[VI] stability. Filters can be pretreated with base to minimize Cr[VI] reduction during sampling in high-iron or acidic environments [6].

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METHOD WRITTEN BY:

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DECABROMODIPHENYL OXIDE 2559

$C_{12}Br_{10}O$ MW: 959.12 CAS: 1163-19-5 RTECS: KN3525000

METHOD: 2559, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no PEL
NIOSH: no REL
ACGIH: WEEL: 5.0 mg/m³

PROPERTIES: solid, white powder; MP 300 °C; sp gr 3.0; decomposes @ ca. 425 °C

SYNONYMS: DBDPO; Pentabromophenyl ether; bis(pentabromophenyl)ether; decabromodiphenyl ether; decabromobiphenyl ether.

SAMPLING

SAMPLER: Filter (Quartz fiber filter, 37-mm)

FLOW RATE: 2.0 L/min

VOL-MIN: 48 L
-MAX: 960 L

SHIPMENT: Ship at ambient temperature.

SAMPLE STABILITY: At least 30 days @ room temp.

BLANKS: 2 to 10 field blanks per set.

ACCURACY

RANGE STUDIED: Generated atmospheres not studied.

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Decabromodiphenyl oxide (DBDPO)

DESORPTION: 1.5 mL DMSO; place on a rotary shaker for minimum of 2 hours.

INJECTION VOLUME: 5 µL

MOBILE PHASE: 98% methanol/2% pH 7 buffer of KH_2PO_4 and Na_2HPO_4 @ 0.225 mL/min; ambient temperature.

COLUMN: C-18, 5 µm, 150 cm x 2.1 mm ID or equivalent .

DETECTOR: UV absorption @ 228 nm.

CALIBRATION: DBDPO dissolved in DMSO.

RANGE: 2 to 240 µg per sample.

ESTIMATED LOD: 1.0 µg per sample.

PRECISION ($\hat{S}_r$): 0.038 @ 2.6 to 240 µg per sample. [1]

APPLICABILITY: The working range is 0.002 to 5.0 mg/m³. An appropriate range of calibration standards should be used to bracket the expected analyte concentration range. To prevent the need to switch detector sensitivity settings for field samples with higher levels of DBDPO, a calibration curve made from standards containing greater levels of DBDPO may be appropriate. This method was developed to analyze DBDPO in an air sample.

INTERFERENCES: None identified - however, compounds with a similar retention time may interfere. Positive identification may be confirmed by dual column chromatography using an appropriate alternative LC column. Identification can also be confirmed by mass spectrometry.

OTHER METHODS: None identified.

REAGENTS:

1. Methanol, HPLC grade.*
2. Dimethyl Sulfoxide (DMSO), HPLC grade.*
3. Decabromodiphenyl oxide, 98%. Sold as Pentabromophenyl ether (Sigma-Aldrich, Milwaukee, WI., or equivalent).*
4. Potassium dihydrogen phosphate (KH_2PO_4). (Sigma-Aldrich, Milwaukee, WI., or equivalent).
5. Disodium hydrogen phosphate (Na_2HPO_4). (Sigma-Aldrich, Milwaukee, WI., or equivalent).
6. Mobile phase buffer: 1.509 g KH_2PO_4 and 2.477 g Na_2HPO_4 in 1 L deionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: quartz fiber filter, 37-mm diameter, 0.45 mm thick (SKC, Eighty Four, PA, or equivalent), backed by a cellulose support pad 37-mm OD, in a two part, 37-mm cassette filter holder.
2. For calibration and QC samples, filter spacer rings are used instead of a support pad. Spacer Ring, 37 mm (SKC, Eighty Four, PA).
3. Personal sampling pump capable of operating for 8 hr at 2 L/min., with flexible connecting tube.
4. Labquake rotary shaker or equivalent.
5. Vials, Autosampler, glass with PTFE lined crimp or screw top cap.
6. Forceps.
7. Syringes, glass: 5-µL, 10-µL, 1-mL, other sizes as needed.
8. Liquid Chromatograph: Shimadzu LC-10ADvp pump, SIL-10ADvp auto injector, and SPD-10AVvp UV detector (or equivalent), Alltech Alltima C-18 5µ, 150 X 2.1 mm column (or equivalent).

SPECIAL PRECAUTIONS: Decabromodiphenyl Oxide is a cancer suspect agent and irritant. Methanol is a flammable liquid, toxic. DMSO is an irritant, wear protective clothing as it can penetrate the skin.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate of 1.0 to 2.0 L/min for a volume of 48 to 960 L.
3. After the sample is collected, place the plastic plugs in the tubing connector stubs on the sampling cassette.

SAMPLE PREPARATION:

4. Extract Filters:
   a. Remove the filter from the cassette with a pair of forceps, discard the support pad, fold the filter and transfer to an autosampler vial.
   b. Add 1.5 mL of DMSO and cap the vial with the appropriate top.
   c. Place the vial on the labquake rotary shaker (VWR Scientific, Batavia, IL). Rotate the samples for a minimum of 2 hours. Place samples in an ultrasonic bath for 30 minutes.
      NOTE: Decabromodiphenyl oxide is not a highly soluble compound. To insure complete solubility, both manual agitation and sonication are used on the samples to solubilize the decabromodiphenyl oxide.
5. Prepare the filter extract for analysis.
   a. Carefully remove the septum cap from the vial containing the extracted filter.
   b. Using a transfer pipette, remove as much liquid extract from the extraction vial as possible and transfer to an autosampler vial. Cap the vial with an appropriate septum cap.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six calibration standards to cover the concentration range of the samples. A typical liquid chromatogram of a DBDPO standard is shown in Figure 1.
   a. Prepare calibration standards by adding known amounts of the DBDPO standard solution or a secondary stock solution prepared from the standard solution to an autosampler vial containing 1.5 mL DMSO.
   b. Analyze with samples and blanks (steps 9 & 10).
   c. Prepare a calibration graph (peak area vs. µg DBDPO).
7. Determine the recovery (R) of the analyte from the sampling media using the quartz fiber filters with analyte spikes in the concentration range of the samples (see step 6). Prepare three filters at each of five levels plus two media blanks.
   a. Place a filter spacer ring in the bottom section of a two part 37-mm filter cassette. Place a 37-mm quartz fiber filter on top of the spacer ring (do not use a support pad).
   b. Inoculate the filter with a known amount of calibration stock solution with a microliter syringe, place the top section of the cassette in place and seal the filter in place by squeezing the two sections together.
   c. Place the plugs in the inlet and outlet tubing stubs and set the cassettes aside for a minimum of twelve hours.
   d. Prepare the filter samples (steps 4 & 5) and analyze with the calibration standards.
   e. Prepare a graph of R vs. µg DBDPO.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set the liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2559-1. Inject sample with autosampler or by manual injection.
   NOTE: If peak area is above the linear range of the calibration standards, dilute the sample with DMSO, reanalyze, and apply the appropriate dilution factor in calculations. Or, prepare a calibration curve with standards of higher levels of DBDPO.
10. Measure peak area of DBDPO peak and determine µg per sample from calibration graph.

CALCULATIONS:

11. From the calibration graph, determine the mass, µg (corrected for R) for the sample (W), and average media blank (B).
12. Calculate concentration, C, of decabromodiphenyl oxide in the air volume sampled, V(L):

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method was not evaluated with laboratory generated air samples. All of the recovery and storage study determinations have been performed with laboratory spiked filters in the development of this method. Air was not pulled through the filters prior to analysis.

The LOD/LOQ values are 1.0 µg/sample and 3.3 µg/sample respectively, based on a liquid standard calibration curve.

Recovery of spiked quartz fiber filters ranged from 94.5% to 104.2% for analyte quantities of 2.63 to 25.1 µg/filter using liquid standards as the spiking solution.

A thirty day storage stability study of DBDPO spiked on quartz fiber filters indicates that the recovery of the analyte at a level of 5.01 µg/filter (N=12) is 103.0%. The samples were stored in a closed cardboard container at room temperature for the duration of the study.

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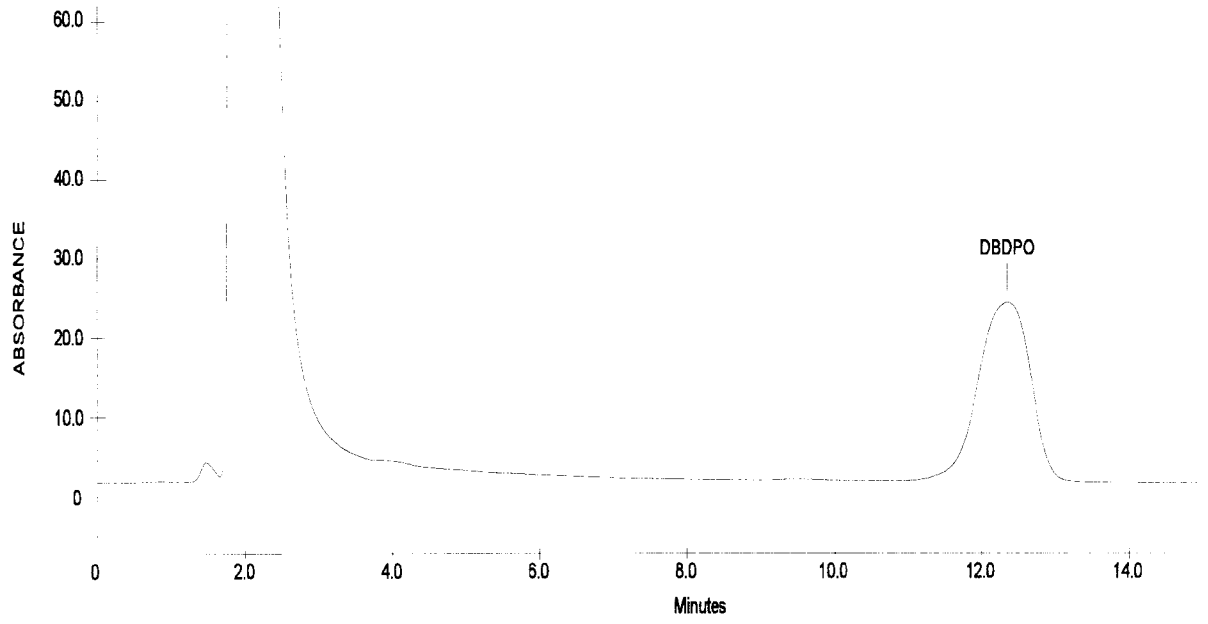

FIGURE 1: This chromatogram shows a standard of decabromodiphenyl oxide at 22.0 ug/sample. The major peak at approximately 12.2 minutes is DBDPO.

DIACETYL 2557

$C_4H_6O_2$ MW: 86.09 CAS: 431-03-8 RTECS: EK2625000

METHOD: 2557, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: yellowish liquid; d = 0.981 g/mL @ 20 °C; BP 88 °C; VP 52 mm Hg @ 20 °C; FP 7 °C; flash point 21 °C

SYNONYMS: biacetyl; 2,3-butadione; 2,3-diketobutane; dimethyl diketone; dimethylglyoxal

SAMPLING

SAMPLER: SORBENT TUBE (Anasorb CMS Solid Sorbent Tube, 150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 10 L

SHIPMENT: Ship cold (5 °C) and store in dark

SAMPLE STABILITY: 7 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{r,T}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: diacetyl

DESORPTION: 1 mL of acetone/methanol (99:1) on rotary mixer for 1.5 hours

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 35 °C (hold 3 min) to 200 °C (6 °C/min)

CARRIER GAS: He (2.8 mL/min)

COLUMN: capillary, fused silica, 30 m x 0.32-mm ID; 1-µm film, Stabilwax-DA or equivalent

CALIBRATION: standard solutions of diacetyl in acetone/methanol (99:1) solvent

RANGE: 2 to 470 µg/sample

ESTIMATED LOD: 0.6 µg/sample

PRECISION ($\hat{S}_r$): 0.018

APPLICABILITY: The working range for diacetyl was 0.057 to 13.4 ppm (0.20 to 47.2 mg/m^3) for a 10-L air sample.

INTERFERENCES: Any compound with a similar retention time to diacetyl.

OTHER METHODS: None determined.

REAGENTS:

1. Diacetyl, chromatographic grade*
2. Acetone, pesticide grade*
3. Methanol, pesticide grade*
4. Helium, pre-purified and filtered.
5. Hydrogen, pre-purified and filtered.
6. Air, compressed, purified, and filtered.
7. Desorbing solvent: acetone/methanol (99:1)
8. Calibration stock solution: Add known amount of diacetyl to desorbing solvent in 10- mL volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Anasorb CMS solid sorbent tube (SKC, Inc. # 226-121).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph equipped with FID, integrator, and capillary column with a deactivated glass inlet liner (page 2557-1).
4. Vials, autosampler, 2-mL, amber glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipettes, 3-mL and 5-mL.
7. Volumetric flasks, 10-mL, amber.

SPECIAL PRECAUTIONS: Diacetyl is flammable, toxic, and forms explosive mixtures in air. Acetone and methanol are flammable and pose a fire hazard. Work with all chemicals in a well ventilated laboratory safety hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampling tube immediately before sampling. Attach sampling tube to personal sampling pump with flexible tubing.
3. Sample at an accurately know flow rate between 0.01 and 0.2 L/min for a total sample size of 10 L.
4. Cap the samplers with plastic caps, pack in a manner to insure that the samplers are kept in the dark, and are shipped cold (5 °C).

SAMPLE PREPARATION:

5. Place the front and back sorbent sections in separate amber vials (due to photosensitivity of diacetyl). Place the glass wool plug preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of the acetone/methanol (99:1) solvent into each vial. Securely attach crimp caps to each vial.
7. Place each vial on a rotary mixer for 1.5 hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of diacetyl to the solvent in a 10-mL volumetric flask and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg diacetyl).
9. Determine the desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount (5 to 20 µL) of DE stock solution directly onto the front section of each Anasorb CMS tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE vs µg diacetyl recovered.
10. Analyze a minimum of 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 the conditions listed on page 2557-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of diacetyl 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 diacetyl in the air volume sampled, V(L):

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method was developed in response to a request to identify and quantitate possible hazardous chemicals in food packaging facility. Diacetyl, a toxic and reactive compound [2], was identified as a possible suspect chemical in the facility.

Because of the reactivity of diacetyl, several specialized analytical conditions were required during the method development. The use of a deactivated glass inlet liner and a Stabilwax-DA capillary column were required to prevent the reaction of diacetyl in the injection port and with the column which resulted in tailing peaks and decomposition of the analyte. It was further determined that the reactivity of diacetyl could be inhibited or slowed down by storage in the dark at 5 °C. Standards prepared in amber volumetric flasks were stable for a couple days. Even with storage under these conditions, collected samples containing diacetyl were only stable for 7 days (95%). The average DE recovery for diacetyl was 90% over a range from 47 to 470 µg [1].

A user check of this method for diacetyl verified that it passed the performance criteria for a NIOSH method. The mean recovery was 103.1% (n=12) with a standard deviation of 4.45%. The precision of an average test result was 9.79% [3].

NOTE: While this method can be used of the sampling and analysis of acetoin, recovery is not optimized and is 65%-70%, which is below the acceptable recovery criteria of ≥75% for NMAM methods [4].

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

DIESEL PARTICULATE MATTER (as Elemental Carbon) 5040

C AW: 12.01 CAS: none RTECS: none

METHOD: 5040: Issue 3 **EVALUATION: FULL** **Issue 1: 15 May 1996**
Issue 3: 15 March 2003

OSHA: no PEL
NIOSH: no REL
ACGIH: 20 µg/m³ as elemental carbon (proposed [1])

PROPERTIES: nonvolatile solid

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

SAMPLING

SAMPLER:	FILTER: quartz-fiber, 37-mm; size-selective sampler may be required [2].
FLOW RATE:	2 to 4 L/min (typical)
VOL-MIN:	142 L @ 40 µg/m³
-MAX:	19 m³ (for filter load of ~ 90 µg/cm²)
SHIPMENT:	Routine
SAMPLE STABILITY:	Stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	23 to 240 µg/m³ (See also ref. [2].)
BIAS:	None (See also ref. [2].)
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.085 at 23 µg/m³ (See also ref. [2].)
ACCURACY:	± 16.7% at 23 µg/m³ (See also ref. [2].)

MEASUREMENT

TECHNIQUE:	Thermal-optical analysis; flame ionization detector (FID)
ANALYTE:	Elemental carbon (EC). Total carbon is determined, but an EC exposure marker was proposed. See [2] for details.
FILTER PUNCH SIZE:	1.5 cm² (or other [2])
CALIBRATION:	Methane injection
RANGE:	1 to 105 µg per filter portion (See also [2].)
ESTIMATED LOD:	0.3 µg per filter portion
PRECISION ($\bar{S}_r$):	0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C

APPLICABILITY: The working range is approximately 6 to 630 µg/m³, with an LOD of ~ 2 µg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.5 cm² punch from the sample filter. If a lower LOD is desired, a larger sample volume and/or 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.4 µg/m³). The split between organic carbon (OC) and EC may be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on laser intensity. In general, the OC-EC split may be inaccurate when EC loadings are above 20 µg/cm². High loadings can give low (and variable) EC results because the transmittance remains low and relatively constant until some of the EC is oxidized. The split should be reassigned (prior to EC peak) in such cases [3]. An upper EC limit of 800 µg/m³ (90 µg/cm²) can be determined.

INTERFERENCES: Total carbon (as OC and EC) is determined by the method, but EC was recommended as a measure of workplace exposure because OC interferences may be present [2, 3]. Cigarette smoke and carbonates ordinarily do not interfere in the EC determination. Less than 1% of the carbon in cigarette smoke is elemental. If heavy loadings of carbonate are anticipated, a size-selective sampler (impactor and/or cyclone) should be used [2]. For measurement of diesel-source EC in coal mines, a cyclone and impactor with a submicrometer cutpoint are required to minimize collection of coal dust. A cyclone and/or impactor may be necessary in other workplaces if EC-containing dusts are present.

OTHER METHODS: Other methods for determination of EC and OC have been employed, but these are not equivalent to the method described herein. Information on other methods is summarized elsewhere [2].

REAGENTS:

1. Aqueous solutions of reagent grade (99+%) sucrose, 0.1 to 3 mg C per mL solution. Ensure filter spike loading range brackets that of samples.
2. Ultra pure H_2O, Type I, or equivalent.
3. UHP helium (99.999%), scrubber also required for removal of oxygen.
4. Hydrogen, purified (99.995%), cylinder or hydrogen generator source.
5. Ultra Zero air (low hydrocarbon).
6. 10% oxygen in helium balance, both gases UHP, certified mix.
7. 5% methane in helium balance, both gases UHP, certified mix.

EQUIPMENT:

1. Sampler: Quartz-fiber filter, precleaned (in low temperature asher 2 to 3 h, or muffle furnace for 1 to 2 h at ~ 800 °C), 37-mm, in a 3-piece cassette with filter support (stainless steel screen, cellulose pad, or a second quartz filter). Alternative samplers may be required in dusty environments. See ref. [2] for details.
   NOTE 1: High purity, high efficiency, binder-free quartz-fiber filters must be used (e.g., Pall Gelman Sciences Pallflex Tissuequartz 2500QAT-UP. Precleaned filters are available from several laboratories. Filters also can be purchased and cleaned in-house. Filters should be cleaned in a muffle furnace operated at 800-900°C for 1-2 hours. Check (analyze) filters to ensure removal of OC contaminants. A shorter cleaning period may be effective. OC results immediately after cleaning should be below 0.1 $\mu g/cm^2$. OC vapors readily adsorb onto clean filters. Even when stored in closed containers, OC loadings may range from 0.5 $\mu g/cm^2$ after several weeks.
   NOTE 2: Cellulose supports give higher OC blanks than screens and quartz filters. Bottom quartz filters can be used to correct for adsorbed vapor; see ref. [2].
2. Personal sampling pump with flexible tubing.
3. Thermal-optical analyzer; see ref. [2].
4. Metal punch for removal of 1.5 cm^2 rectangular portion of filter.
   NOTE: A smaller portion (e.g., taken with cork borer) may be used, but the area must be large enough to accommodate the entire laser beam (i.e., beam should pass through the sample, not around it). The area of the portion must be accurately known, and the sample must be carefully positioned (the filter transmittance will decrease dramatically when the sample is properly aligned). A filter portion ≥ 0.5 cm^2 with diameter or width $\leq$ 1 cm is recommended.
5. Syringe, 10-µL.
6. Aluminum foil.
7. Needle (for lifting filter punch portion).
8. Forceps
9. Volumetric flasks, Class A.
10. Analytical balance.

SPECIAL PRECAUTIONS: Hydrogen is a flammable gas. Users must be familiar with the proper use of flammable and nonflammable gases, cylinders, and regulators. According to the instrument manufacturer, the instrument is a Class I Laser Product. This designation means there is no laser radiation exposure during normal operation. Weakly scattered laser light is visible during operation, but does not pose a hazard to the user. The internal laser source is a Class IIIb product, which poses a possible hazard to the eye if viewed directly or from a mirror-like surface (i.e., specular reflections). Class IIIb lasers normally do not produce a hazardous diffuse reflection. Repairs to the optical system, and other repairs requiring removal of the instrument housing, should be performed only by a qualified service technician.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Both open- and closed-faced cassettes have been used. Both configurations generally give even deposits. At higher flow rates (e.g., 4 L/min), small spots occasionally have been observed in the center of the filters when closed-faced cassettes are used. This material likely consisted of impacted diesel agglomerates and/or non-diesel particulate matter. EC results for multiple portions of the filters were in good agreement, so the spots had little analytical impact. Other samplers also can be used (see ref. [2]) provided an even deposit of diesel particulate results. An even deposit is necessary because the sample portion analyzed must be representative of the entire deposit. If the deposit is not homogeneous, the entire sample must be analyzed. An impactor/cyclone may be needed in some cases. [2]
2. Attach sampler outlet to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate. Typical rates are 2-4 L/min (note: Lower flows (e.g., 1 L/min) have been used in mines to prevent overloading).
4. After sampling, replace top piece of cassette, if removed, and pack securely for shipment to laboratory.
   NOTE: Diesel particulate samples from occupational settings generally do not require refrigerated shipment unless there is potential for exposure to elevated temperatures (that is, well above collection temperature). Filter samples normally are stable under laboratory conditions. Some OC loss may occur over time if samples contain OC from other sources (for example, cigarette smoke). Sorption of OC vapor after sample collection has not occurred, even with samples having high (e.g., 80%) EC content.

SAMPLE PREPARATION:

5. Place sample filter on a freshly cleaned aluminum foil surface. Isopropyl alcohol or acetone can be used to clean the foil. Allow residual solvent to vaporize from the surface prior to use. Punch out a representative portion of the filter. Take care not to disturb deposited material and avoid hand contact with sample. A needle inserted at an angle is useful for removal of the filter portion from the punch body. Newer instruments have an externally mounted bracket to support the quartz sample holder while the previous sample is removed and a new one is loaded. Through a hole in the side of the standard punch, a needle can be used to push the filter portion from the punch onto the sample holder. Alternative approaches also can be used, depending on the user's preference, as long as contamination is avoided.

CALIBRATION AND QUALITY CONTROL:

6. Analyze at least one replicate sample. For sets of up to 50 samples, replicate 10% of the samples. For sets over 50 samples, replicate 5% of the samples. If a filter deposit appears uneven (this should not be the case if the cassette is sealed properly), take a second portion (step 5) for analysis to check evenness of deposition.
   NOTE: Precision of replicate analyses of a filter is usually better than 5% (1 to 3% is typical).

7. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. With 10-µL (or other) syringe, apply an aliquot of OC standard solution directly to filter portion taken (step 5) from a precleaned filter. For best results, the precleaned filter punch should be cleaned again in the sample oven prior to application of the aliquot.
      NOTE: With small aliquots (e.g., ≤ 10 µL), disperse standard solution over one end of filter portion to ensure standard is in laser beam. To prevent possible solution loss to surface, hold the portion off the surface. Larger volumes can easily penetrate to the underside of the filter portion.
   b. Allow water to evaporate and analyze spikes with samples and blanks (steps 9 and 10).
      NOTE: A pronounced decrease in filter transmittance during the *first* temperature step of the analysis indicates water loss. Allow portions to dry longer if this occurs. Spiked punches also can be dried in the oven, if desired. For quick drying, the 'clean oven' command on the menu can be selected and canceled after about 4 seconds. The time allowed may depend on instrument, but oven temperatures should be below 100 °C to avoid boiling the solution. This approach is convenient and prevents potential adsorption of organic vapors in laboratory air.
8. Determine instrument blank (results of analysis with freshly cleaned filter portion) for each sample set.

MEASUREMENT:

9. Adjust analyzer settings according to manufacturer's recommendations (see instrument operation manual and background information in ref. [2]). Place sample portion into sample oven.
   NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require a longer period and higher temperature during the oxidative mode to ensure that all EC is removed (the EC peak should never merge with the calibration peak). Adjust time and temperature accordingly. A maximum temperature above 940 °C should not be required.
10. Determine EC (and OC) mass, µg. Analyzer results are reported in units µg/cm^2 of C. The reported values are normally based on a sample portion of about 1.5 cm^2, which is the area of the standard punch provided by the manufacturer. If the portion area used differs from the value entered in the ocecpar.txt file, multiply the result by 1.5 (or value in ocecpar.txt file) and divide the product by the actual area analyzed to obtain the area-corrected result (i.e., reported result x 1.5/portion area = corrected result in µg/cm^2). This is most easily done in the data spreadsheet. Alternatively, the correct results will be obtained with the data calculation program if the portion area is entered in the parameter file (ocecpar.txt), but this approach is cumbersome when punches of different areas are used because correct results will not be obtained for all punch sizes.

CALCULATIONS:

11. Multiply the reported (or area-corrected) EC result (µg/cm^2) by filter *deposit area*, cm^2, (typically 8.5 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each filter sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b). The mass of OC is calculated similarly, but the mean OC field blank may underestimate the amount of OC contributed by adsorbed vapor. A quartz filter placed beneath the sample filter can provide a better estimate of the adsorbed OC. [2]
12. Calculate the 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:

Details on the evaluation of this method are provided in a chapter of this NMAM Supplement. [2] The chapter includes a summary of interlaboratory comparison work conducted since the initial publication of the method. Background information and guidance on method use, including sampling requirements, also are provided. In general industry, 37-mm cassettes are normally suitable for air sampling, but there are exceptions. A cyclone in series with an impactor having a submicrometer cutpoint must be used in coal mines, and the Mine Safety and Health Administration (MSHA) has recommended use of a cyclone-impactor sampler in metal and nonmetal mines. [5] The impactor is commercially available [6]. A size-selective sampler (either impactor and/or cyclone) also may be required in other dusty environments [2], particularly if the dust is carbonaceous. If a sample contains carbonate, the carbonate carbon (CC) will be quantified as OC. A carbonate-subtracted result can be obtained through acidification of the sample portion or through separate integration of the carbonate peak [2] (*note: Trona and other compounds containing sodium can etch the quartz oven wall at elevated temperatures. Avoid spillage of these materials in the sample oven.*) These procedures are described in a Chapter of this Supplement. [2] The thermal-optical method is applicable to nonvolatile carbon species (i.e., particulate OC, CC and EC). The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection.

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NOTE: Recently, diesel exhaust has been taken off the ACGIH Notice of Intended Changes list. See reference [2].
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[6] SKC, Eight Sixty Three Valley View Road, Eighty Four, PA 15330.

METHOD WRITTEN BY:

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

(1) 2-(DIMETHYLAMINO)ETHANOL
(2) 1-DIMETHYLAMINO-2-PROPANOL

FORMULAS: TABLE 1 MW: TABLE 1 CAS: TABLE 1 RTECS: TABLE 1

METHOD: 2561, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no REL
NIOSH: no PEL
ACGIH: no TLV

PROPERTIES: Table 1

COMPOUNDS: (1) 2-(dimethylamino)ethanol: dimethylethanol amine
(2) 1-dimethylamino-2-propanol: dimethylisopropanolamine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-7, 60 mg/30 mg)

FLOW RATE: 0.02 to 0.1 L/min

VOL – MIN: 10 L
– MAX: 24 L

SHIPMENT: Cold

SAMPLE STABILITY: Stable stored in freezer

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

OVERALL PRECISION (S_{rt}): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Compounds above

DESORPTION: 1 mL methanol, 60 min

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C for 6 min then up to 200 °C for 4 minutes at a rate of 15 °C per minute

CARRIER GAS: Helium, 1-2 mL/min

COLUMN: Capillary, fused silica, 30-m x 0.25-mm ID; 1.0-µm film dimethylpolysiloxane, DB-1 or equivalent

CALIBRATION: Solutions of compounds in methanol

RANGE: 0.004 to 2 mg per sample [1, 2, 3]

ESTIMATED LOD: See Table 2

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

APPLICABILITY: This method can be used for simultaneous analysis of both amino compounds. The method was field tested for almost 300 samples containing both compounds with little or no breakthrough [2, 3]. Up tp 4 mg of dimethylethanolamine (no isopropanolamine present) and up to 1200 µg dimethylisopropanol (140 µg dimethylethanolamine present) were reported on the field samples with little breakthrough. For higher capacity, a larger XAD-7 sorbent bed tube can be used.
NOTE: During method development, a capillary Rtx-5Amine (cross-linked 5% diphenyl/95% dimethyl polysiloxane) column with deactivated injection port liner was also used successfully.

INTERFERENCES: None identified.

OTHER METHODS: This method may be applicable to other amino alcohols such as those in method 2007 [4].

REAGENTS:

1. Eluent: methanol* (chromatographic grade).
2. Analytes, 99+% grade*.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 6-mm OD, flame-sealed ends, containing two sections of XAD-7 resin (front = 60 mg; back = 30 mg) separated by glass wool. Pressure drop across the tube at 0.1 L/min. airflow must be less than 3.2 kPa. Tubes are commercially available (SKC, Inc. #226-94).
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 2561-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringes, 10-µL to 500-µL.
7. Volumetric flasks, 10-mL.
8. Pipet, volumetric, 1-mL, with pipet bulb or repipet.

SPECIAL PRECAUTIONS: Methanol is toxic and flammable. The analytes are eye irritants [2]. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.1 L/min for a total sample size of 10 to 24 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. The initial glass wool plug may be discarded.
6. Add 1.0 mL of methanol eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate with at least six working standards over the range 4 to 4000 µg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte vs. µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of XAD-7 used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to 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 2561-1. Inject sample aliquot with autosampler, or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, 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.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Current Validation

This method was developed in response to a request for a method to use in a field study. The method for dimethylethanolamine and dimethylisopropanolamine was validated using analytes fortified on XAD-7 sorbent tubes (SKC, Inc. #226-94, Lot 1994). Desorption efficiency (DE) and precision are listed in Table 2.

Storage stability studies were done at approximately 100 µg each analyte/sample. The samples were stored for up to 5 weeks in the freezer (-4°C). The recovery for dimethylethanolamine (110.9 µg/sample) was 98.4% and for dimethylisopropanolamine (104.6 µg/sample) was 100.2%.

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METHOD WRITTEN BY:

Ardith A. Grote, NIOSH/DART

TABLE 1. Structural Formulas, Molecular Weights, and Properties

Compound	CAS	RTECS	Formula	MW	mg/m³= 1 ppm	BP (°C)	VP (mm Hg)	Density (g/mL)
2-(dimethylamino)ethanol	108-01-0	KK6125000	$HOCH_2CH_2N(CH_3)_2$	89.14	0.274	133	6.12	0.887
1-dimethylamino-2-propanol	108-16-7	UB3150000	$(CH_3)_2NCH_2CH(OH)CH_3$	103.17	0.237	124	8.0	0.837

TABLE 2. Current Validation

Compound	Range Studied (µg / sample)	LOD (µg / sample)	Average DE[1]	Measurement Precision ($\hat{S}_r$)
2-(dimethylamino)ethanol	22-554	4	0.930	0.026
1-dimethylamino-2-propanol	21-523	4	0.894	0.029

[1] Averaged over mass range shown.

ELEMENTS by ICP (Nitric/Perchloric Acid Ashing)

7300

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

METHOD: 7300, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

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

PROPERTIES: Table 1

ELEMENTS:

aluminum*	calcium	lanthanum	nickel	strontium	tungsten*
antimony*	chromium*	lithium*	potassium	tellurium	vanadium*
arsenic	cobalt*	magnesium	phosphorus	tin	yittrium
barium	copper	manganese*	selenium	thallium	zinc
beryllium*	iron	molybdenum*	silver	titanium	zirconium*
cadmium	lead*				

*Some compounds of these elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride membrane)

FLOWRATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: elements above

ASHING REAGENTS: conc. HNO_3/ conc. $HClO_4$ (4:1), 5 mL; 2mL increments added as needed

CONDITIONS: room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 25 mL

WAVELENGTH: depends upon element; Table 3

BACKGROUND CORRECTION: spectral wavelength shift

CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$

RANGE: varies with element [1]

ESTIMATED LOD: Tables 3 and 4

PRECISION ($\bar{S}$): Tables 3 and 4

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m³ for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].

OTHER METHODS: This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

REAGENTS:

1. Nitric acid (HNO_3), conc., ultra pure.
2. Perchloric acid ($HClO_4$), conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3, 1% $HClO_4$. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size; or polyvinyl chloride membrane, 5.0-µm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10-, 25-,100-mL., and 1-L**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
    NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO_3/1% $HClO_4$:
    a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
    b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
    c. Mo, Sb, Sn, Te, Ti, W, Zr
    d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked blank filters per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, mg / m^3$$

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

Issues 1 and 2

Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

Issue 3

In this update of NIOSH Method 7300, the precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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METHOD REVISED BY:

Mark Millson and Ronnee Andrews, NIOSH/DART.

Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Labortories, Salt Lake City, UT.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties: Atomic Weight	Properties: MP, °C	Air Volume, L @ OSHA PEL: MIN	Air Volume, L @ OSHA PEL: MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.34	710	50	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
Potassium (K)	39.10	63.65	5	1000
Lanthanum	138.91	920	5	1000
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
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
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
Tungsten (W)	183.85	3410	5	1000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m³ (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
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)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--			--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	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 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6				--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	--	C 0.05	--
Tungsten	7440-33-7		5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000		--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45 µm)

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
Sb	206	0.192	7.7	3.08	90.2	11.4	12.9	**41.3**	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
Sn	189	0.040	1.6	0.77	90.2	18.0	3.21	**49**	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
W	207	0.075	3.0	1.54	**72.2**	10.1	6.40	**57.6**	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
Zr	339	0.022	0.9	0.31	88.0	19.4	1.29	**25**	57.87

(a) Bold values are qualitative only because of low recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified[17] 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
Ca	317	0.908	36.3	15.6	**68.1**	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
La	408	0.048	1.9	0.78	**45.5**	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
Mg	279	0.098	3.9	1.56	**54.8**	20.59	6.40	**64.5**	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
Sb	206	0.192	7.7	3.10	**64.6**	22.54	12.70	**38.1**	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
Sn	189	0.040	1.6	0.78	85.7	27.29	3.18	**52.0**	29.4
Sr	407	0.005	0.2	0.31	**71.8**	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
W	207	0.075	3.0	1.56	**74.9**	15.79	6.40	**44.7**	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
Zr	339	0.022	0.9	0.31	**70.7**	54.20	1.27	**40.4**	42.1

(a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
(c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.

ELEMENTS by ICP (Aqua Regia Ashing) 7301

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

METHOD: 7301, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

ELEMENTS:						
	aluminum*	calcium	lead*	phosphorus	thallium	zinc
	antimony*	chromium*	lithium	potassium	tin	zirconium*
	arsenic	cobalt	magnesium	selenium	titanium	
	barium	copper	manganese	silver	tungsten*	
	beryllium	iron*	molybdenum	strontium	vanadium	
	cadmium	lanthanum	nickel	tellurium	yttrium	

* Some compounds of those elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not determined

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: Elements above

ASHING REAGENTS: Aqua regia (1 HNO_3: 3 HCl)

CONDITIONS: Room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 5% aqua regia, 25 mL

WAVELENGTH: Depends upon element, Table 3

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 5% aqua regia

RANGE: Varies with element [1]

ESTIMATED LOD: Tables 3 and 4

PRECISION ($\hat{S}_r$): Tables 3 and 4

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m³ for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected. This method does not digest PVC filters completely.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].

OTHER METHODS: Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive. NIOSH Methods 7300 & 7302 are alternative digestion procedures.

REAGENTS:

1. Nitric acid (HNO_3), conc.*, ultra pure.
2. Hydrochloric acid (HCl), conc.*, ultra pure.
3. Ashing acid (Aqua Regia): 1:3 (v/v) HNO_3:HCl. Mix 1 volume conc. HNO_3 with 3 volumes conc. HCl.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 1% HNO_3, 3% HCl. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size; or polyvinyl chloride (PVC) membrane, 5.0-µm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10-, 25-,100-mL., and 1-L**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: Concentrated acids are powerful oxidizers, toxic, and corrosive liquids. Wear protective clothing and work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mo, Sb, W, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
   NOTE: PVC filters will not completely dissolve after repeated additions of ashing acid.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturer's recommendations.
    NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 5% Aqua Regia:
    a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
    b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
    c. Mo, Sb, Sn, Te, Ti, W, Zr
    d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked media blanks per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards, samples, and blanks.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations. If more sensitivity is required, the final sample volume may be held to 10.0 mL.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{C_S V_S - C_b V_b}{V}, mg / m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. The precision and recovery data, instrumental detection limits, and analytical wavelengths are listed in Tables 3 and 4. In general, better recoveries were obtained from MCE filters than from PVC filters. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments model EOP operated according to manufacturer's instructions.

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METHOD WRITTEN BY:

Mark Millson, NIOSH/DART, and Ronnee Andrews, NIOSH/DART.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties: Atomic Weight	Properties: MP, °C	Air Volume, L @ OSHA PEL: MIN	Air Volume, L @ OSHA PEL: MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.34	710	50	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
Potassium (K)	39.10	63.65	5	1000
Lanthanum (La)	138.91	920	5	1000
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
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
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
Tungsten (W)	183.85	3410	50	1000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m³ (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
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)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--			--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	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 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6				--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	--	C 0.05	--
Tungsten	7440-33-7		5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000		--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45µm)

Element (a)	wavelength (nm)	Est.LOD (µg/ Filter)	LOD (ng/mL)	Certified 3x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	100.3	2.39	3.21	93.4	4.95
Al	167	0.115	4.6	1.54	**208.1**	42.4	6.40	99.6	9.43
As	189	0.140	5.6	3.08	97.6	4.71	12.90	95.1	1.14
Ba	455	0.005	0.2	0.31	104.3	1.65	1.29	100.8	1.54
Be	313	0.005	0.2	0.31	99.6	1.42	1.29	100.6	0.68
Ca	317	0.908	36.3	15.4	101.6	5.01	64.00	101.6	1.42
Cd	226	0.0075	0.3	0.31	106.8	2.60	1.29	99.2	0.76
Co	228	0.012	0.5	0.31	105.6	1.64	1.29	100.4	0.87
Cr	267	0.020	0.8	0.31	97.0	27.0	1.29	88.0	5.38
Cu	324	0.068	2.7	1.54	118.9	65.2	6.40	102.0	0.68
Fe	259	0.095	3.8	1.54	114.9	43.0	6.40	82.7	7.81
K	766	1.73	69.3	23.00	94.7	2.60	96.40	95.8	0.98
La	408	0.048	1.9	0.77	105.7	1.80	3.21	101.3	0.84
Li	670	0.010	0.4	0.31	104.3	2.37	1.29	99.3	0.89
Mg	279	0.098	3.9	1.54	105.2	4.23	6.40	99.2	1.24
Mn	257	0.005	0.2	0.31	103.5	1.64	1.29	91.2	2.01
Mo	202	0.020	0.8	0.31	108.9	2.70	1.29	97.4	1.25
Ni	231	0.020	0.8	0.31	112.2	2.28	1.29	94.2	1.73
P	178	0.092	3.7	1.54	93.2	10.9	6.40	97.1	5.93
Pb	168	0.062	2.5	1.54	88.0	6.52	6.40	102.2	1.06
Sb	206	0.192	7.7	3.08	**50.1**	54.7	12.90	80.0	19.46
Se	196	0.135	5.4	2.30	93.2	8.38	9.64	89.1	7.23
Sn	189	0.040	1.6	0.77	**25.8**	81.9	3.21	91.7	16.39
Sr	407	0.005	0.2	0.31	100.8	1.27	1.29	99.3	0.66
Te	214	0.078	3.1	1.54	103.1	1.88	6.40	95.0	1.31
Ti	334	0.050	2.0	0.77	98.3	1.88	3.21	96.0	1.06
Tl	190	0.092	3.7	1.54	101.3	3.57	6.40	98.2	0.71
V	292	0.028	1.1	0.77	106.0	1.38	3.21	101.3	0.81
W	207	0.075	3.0	1.54	**64.9**	21.8	6.40	**74.1**	11.34
Y	371	0.012	0.5	0.31	104.3	1.55	1.29	99.3	0.72
Zn	213	0.310	12.4	4.60	99.8	9.73	19.30	98.0	0.86
Zr	339	0.022	0.9	0.31	**52.5**	71.2	1.29	**76.6**	18.19

(a) Bold values are qualitative only, because of poor recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD.
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (a)	wavelength (nm)	Est. LOD (µg/ Filter)	LOD (ng/mL)	Certified 3x LOD (µg/filter) (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (µg/ filter) (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	**57.9**	0.2	3.18	**55.0**	21.7
Al	167	0.115	4.6	1.56	**-1.9**		6.40	112.1	59.6
As	189	0.140	5.6	3.10	78.2	1.6	12.70	80.2	7.9
Ba	455	0.005	0.2	0.31	**73.0**	0.1	1.27	95.7	3.7
Be	313	0.005	0.2	0.31	81.1	0.1	1.27	97.2	4.3
Ca	317	0.908	36.3	15.60	**68.2**	4.9	64.00	97.7	4.5
Cd	226	0.0075	0.3	0.31	86.7	0.1	1.27	97.4	4.3
Co	228	0.012	0.5	0.31	83.8	0.1	1.27	99.2	4.4
Cr	267	0.020	0.8	0.31	80.1	0.1	1.27	94.1	6.8
Cu	324	0.068	2.7	1.56	75.9	0.5	6.40	96.1	4.3
Fe	259	0.095	3.8	1.56	78.4	0.6	6.40	88.4	9.0
K	766	1.73	69.3	23.40	**61.4**	3.1	95.00	91.6	5.7
La	408	0.048	1.9	1.78	**34.4**	0.4	3.18	95.3	3.8
Li	670	0.010	0.4	0.31	76.3	0.0	1.27	96.0	4.7
Mg	279	0.098	3.9	1.56	77.5	0.6	6.40	94.0	4.6
Mn	257	0.005	0.2	0.31	77.4	0.1	1.27	93.4	4.2
Mo	202	0.020	0.8	0.31	79.7	0.2	1.27	89.2	9.8
Ni	231	0.020	0.8	0.31	86.2	0.1	1.27	100.8	4.8
P	178	0.092	3.7	1.56	76.9	0.9	6.40	**69.0**	14.5
Pb	168	0.062	2.5	1.56	82.0	0.9	6.40	99.4	4.4
Sb	206	0.192	7.7	3.10	**40.3**	1.5	12.70	**23.0**	76.5
Se	196	0.135	5.4	2.30	89.4	1.2	9.50	87.5	9.9
Sn	189	0.040	1.6	0.78	101.1	0.4	3.18	**21.1**	124.0
Sr	407	0.005	0.2	0.31	**73.4**	0.1	1.27	95.2	3.9
Te	214	0.078	3.1	1.56	91.8	0.7	6.40	85.3	7.5
Ti	334	0.050	2.0	0.78	**53.4**	0.2	3.18	**46.3**	39.9
Tl	190	0.092	3.7	1.56	**71.6**	0.8	6.40	86.1	9.3
V	292	0.028	1.1	0.78	77.8	0.3	3.18	96.1	4.6
W	207	0.075	3.0	1.56	**51.3**	0.8	6.40	**29.8**	47.0
Y	371	0.012	0.5	0.31	79.6	0.1	1.27	95.8	4.4
Zn	213	0.310	12.4	4.70	80.9	2.2	19.10	94.7	4.2
Zr	339	0.022	0.9	0.31	**46.2**	0.1	1.27	**39.2**	112.7

(a) Bold values are qualitative only because of poor recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD.
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion)

7303

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

METHOD: 7303, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

ELEMENTS:

aluminum	cadmium	indium	nickel	strontium	zinc
antimony*	calcium	iron	palladium	tellurium	
arsenic	chromium	lead*	phosphorus	thallium	
barium	cobalt	magnesium	platinum	tin*	
beryllium	copper	manganese	potassium	titanium	
bismuth*	gallium	molybdenum	selenium	vanadium	
boron	gold	neodymium	sodium	yttrium	

* With certain restrictions (see Table 3)

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 5,000 to 50,000 µg/sample

BIAS: Not determined

OVERALL PRECISION: Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY

ANALYTE: See element list above

REAGENTS: Conc. HCl, 1.25 mL; and conc. HNO_3, 1.25 mL

FINAL SOLUTION: 5% HCl and 5% HNO_3, 25 mL

WAVELENGTH: Element and instrument specific

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 5% HCl, 5% HNO_3

RANGE: LOQ to 50,000 µg/sample [1]

ESTIMATED LOD: Varies with element; Table 1

PRECISION (Š): Not evaluated

APPLICABILITY: The working range of this method is up to 100 mg/m³ for each element in a 500-L sample (the minimum range depends on the LOD for each sample; see Table 1). The analysis is not compound specific. Certain elemental compounds are known to be acceptable or unacceptable by this method (see Table 3). For unverified compounds, a test run should be conducted using a known amount of the compound in question to determine acceptability.

INTERFERENCES: Interferences are spectral in nature and are accounted for by choosing appropriate wavelengths, applying interelement correction factors, and background correction.

OTHER METHODS: Alternative, more sensitive methods exist for some elements by graphite furnace atomic absorption spectroscopy. This method is similar to NIOSH Method 7301, differing only in the use of the hot block for digestion of the sampler.

REAGENTS:

1. Hydrochloric acid,* conc., ultra pure.
2. Nitric acid,* conc., ultra pure.
3. Calibration stock solutions, 50-1000 µg/mL. Commercially available single element solutions or multielement solutions prepared as instructed by the instrument manufacturer.
4. Argon, prepurified.
5. Distilled, deionized, Type II water.
6. Diluting solution: 5% HCl : 5% HNO_3. To about 600 mL of deionized water in a 1-L volumetric flask, slowly add 50 mL conc. HCl and 50 mL conc. HNO3. Dilute to the mark with deionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled argon plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Hot block apparatus at 95 °C.
5. Digestion vessels and caps, 50-mL.
6. Watchglasses.
7. Pipettes, electronic and mechanical.
8. Regulator, two-stage, for argon.
9. Forceps.

SPECIAL PRECAUTIONS: Concentrated acids are powerful oxidizers, toxic, and corrosive liquids. Wear protective clothing and work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holder and with forceps remove the sample filter. Fold the filter into quarters taking care not to lose any sample, and transfer to a clean, 50-mL hot block digestion tube.
4. Add 1.25 mL HCl. Cover with a plastic watchglass. Place in the hot block and heat at an internal temperature of 95 °C for 15 minutes.
   NOTE: The internal temperature may vary from the digital readout. Calibrate the hot block prior to digestion.
5. Remove the sample from the hot block and cool for 5 minutes. Remove watchglass and add 1.25 mL HNO_3. Replace watchglass and return to hot block at 95 °C for 15 minutes.
6. Remove the sample from the hot block and cool for at least 5 minutes. Rinse watchglass into the sample container and discard watchglass.
7. Dilute to 25-mL final volume with distilled, deionized Type II water.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate the spectrometer according to the manufacturer's recommendations. Use standards consisting of the same 5% HCl : 5% HNO_3 matrix as the samples.
9. Analyze a standard every 10 samples.
10. Analyze a media blank every 20 samples, and a reagent blank every 10 samples.
11. Analyze a set of two laboratory control samples every 40 samples of a given matrix for a given analyte.
12. Check recoveries with at least two spiked media blanks per ten samples.
    NOTE: In the determination of lead, there may be a measurement interference (for example, samples with high aluminum levels). More recent instruments have a correction for this.

MEASUREMENT:

13. Set spectrometer to conditions specified by manufacturer.
14. Analyze standards, samples and quality control checks.
    NOTE: If the elemental value for a sample is above the linear range of the element(s) in question, dilute the sample solution with 5% HCl : 5% HNO_3 diluting solution, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
16. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, mg / m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The method was evaluated for all elements and compounds listed in Table 1 and Table 2 between 1999 and 2001 using known amounts of bulk material [4]. Evaluation is ongoing for additional elements and compounds. The limits of detection and quantitation were also determined for each element. Two ICP instruments were used in the evaluation, a Thermal Jarrell Ash Model 61E [5] and a TJA IRIS [6], operated according to the manufacturer's instructions.

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[5] Thermal Jarrell Ash [1991]. ICAP 61E Plasma Spectrometer Operator's Manual, Thermal Jarrell Ash Corp., Part No. 128832-01, Feb., 1991.
[6] Thermal Jarrell Ash [1997]. IRIS Plasma Spectrometer User's Guide, Thermal Jarrell Ash Corp., Part No. 135811-0, Feb. 4, 1997.

METHOD WRITTEN BY:

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TABLE 1: ANALYTE INFORMATION FOR VALID ELEMENTS AND COMPOUNDS

Analyte	Properties		LOD (µg/mL)	LOQ (µg/mL)	Estimated LOQ (µg/sample)*	Minimum** air vol. (L)	Maximum*** air vol. (L)
	MW	MP (°C)					
Al	26.98	660	0.111	0.37	9.25	2	10,000
As	74.92	817	0.009	0.03	0.075	8	5,000,000
Au	196.97	10.63	0.015	0.05	1.25	1	3,300
B	10.81	2177	0.0094	0.0283	0.71	1	3,300
Ba	137.34	3.51	0.0018	0.006	0.15	1	100,000
Be	9.01	2178	0.00075	0.0025	0.062	35	25,000,00
Bi	208.98	271	0.025	0.085	2.12	1	10,000
Ca	40.08	842	0.099	0.33	8.25	2	10,000
CaO	56.08	2927	0.139	0.462	11.6	3	10,000
Cd	112.4	321	0.0037	0.012	0.30	3	500,000
Co	58.93	1495	0.003	0.011	0.27	3	500,000
Cr	52.00	1890	0.009	0.03	0.75	8	500,000
Cu	63.54	1083	0.020	0.060	1.50	15	500,000
Fe	55.85	1535	0.070	0.20	5.00	1	5,000
Fe_2O_3 (as Fe)	159.69	1462	0.070	0.20	5.00	1	5,000
Ga	69.72	29.75	0.03	0.09	2.25	1	3,300
In	114.82	156.3	0.015	0.05	1.25	15	500,000
Mg	24.31	651	0.047	0.14	3.50	1	10,000
MgO	40.32	2825	0.078	0.23	5.75	5	33,000
Mn	54.94	1244	0.0012	0.004	0.10	0.05	10,000
Mo	95.94	651	0.0072	0.024	0.60	0.5	10,000
Nd	92.906	2477	0.01	0.03	0.75	0.1	3,300
Ni	58.71	1453	0.012	0.039	0.98	1	50,000
P	30.97	44	0.3	1.0	25	250	500,000
Pb	207.19	328	0.023	0.07	1.75	35	100,000
Pd	106.4	1550	0.009	0.03	0.75	0.1	3,300
Pt	195.09	1769	0.0045	0.015	0.38	200	25,000,000
Sb	121.75	630.5	0.018	0.06	1.50	3	100,000
Se	78.96	217	0.021	0.064	1.60	8	250,000
Sn	118.69	232	0.015	0.05	1.25	1	25,000
Sr	87.62	769	0.002	0.006	0.15	300	100,000,000
Te	127.60	450	0.15	0.5	12.5	125	500,000
Ti	47.90	1675	0.005	0.016	0.40	0.1	10,000
Tl	204.37	304	0.044	0.133	3.32	35	500,000
V	50.94	1890	0.003	0.01	0.25	2.5	500,000
Y	88.91	1495	0.001	0.003	0.075	0.1	50,000
Zn	65.37	419	0.022	0.066	1.65	0.5	10,000
ZnO	81.37	1970	0.027	0.082	2.05	0.5	10,000

* Value based on a 25-mL sample volume.

** The minimum sampling volume needed to obtain the OSHA PEL at the LOQ for the element/compound at a sample digestion volume of 25 mL.

*** The maximum sampling volume for a given sample, calculated by taking 50,000 µg as the limit for the element/compound per sample.

NOTE: The LOD and LOQ values are dependent on the particular analytical instrument used. Also, LOD and LOQ values may vary for a particular element due to certain interelement interferences.

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 dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
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)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	–	–	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	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 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	–	–	–	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	--	C 0.05	--
Tungsten	7440-33-7	–	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	–	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3: VALIDATION SUMMARY

Analyte	Status[1]	Analyte	Status	Analyte	Status
Ag	Not Valid	CuO	Valid	S	Not Valid
Al	Valid	Fe	Valid	Sb	Partially Valid[4]
Al_2O_3	Not Valid	Fe_2O_3	Valid	Sb_2O_3	Partially Valid[5]
As	Valid	Ga	Valid	Se	Valid
Au	Valid	In	Valid	Si	Not Valid
B	Valid	KCl	Pending	Sn	Partially Valid[6]
Ba	Pending	Mg	Valid	SnO	Pending
BaO	Pending	MgO	Valid	SnO_2	Pending
BaO_2	Pending	Mn	Valid	Sr	Valid
$BaCl_2$	Valid	MnO	Valid	$SrCrO_4$	Valid (by Cr)
$BaSO_4$	Pending	Mo	Valid	Te	Valid
Be	Valid	NaCl	Pending	Ti	Valid
Bi	Partially Valid[2]	Nd	Valid	Tl	Valid
Ca	Valid	Ni	Valid	V	Valid
$CaCO_3$	Valid	P	Valid	V_2O_5	Valid
CaO	Valid	Pb	Partially Valid[3]	Y	Valid
Cd	Valid	$PbCrO_4$	Valid (by Cr)	Zn	Valid
Co	Valid	PbO	Valid	ZnO	Valid
Cr	Valid	Pd	Valid	Zr	Not Valid
Cu	Valid	Pt	Valid	ZrO	Not Valid

[1] Status definitions

Valid: The method is suitable for samples up to at least 0.0500 g bulk material with recoveries of between 90 and 110 percent. This weight exceeds most expected levels encountered in work environments.

Partially Valid: The method is suitable with bulk-material recoveries of between 90 and 110 percent under certain conditions (as footnoted above).

Not Valid: The method procedure is not suitable for samples at any weight with recoveries of between 90 and 110 percent. An alternative method should be used.

[2] Valid up to 10,000 µg/sample and within 7 days of sample digestion.

[3] Valid up to 50,000 µg/sample and at least 24 hours after sample digestion; Valid up to 15,000 µg/sample within 24 hours of sample digestion.

[4] Valid up to 25,000 µg/sample and within 7 days of sample digestion.

[5] Valid up to 25,000 µg/sample and within 7 days of sample digestion.

[6] Valid up to 30,000 µg/sample and within 7 days of sample digestion.

NOTE: The upper limits of the method can be extended by serial dilution of the samples at the time of analyses.

ELEMENTS ON WIPES 9102

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

METHOD: 9102, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: N/A
NIOSH: N/A
ACGIH: N/A

PROPERTIES: Table 1

ELEMENTS:

Arsenic	Iron	Selenium	Zinc
Barium	Lanthanum	Silver	Zirconium
Beryllium	Lead	Strontium	
Cadmium	Manganese	Tellurium	
Cobalt	Molybdenum	Thallium	
Copper	Nickel	Vanadium	
Chromium	Phosphorus	Yttrium	

SAMPLING

SAMPLER: WIPE

FLOW RATE: N/A

VOL-MIN: N/A
-MAX:

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not Studied

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: Elements above

ASHING REAGENTS: Conc. HNO_3, 20 mL; and conc. $HClO_4$, 1 mL

CONDITIONS: Room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 10 mL

WAVELENGTH: Table 2

BACKGROUND CORRECTION: Spectral wavelength shift

CALIBRATION: Elements in 4% HNO_3, 1% $HClO_4$

RANGE: Table 2

ESTIMATED LOD: Table 2

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

APPLICABILITY: This method is a simultaneous elemental analysis, not compound specific. *Verify that the types of compounds in the samples are soluble with the ashing procedure selected.* Because this method deals with wipes samples it is important to keep in mind that the values obtained are qualitative.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction.

OTHER METHODS: This method supplements NMAM Method 7300 [1]. Additional element methods, whether single element or multi-element, may be found in NMAM. Alternate instrumentation includes flame atomic absorption spectroscopy for certain elements and graphite furnace AAS for increased sensitivity.

REAGENTS:

1. Nitric acid (HNO_3), conc., ultra pure.*
2. Perchloric acid ($HCLO_4$), conc., ultra pure.*
3. Calibration stock solutions, 1000 µg/mL commercially available, or prepared per instrument manufacturer's recommendation (see step 20).
4. Dilution acid, 4:1 HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
5. Argon.
6. Distilled, de-ionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Wash 'n Dri or ASTM equivalent[2] [pre-packaged moist disposable towelette (wipe)].
2. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
3. Regulator, two-stage for argon.
4. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
5. Volumetric flasks, 10- and 100-mL.**
6. Assorted volumetric pipettes as needed.**
7. Hotplate, surface temperature 150°C.
8. Polystyrene centrifuge tubes, 50-mL and 15-mL .
9. Hard-walled sample container.

** Clean all glassware with conc. nitric acid and rinse thoroughly in de-ionized water.

SPECIAL PRECAUTIONS: Nitric and perchloric acids are strong oxidizers and extremely corrosive. Perform all perchloric acid digestions in a perchloric acid hood. When working with acids use gloves and avoid inhalation or contact with skin or clothing.

SAMPLING:[3]

1. Wearing a clean pair of powder-less, plastic gloves, place the template over the area to be sampled and secure it. If the area to be sampled is in a confined area and a template cannot be used, measure the sampling area, and delineate the area to be sampled with masking tape.
2. Remove a wipe from its package, and unfold it.
3. Wipe the surface to be sampled using fingertips held together and applying firm pressure. Use an overlapping 'S' pattern to cover the entire surface with horizontal strokes.
4. Fold the exposed side of the wipe in, and wipe the same area using vertical 'S'-strokes.
5. Fold the wipe again to reveal an unexposed surface, and wipe the surface a third time as described in step 3.
6. 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 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.
7. Clean the template in preparation for the next wipe sample using water or a wipe. A disposable template may also be used.
8. Remove gloves and discard. Clean gloves should be worn for each new sample.
9. Field blanks: 10% of samples, at least three per batch. Remove unexposed wipes from packaging and place into sample containers. The field blanks should be collected at the beginning, middle, and end of sampling.

SAMPLE PREPARATION:

10. Transfer the samples and blanks to clean beakers.
11. Add 20 mL concentrated nitric acid and 1 mL concentrated perchloric acid. Cover beaker with a watchglass. Let stand 30 min at room temperature. Start a reagent blank at this step.
12. Allow samples to heat for approximately 8 hours @150 °C.
13. Remove watchglass and rinse into the beaker with de-ionized water.

14. Continue to heat on hotplate (120 °C).
    NOTE: Some species will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere.
15. Add additional amounts of HNO_3, if necessary, until the solution is clear and the wipe media is completely destroyed.
16. Take the sample to near dryness (ca. 0.5 mL).
17. Dissolve the residue in 0.5 mL dilution acid.
18. Transfer the solutions quantitatively to 15-mL centrifuge tubes or 10 mL volumetric flasks.
19. Dilute to 10 mL with de-ionized water.

CALIBRATION AND QUALITY CONTROL:

20. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 10 µg/mL multi-element working standards are used. The following multi-element combinations are chemically and spectrally compatible in 4% HNO_3/1% $HClO_4$:
    a. Al, As, Ba, Be, Cd, Ca, Cr, Co, Cu, In, Fe, La;
    b. Pb, Li, Mg, Mn, Ni, P, K, Sc, Se, Ag, Sr, Tl, V, Y, Zn;
    c. Sb, Mo, Te Sn, Ti, W, Zr;
    d. Pt
21. Analyze a standard for every six samples.
22. Check recoveries with at least two spiked media blanks per ten samples.

MEASUREMENT:

23. Set spectrometer to conditions specified by manufacturer.
24. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, re-analyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

25. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
26. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (µg/cm^2), of each element on the surface area sampled, S (cm^2):

$$C = \frac{C_s V_s - C_b V_b}{S}, \mu g / cm^2.$$

EVALUATION OF METHOD:

This method was evaluated using wipe media spiked with aqueous standards (fortified samples) and wipe media spiked with SRM 2711 (Montana Soil). Recoveries for the twenty-three elements listed on page 9201-1 were within the range of 75-115% for the fortified samples. Ten of the elements found in SRM 2711 were recoverable within the same range. These are: silver, arsenic, cadmium, cobalt, copper, manganese, nickel, phosphorus, lead, and zinc.

Because this method is a simultaneous elemental analysis, it is not compound specific. The data provided is for those compounds compatible with the acids used in the digestion. Verification of the solubility of specific compounds of interest should be completed and the sample matrix carefully examined. For example, if silicates are present total elemental values will not be measured without the use of hydrofluoric acid in the digestion process.

REFERENCES:

[1] NIOSH [1994]. Elements by ICP, Method 7300 in: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed., Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 94-113.
[2] ASTM [2002]. Annual Book of ASTM Standards, Standard Specification for Wipe Sampling Materials for Lead in Surface Dust. West Conshohocken, PA: ASTM International, E 1792-01.
[3] ASTM [2002]. Annual Book of ASTM Standards, Standard Practice for Field Collection of Settled Dust Samples Using Wipe Sampling Methods for Lead Determination by Atomic Spectrometry Techniques. West Conshohocken, PA: ASTM International, E 1728-99.

METHOD WRITTEN BY:

Ronnee N. Andrews, Mark Millson, and Donald D. Dollberg, NIOSH/DART

TABLE 1. PROPERTIES

Element (Symbol)	Atomic Weight	MP (° C)	CAS #	RTECS
Silver (Ag)	107.87	961	7440-22-4	VW3675000
Arsenic (As)	74.92	817	7440-38-2	CG0525000
Barium (Ba)	137.33	725	7440-39-3	CQ8370000
Beryllium (Be)	9.01	1287	7440-41-7	DS1750000
Cadmium (Cd)	112.41	321	7440-43-9	EU9800000
Cobalt (Co)	58.93	1493	7440-48-4	GF8750000
Chromium (Cr)	52.00	1900	7440-47-3	GB4200000
Copper (Cu)	63.54	1083	7440-50-8	GL5325000
Iron (Fe)	55.85	1535	7439-89-6	NO4565500
Lanthanum (La)	138.91	920	7439-91-0	
Manganese (Mn)	54.94	1244	7439-96-5	OO9275000
Molybdenum (Mo)	95.94	2622	7439-98-7	QA4680000
Nickel (Ni)	58.69	1555	7440-02-0	QR5950000
Phosphorus (P)	30.97	44	7723-14-0	TH3495000
Lead (Pb)	207.2	328	7439-92-1	OF7525000
Selenium (Se)	78.96	217	7782-49-2	VS7700000
Strontium (Sr)	87.62	769	7440-24-6	WK7849000
Tellurium (Te)	127.60	450	13494-80-9	WY2625000
Thallium (Tl)	204.38	304	7440-28-0	XG3425000
Vanadium (V)	50.94	1917	7440-62-2	YW1355000
Yttrium (Y)	88.91	1509	7440-65-5	ZG2980000
Zinc (Zn)	65.39	420	7440-66-6	ZG8600000
Zirconium (Zr)	91.22	1857	7440-67-7	ZH7070000

TABLE 2. WAVELENGTH, LIMITS OF DETECTION (LOD), RANGE & PRECISION

Element (Symbol)	Wavelength (nm)	Instrumental LOD (µg/wipe)	Range (µg/wipe)	Precision* (S_r)
Silver (Ag)	328	0.035	0.118-25.0	0.0701
Arsenic (As)	189	0.078	0.261-105.	0.0549
Barium (Ba)	455	0.010	0.0333-10.0	0.0370
Beryllium (Be)	313	0.010	0.0333-10.0	0.0267
Cadmium (Cd)	226	0.010	0.0333-41.7	0.0273
Cobalt (Co)	228	0.010	0.0333-10.0	0.0301
Chromium (Cr)	267	0.010	0.0333-10.0	0.0287
Copper (Cu)	324	0.042	0.141-114.	0.0317
Iron (Fe)	259	0.074	0.246-50.0	0.0516
Lanthanum (La)	408	0.018	0.0593-25.0	0.0279
Manganese (Mn)	257	0.010	0.0333-638.	0.0333
Molybdemum (Mo)	202	0.010	0.0333-10.0	0.0441
Nickel (Ni)	231	0.010	0.0340-20.6	0.0629
Phosphorus (P)	178	0.043	0.142-860.	0.128
Lead (Pb)	168	0.042	0.141-1160	0.0267
Selenium (Se)	196	0.10	0.338-75.0	0.0364
Strontium (Sr)	407	0.010	0.0333-10.0	0.0368
Tellurium (Te)	214	0.047	0.156-50.0	0.0359
Thallium (Tl)	190	0.041	0.136-50.0	0.0256
Vanadium (V)	292	0.010	0.0333-25.0	0.0284
Yttrium (Y)	371	0.010	0.0333-10.0	0.0280
Zinc (Zn)	213	0.77	2.56-350.	0.101
Zirconium (Zr)	339	0.026	0.0877-10.0	0.344

* Values were obtained with a Spectro ICP-AES; LOD may vary with instrument and should be independently verified.

ESTERS 1 1450

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

METHOD: 1450, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 March 2003

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

PROPERTIES: Table 1

COMPOUNDS:

n-amyl acetate	1-butyl acetate	isobutyl acetate	ethyl acrylate
2-ethoxyethyl acetate	methyl isoamyl acetate	n-butyl acetate	
n-propyl acetate	sec-butyl acetate	isoamyl acetate	

SYNONYMS: See Table 1

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ OSHA PEL
-MAX: 10 L

SHIPMENT: Refrigerated

SAMPLE STABILITY: See EVALUATION OF METHOD

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 2x OSHA PEL[1]

ACCURACY: See EVALUATION OF METHOD

BIAS: See EVALUATION OF METHOD

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

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Compounds referenced above

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 200 - 225 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 50 °C for 2 minutes, then up to 110 °C at a rate of 5 °C per minute, holding at 110 °C for 3 minutes.

CARRIER GAS: 4 mL/min, Helium

COLUMN: Capillary, fused silica, 30m x 0.32-mm ID; 0.5 µm film DB-Wax or equivalent.

CALIBRATION: Solutions of compounds in CS_2

RANGE: See EVALUATION OF METHOD and Table 1.

LOD: See EVALUATION OF METHOD

PRECISION ($\hat{S}_r$): See EVALUATION OF METHOD [1]

APPLICABILITY: This method can be used for simultaneous analysis of all analytes. High humidity greatly reduces sampler capacity and breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This method, NMAM 1450, Issue 3 is an updated analytical procedure [5]. This method originally combined and replaced the NMAM 2nd edition Methods S31, S32, S35, S37, S41, S44 through S48, and S51 [3]. Estimated LOD for each analyte is approximately 10 times lower than that of the previous methods.

REAGENTS:

1. Desorbing solution: Carbon disulfide* (chromatographic grade) with 0.05% (v/v) n-hexane or other suitable internal standard.
2. Analyte, reagent grade.
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front - 100 mg; back - 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1450-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-µL, readable to 0.1 µL, 25-, 50- and 100-µL.
7. Volumetric flasks, 10-mL.
8. Pipet, volumetric, 1-mL, with pipet bulb or repipet.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood. Wear appropriate protective clothing and gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler tube in line.
2. Break the ends of the sampler tube immediately before sampling. Attach sampler tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 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 desorbing solution to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.
   NOTE: The desorption efficiency of 2-ethoxyethyl acetate has been found to decrease with the resident time of the desorbed solution with charcoal [4]. After 30 min desorption transfer the supernatant solution of 2-ethoxyethyl acetate to a clean 2-mL vial and seal with a crimp cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.001 to 10 mg analyte per sample.
   a. Add known amounts of analyte to desorbing solution in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs.mg analyte).

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1450-1. Inject sample aliquot with autosampler, or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with desorbing solution, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Previous Evaluation

The original methods for S31 (sec-amylacetate), S47 (n-butyl acetate), S46 (sec-butylacetate), S32 (t-butyl acetate), S41 (2-ethoxy acetate), S35 (ethyl acrylate), S45 (isoamyl acetate), S44 (isobutyl acetate), S37 (methyl isoamyl acetate), S48 (n-propyl acetate) were issued on December 6, 1974, except for S51 (n-amyl acetate), which was issued on January 17, 1975 [3]. Atmospheres of each compound were generated in dry air by calibrated syringe drive and 10-L air samples were taken [1]. Collection efficiency in humid air and sample storage stability were not tested. Spiked samplers were used to study measurement precision and desorption efficiency (DE).

Current Evaluation

Methods for esters (n-amyl acetate, n-butyl acetate, sec-butyl acetate, t-butyl acetate, 2-ethoxyethyl acetate, ethyl acrylate, isoamyl acetate, isobutyl acetate, methyl isoamyl acetate, n-propyl acetate) were evaluated [5] using analytes fortified on Anasorb CSC sorbent tubes (Lot #2000). Desorption efficiency (DE) and precision are shown in Table 2. Sec-amyl acetate was evaluated in the previous issue of this method but it was not included in this current update.

Storage stability studies were performed on Anasorb CSC tubes (Lot #2000) at approximately 150 µg each analyte/sample. The samples were stored for up to 30 days at 4 °C. The recoveries of 30-day storage are summarized in Table 2.

REFERENCES:

[1] NIOSH [1977]. Documentation of the NIOSH Validation Tests. U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185.
[2] UTBL [1983]. UTBL user check, NIOSH Sequence #4121-N (unpublished), November 15.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd ed., V.2., U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-157-B.
[4] Corelson D [1988]. Menlo Park, CA., SRI. Personal communication with NIOSH.
[5] Yoon YH, Perkins JB, Reynolds JM [2002]. Back-up Data Report for Esters 1, DataChem Laboratories, Inc. under NIOSH contracts CDC-200-95-2955 and CDC 200-2001-08000.

PREVIOUS REVISION BY:

Robert W. Kurimo, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC 99-74-45.

METHOD REVISED BY:

Young Hee Yoon, Ph.D., James B. Perkins and John M. Reynolds, DataChem Laboratories, Inc., Salt Lake City, Utah.

Table 1. General Information

Compound, Formula and RTECS	Synonyms	M.W.	OSHA/NIOSH/ACGIH, ppm	BP, °C	VP @ 20 °C, kPa (mm Hg)	Liquid Density, g/mL @ 20 °C
n-amyl acetate $CH_3COO(CH_2)_4CH_3$; $C_7H_{14}O_2$ AJ1925000	acetic acid 1-pentanol ester; CAS #628-63-7	130.18	TWA (STEL) 100/100/100	149	0.5(4)	0.876
sec-amyl acetate $CH_3COOCHCH_3(CH_2)_2CH_3$; $C_7H_{14}O_2$ AJ2100000	acetic acid 2-pentanol ester; CAS #626-38-0	130.18	125/125/125	134	0.9(7)	0.866
n-butyl acetate $CH_3COO(CH_2)_3CH_3$; $C_6H_{12}O_2$ AF7350000	acetic acid butyl ester; CAS #123-86-4	116.16	150/150(200)/150(200)	126	1.3(10)	0.883
sec-butyl acetate $CH_3COOCH(CH_3)CH_2CH_3$; $C_6H_{12}O_2$ AF7380000	acetic acid 1-methyl propyl ester; CAS #105-46-4	116.16	200/200/200	112	1.3(10)	0.865
t-butyl acetate $CH_3COOC(CH_3)_3$; $C_6H_{12}O_2$ AF7400000	acetic acid 1, 1-dimethylethyl ester; CAS #540-88-5	116.16	200/200/200	98	not available	0.867
2-ethoxyethyl acetate $CH_3COO(CH_2)_2OCH_2CH_3$; $C_6H_{12}O_3$ KK8225000	Cellosolve acetate; acetic acid ethylene glycol monoethyl ether ester; CAS #111-15-9	132.16	100[a]/0.5[a]/5[a]	156	0.3(2)	0.973
ethyl acrylate $CH_2=CHCOOCH_2CH_3$; $C_5H_8O_2$ AT0700000	2-propenoic acid ethyl ester; CAS #140-88-5	100.11	25[a]/4 LOQ[b]/5[ab](15 ppm)	99	3.9(30)	0.923
isoamyl acetate $CH_3COO(CH_2)_2CH(CH_3)_2$; $C_7H_{14}O_2$ NS9800000	acetic acid 3-methyl-1-butanol ester; CAS #123-92-2	130.18	100/100/100	142	0.5(4)	0.876
isobutyl acetate $CH_3COOCH_2CH(CH_3)_2$; $C_6H_{12}O_2$ AI4025000	acetic acid isobutyl ester; CAS #110-19-0	116.16	150/150/150	117	1.7(13)	0.871
methyl isoamyl acetate $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$; $C_8H_{16}O_2$ SA7525000	acetic acid 4-methyl-2-pentanol ester; 1,3-dimethyl butyl acetate; "sec-hexyl acetate;" CAS #108-84-9	144.22	50/50/50	146	0.5(3.8)	0.858
n-propyl acetate $CH_2COO(CH_2)_2CH_3$; $C_5H_{10}O_2$ AJ3675000	acetic acid n-propyl ester; CAS #109-60-4	102.13	200/200 (250)/200 (250)	102	3.3(25)	0.890

[a] Skin

[b] Carcinogen

Table 2. Current Method Evaluation

	Overall Method					Analytical Method				Storage Stability Study	
Compound	Range (mg/m^3)	Accuracy	Breakthrough[1] at 2 x OSHA PEL (≤)	Bias (%)	S_{RT}	Range Studied (µg/sample)	LOD (µg/sample)	Average DE	Measurement Precision ($\hat{S}_r$)	Levels (µg/sample)	Recovery (%)
n-amyl acetate	208-871	0.163	34.2 L	0.3	0.0831	14-440	0.9	0.96	0.0072	140	98
n-butyl acetate	352-1475	0.136	20.5 L	0.3	0.0691	15-440	0.9	0.96	0.0087	140	98
sec-butyl acetate	478-2005	0.116	16.5 L	-2.4	0.0539	14-440	0.9	0.97	0.0062	140	98
t-butyl acetate	424-1780	0.234	14.3 L	-8.6	0.0897	14-430	0.9	0.98	0.0052	140	98
2-ethoxyethyl acetate	262-1100	0.203	34.6 L	-9.6	0.0648	16-340	1	0.82	0.020	160	96
ethyl acrylate	50-210	0.162	>45 L	-7.1	0.0550	31-300	2	0.86	0.015	150	90
isoamyl acetate	208-874	0.195	32.3 L	-7.1	0.0750	14-430	0.9	0.97	0.0066	140	98
isobutyl acetate	306-1280	0.133	21.5 L	1.8	0.0656	14-440	0.9	0.97	0.0084	140	98
methyl isoamyl acetate	143-601	0.126	>45 L	-2.6	0.0590	14-280	0.9	0.81	0.015	140	95
n-propyl acetate	384-1610	0.162	17.9 L	6.9	0.0566	15-450	0.9	0.95	0.0091	140	98

[1]The values for these categories were taken from the original methods validation, see ref [1].

ESTROGENIC COMPOUNDS 5044

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

METHOD: 5044, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

Synonyms: Table 2

SAMPLING

SAMPLER:	FILTER, PTFE (37-mm, 2-µm)
FLOW RATE:	1 L/min
VOL.-MIN:	150 L
-MAX:	1000L
SHIPMENT:	Ship at ambient temperature.
SAMPLE STABILITY:	30 days at 25 °C [1]
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	Not determined
BIAS:	Not determined
OVERALL PRECISION(S_{rT}):	Not determined
ACCURACY:	Not determined

MEASUREMENT

TECHNIQUE:	HPLC, UV detection
ANALYTE:	See Table 1
EXTRACTION:	Methanol, extraction overnight at room temperature
INJECTION VOLUME:	25 µL
MOBILE PHASE:	60% acetonitrile / 40% water @ 26 °C, 1.75 mL/min
COLUMN:	C18 reversed phase, 150 x 4.6-mm, 5-µm; in-line pre-filter, 2.0- µm
DETECTOR:	UV/Vis at 200 nm and 237 mµ
CALIBRATION:	Standards in methanol
RANGE:	β-Estradiol 0.3 to 44 µg/sample Estrone 0.2 to 64 µg/sample Progesterone 0.5 to 64 µg/sample β-Estradiol 3-Benzoate 0.5 to 64 µg/sample [1]
ESTIMATED LOD:	Table 3
PRECISION (S_r):	β-Estradiol 0.040 Estrone 0.039 Progesterone 0.030 β-Estradiol 3-Benzoate 0.032 @ 0.5 - 64 µg/sample [1]

APPLICABILITY: This method has not been used to evaluate field air samples. The method is based on a preliminary investigation analyzing field wipe samples collected during a health hazard evaluation at a facility producing birth control pills [1]. Appendix 1 contains information on recovery of analytes from wipe samples.

INTERFERENCES: Any compound that elutes at the same HPLC retention times may interfere.

OTHER METHODS: No validated methods were found.

REAGENTS:

1. Water, distilled, deionized, degassed
2. Acetonitrile, HPLC grade, degassed.*
3. Methanol, HPLC grade.*
4. β-Estradiol (Sigma E8875 or equivalent)*
5. Estrone (Sigma E9750 or equivalent)*
6. Progesterone (Sigma P0130 or equivalent)*
7. β-Estradiol 3-Benzoate (Sigma E8515 or equivalent)*
8. Stock standard solutions: place approximately 40 mg of each analyte, weighed to 0.001 mg, in separate 20-mL vials and dissolve in 20-mL methanol.
9. Estrogen mixed standards: combine 4 mL of each stock standard solution in a 20-mL vial. Prepare serial dilutions of this mixture in methanol to 0.05 µg/mL.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Filters: PTFE-laminate, 37-mm, 2-µm pore size (SKC Inc., Cat No. 225-17-07 or equivalent), cellulose spacer ring, 37-mm OD, 32-mm ID (SKC Inc., Cat. No. 225-23 or equivalent) in a 37-mm cassette filter holder.
2. Culture tubes, PTFE-lined screw cap, 16-mm x 100-mm.
3. Vials, auto-sampler, 4-mL, with PTFE-lined septa.
4. Pipets, volumetric (0.5- to 20-mL)
5. Vials, PTFE-lined screw cap, 20-mL.
6. Forceps.
7. Hamilton syringes, 50-µL and 100-µL.
8. Syringe, disposable, 10-mL.
9. Syringe filter, PTFE, 0.45-µm
10. HPLC with integrator and autosampler; UV/Vis detectors in series (200-nm and 237-nm); C18 column, 150x4.6-mm (Alltima; Alltech Associates Inc., State College PA, Cat. No. 88053, or equivalent); in-line pre-filter, 2.0 µm (Opti-Solv; Optimize Technologies, or equivalent).
11. Rotator, rotating tube shaker (Labquake-Thermolyne or equivalent).

SPECIAL PRECAUTIONS: Acetonitrile and methanol are flammable and health hazards. Methanol is a cumulative poison. Estrogenic compounds may be carcinogens [3]. Handle in a well ventilated hood and wear protective clothing.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 1 L/min for a total sample size of 150 to 1000 L.
3. Pack filter cassettes securely for shipment (unrefrigerated).
4. Store samples at ambient temperature upon receipt at the laboratory.

SAMPLE PREPARATION:

5. Remove each filter from the cassette holder, roll with forceps and place in a 16 x 100 mm culture tube.
6. Add 4.0 mL methanol to each tube.
7. Prepare media and reagent blanks in the same manner.
8. Cap each tube tightly and place on rotator. Rotate ≥8 hr at room temperature.
9. Filter extracts, if necessary, using a disposable syringe fitted with a 0.45-µm PTFE filter into a clean vial.
10. Transfer all extracts to labeled autosampler vials.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards over the range of interest.
    a. Prepare serial dilutions of the stock mixture in the range of 0.08 to 80 µg/mL
    b. Analyze with samples and blanks (steps 15 and 16).
    c. Prepare a calibration graph (peak area vs mass of analyte, µg per sample).

12. Determine the desorption efficiency and recovery in the range of interest for each lot of filters used for sampling.
    a. Prepare four tubes at each of three levels plus three media blanks.
    b. Add known amounts of the analyte or analyte mixture in methanol to the filters.
    c. Allow to stand >2 hr for solvent evaporation.
    d. Prepare samples (steps 6 through 10) and analyze together with standards (steps 15 and 16).
    e. Determine recovery.
13. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

MEASUREMENT:

14. Set HPLC according to manufacturer's instructions and conditions on page 5044-1.
15. Inject sample aliquot manually or with autosampler.
16. Measure peak areas.

CALCULATIONS:

17. Determine the mass in µg of analytes found on the sample filter, W, and on the average blank filter, B.
18. Calculate concentration, C, of analytes in the air volume sampled, V (L):

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

This method has been used to analyze field-generated wipe samples [2]. It was not evaluated with laboratory-generated air samples. LOD/LOQ, extraction efficiency, sampling stability and storage stability studies were performed with laboratory-spiked filters.

LOD/LOQ values (in µg/filter) for β-Estradiol were 0.8/2.5; for Estrone, 0.2/0.5; for Progesterone, 0.5/1.7; and for β-Estradiol 3-Benzoate, 0.5/1.7.

Extraction efficiency for β-Estradiol ranged from 94 to 103%; for Estrone, 95 to 104%; for Progesterone; 97 to 102%; for β-Estradiol 3-Benzoate, 95 to 101%. An additional recovery study using Wash 'n Dri® wipes gave extraction efficiencies of 97 to 100%.

The stability of the analytes on the filter media (static efficiency) was evaluated by drawing air through spiked filters. Recoveries ranged from 94 to 102% for β-Estradiol; for Estrone, from 96 to 101%; for Progesterone, from 99 to 102%; and for β-Estradiol 3-Benzoate, from 92 to 101%.

Recovery after 30-day storage at 25 °C was 93% for β-Estradiol, 94% for Estrone, 98% for Progesterone, and 111% for β-Estradiol 3-Benzoate.

REFERENCES:

[1] Mathews ES and Neumeister CE [2000]. Backup Data Report for Method 5044, Estrogenic Compounds by HPLC (unpublished), NIOSH, DART.
[2] Neumeister CE [1983]. Analytical Report for Sequence 1400. Cincinnati, OH: National Institute of Occupational Safety and Health (unpublished).
[3] Sixth Annual Report on Carcinogens [1991]. USDHHS/PHS, National Toxicology Program

METHOD WRITTEN BY: Elaine S. Mathews and Charles E. Neumeister NIOSH, DART

TABLE 1. PROPERTIES

Compound	Formula	M.W.	M.P. (°C)	UV Max (nm)
β-Estradiol	$C_{18}H_{24}O_2$	272	173-179	206
Estrone	$C_{18}H_{22}O_2$	270	254-256	198
Progesterone	$C_{21}H_{30}O_2$	314	127-131	237
β-Estradiol-3-Benzoate	$C_{25}H_{28}O_3$	376	191-196	201

TABLE 2. GENERAL INFORMATION

Compound	Synonyms	CAS	RTECS	Exposure Limit
β-Estradiol	dihydroxyfollicular hormone dihydroxyestrin oestra-1,3,5(10) triene-3,17-betadiol	50-28-2	KG2975000	None Specified
Estrone	3-hydroxyestra-1,3,5(10)-trien-17-one 1,3,5-estratrien-3-ol-17-one oestrone folliculin	53-16-7	1009137ES	None Specified
Progesterone	pregn-4-ene-3,20-dione luteohormone Corlutin	57-83-0	TW0175000	None Specified
β-Estradiol-3-Benzoate	estradiol benzoate oestradiol monobenzoate (17β)-estra-1,3,5(10)-triene-3,17-diol 3-benzoate Benovocylin	50-50-0	KG4050000	None Specified

TABLE 3. LOD/LOQ DETERMINATION

Compound	LOD µg/filter	LOQ µg/filter
β-Estradiol	0.8	2.5
Estrone	0.2	0.5
Progesterone	0.5	1.7
β-Estradiol 3-Benzoate	0.5	1.7

APPENDIX 1: PREPARATION OF SPIKES ON WIPES:

Wipe media (Wash 'n Dri® Moist Disposable Towelettes) were opened and spread to evaporate to dryness. Dried towelettes were rolled and inserted into 16x100-mm PTFE-lined screw cap tubes. A Hamilton syringe was used to place measured amounts of stock solution in methanol (50 µL containing 40 µg of each analyte) on each wipe. After allowing the spikes to evaporate, 8 mL of methanol was added to each tube, and the tubes were capped and rotated overnight at room temperature to extract the spiked analyte from the wipes.

EFFICIENCY OF EXTRACTION:

Compound	Efficiency of Extraction (%) (n=6)	S_r
β-Estradiol	100	1.4
Estrone	97	3.1
Progesterone	99	0.82
β-Estradiol 3-Benzoate	99	0.76

ETHYL ETHER 1610

$(C_2H_5)_2O$ MW: 74.14 CAS: 60-29-7 RTECS: KI5775000

METHOD: 1610, Issue 3 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 3: 15 March 2003

OSHA : 400 ppm
NIOSH: no REL
ACGIH: 400 ppm; STEL 500 ppm

(1 ppm = 3.03 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.7134 g/mL @ 20 °C; BP 34.6 °C; MP - 116 °C; VP 59 kPa (440 mm Hg; 58% v/v) @ 20 °C; explosive range 1.7 to 48% v/v in air

SYNONYMS: diethyl ether; 1,1'-oxybisethane; ethyl oxide

SAMPLING

SAMPLER: Solid Sorbent Tube (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.25 L @ 400 ppm
-MAX: 3 L

SHIPMENT: routine

SAMPLE STABILITY: 14 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 606 to 2400 mg/m³ (3-L samples)[2]

BIAS: 5.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.088

ACCURACY: ± 20%

MEASUREMENT

TECHNIQUE: GAS CHROMOTOGRAPHY, FID

ANALYTE: ethyl ether

DESORPTION: 1.0 mL CS_2; 30 min with agitation

INJECTION VOLUME: 1 µL

TEMPERATURE:
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (1 min) - 150 °C @ 10 °C/minute, (split 5:1)

CARRIER GAS: helium (1-2 mL/min)

COLUMN: capillary, fused silica 30 m x 0.32-mm ID; 1-µm film 100% dimethyl polysiloxane, Rtx-1 or equivalent

CALIBRATION: solutions of ethyl ether in CS_2

RANGE: 2 to 430 µg per sample (capillary column); 1800 to 7100 µg per sample (packed column)

ESTIMATED LOD: 0.2 µg per sample

PRECISION ($\hat{S}_r$): 0.071 @ 9 to 400 µg per sample

APPLICABILITY: The working range is 100 to 2700 mg/m³ (33 to 880 ppm) for a 3-L air sample. During sampling, high humidity may greatly decrease the breakthrough volume. A sampling period of 15 min may be monitored for STEL compliance using a flow rate of 0.2 L/min.[3]

INTERFERENCES: Any compound, such as pentane, with similar retention times.

OTHER METHODS: This revises Method S80 [4] and NMAM 1610 (issue 2) [4].

REAGENTS:

1. Carbon Disulfide, low benzene grade.*
2. Ethyl ether, reagent grade.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front=100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (see page 1610-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, 25-µL, 250-µL.
6. Flasks, volumetric 10-mL.
7. Pipet, volumetric, 1-mL with pipet bulb.

SPECIAL PRECAUTIONS: Ethyl ether is a dangerous fire and explosion hazard (flash point = -45 °C) and tends to form explosive peroxides. Carbon disulfide is toxic and flammable (flash point = -30 °C). Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.25 to 3 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Include the glass wool plug in the vial with the front sorbent section.
6. Add 1.0 mL carbon disulfide to each vial. Attach cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of ethyl ether to carbon disulfide in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards as needed by serial dilution.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg ethyl ether per sample).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Remove and discard the back sorbent section of a blank sampler.
   c. Inject a known amount (1 to 20 µL) of ethyl ether or a standard solution of ethyl ether in carbon disulfide directly onto the front sorbent section with a microliter syringe.
   d. Cap the tube. Allow to stand overnight.
   e. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   f. Prepare a graph of DE vs. µg ethyl ether recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1610-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed sample with carbon disulfide, reanalyze, and apply the appropriate dilution factor in the calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Issues 1 and 2

Method S80 was issued on February 14, 1975 [4], and evaluated over the range 630 to 2500 mg/m^3 at 22 °C and 766 mm Hg for 3-L air samples desorbed in 0.5 mL ethyl acetate [2]. The concentrations were verified by using a total hydrocarbon analyzer. Breakthrough (5% on the backup section) occurred at 33 min when sampling a concentration of 2470 mg/m^3 in dry air at a flow rate of 0.185 L/min., corresponding to a capacity of 15 mg. The average DE was 98% over the range 1.8 to 7.1 mg ethyl ether per sample. Sample storage stability was not determined.

Issue 3

The sensitivity of this method for ethyl ether was lowered to cover a range from approximately 10 times the LOQ (based upon an improved LOD of 0.2 µg/sample) to 500 times (0.25 REL) the LOQ. The desorption efficiency was tested at four levels over the range of 8 - 428 µg/sample. The average recovery for ethyl ether over this range was 102.5%. A 30-day storage stability study for ethyl ether was completed during the method development. The storage stability was determined at a level approximately 0.2 REL. The analyte was determined to be stable for 14 days when stored at 5°C with an average recovery of 90.3% [1].

REFERENCES:

[1] Pendergrass SM, May LR [2000]. NMAM 1610, Issue 3, Backup Data Report. Cincinnati, OH: National Institute for Occupational Safety & Health, DART (unpublished), April.
[2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S80, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185, available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[3] NIOSH/OSHA [1981]. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, January 1981, Publ. (NIOSH) 81-123, available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
[4] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S80, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B. S80 originally validated under NIOSH Contract CDC-99-74-45.

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Method originally written by Robert W. Kurimo, NIOSH/DART.

FORMALDEHYDE 2016

$H_2C=O$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2016, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 January 1998 **Issue 2:** 15 March 2003

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/m³ @ NTP)

PROPERTIES: Gas; BP -19.5 °C; specific gravity 1.067 (air = 1); explosive range 7 to 73% (v/v) in air

NAMES & SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v formaldehyde); methylene oxide

SAMPLING

SAMPLER: CARTRIDGE
(Cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine)

FLOW RATE: 0.03 to 1.5 L/min

VOL-MIN: 1 L @ 0.25 mg/m³
-MAX: 15 L @ 2.5 mg/m³

SHIPMENT: Place caps onto cartridge. Ship on ice.

SAMPLE STABILITY: 34 days @ 5 °C [1]

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

ACCURACY

RANGE STUDIED: 0.025 to 2.45 mg/m³ (22-L samples) [2]

BIAS: +4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1,2]

ACCURACY: ±19.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone of formaldehyde

EXTRACTION: Elution with 10 mL of carbonyl-free acetonitrile

INJECTION VOLUME: 20 µL

MOBILE PHASE: 45% acetonitrile/55% water (v/v), 1.3 mL/min

COLUMN: 3.9 x 150-mm, stainless steel, packed with 5-µm C-18, Symmetry™ or equivalent

DETECTOR: UV @ 360 nm

CALIBRATION: Samplers fortified with standard solutions of formaldehyde in water

RANGE: 0.23 to 37 µg per sample [1,2]

ESTIMATED LOD: 0.07 µg/sample [1]

PRECISION ($\hat{S}_r$): 0.032 @ 1.0 to 20.0 µg/sample [1]

APPLICABILITY: The working range is 0.015 to 2.5 mg/m³ (0.012 to 2.0 ppm) for a 15-L sample. This method can be used for the determination of formaldehyde for both STEL and TWA exposures [1,2].

INTERFERENCES: Ozone has been observed to consume the 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent and to degrade the formaldehyde derivative [3]. Ketones and other aldehydes can react with 2,4-DNPH; the derivatives produced, however, are separated chromatographically from the formaldehyde derivative.

OTHER METHODS: NIOSH methods 2541 [4] and 3500 [5] and OSHA method 52 [6] are other methods for determination of formaldehyde in air. NIOSH method 5700 employs 2,4-DNPH and HPLC for determination of formaldehyde on textile or wood dust [7]. A journal method employs the same procedure for formaldehyde in automobile exhaust [8].

REAGENTS:

1. Formaldehyde stock solution,* aqueous, standardized, 1 mg/mL (see APPENDIX A). Alternatively, standardized formaldehyde solution, aqueous, 4 mg/mL, is available commercially from Hach Co., Loveland, CO.
2. Acetonitrile,* distilled in glass, low carbonyl content.**
3. Water, deionized and distilled.
4. Sulfuric acid, 0.02 N (pH standardization procedure) or 0.1 N (colorimetric procedure).
5. Sodium hydroxide, 0.01 N.
6. Sodium sulfite (Na_2SO_3), 1.13 M (pH procedure) or 0.1 M (colorimetric procedure). Prepare fresh immediately before use.
7. Thymophthalein indicator solution, 0.04% (w/v) in 50:50 ethanol:water.

* See SPECIAL PRECAUTIONS.

** Carbonyl content of acetonitrile can be determined by passing 10 mL of the solvent through a cartridge of DNPH-coated silica gel and analyzing by HPLC. Formaldehyde content should be below the LOD.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 150-250 µm (60-100 mesh) silica gel coated with 1.0 mg of acidified 2,4-dinitrophenylhydrazine. Pressure drop across sampler should be less than 28 inches of water (7 kPa) at 1.5 L/min. Samplers are commercially available, [Supelco S10 LpDNPH cartridge, cat. No. 2-1014; Waters Corp. Sep-Pak XPoSure Aldehyde Sampler, part No.WATO47205; see APPENDIX B for SKC sampler].
2. Personal sampling pump, 0.03 to 1.5 L/min with flexible connecting tubing.
3. Vials, 4-mL, glass with PTFE-lined rubber septa caps.
4. Vials, 20-mL, glass.
   NOTE: Do not use vials with "polycone" liners (sources of high formaldehyde blanks)[5,9].
5. Liquid chromatograph with UV detector, recorder, integrator, and column (page 2016-1).
6. Syringes, 100-µL, 500-µL and 10-mL.
7. Volumetric flasks, 10-mL, 25-mL, and 1-L.
8. Burets, 50-mL.
9. pH meter.
10. Magnetic stirrer.
11. Beaker, 50-mL.
12. Flask, Erlenmeyer, 250-mL.
13. Ozone scrubber (Waters Corp.)(optional).
14. Aluminum foil or black electrical tape (optional).

SPECIAL PRECAUTIONS: Formaldehyde is a suspect carcinogen and a proven human sensitizer; it should be handled in a fume hood [10-12].
Acetonitrile is toxic and is a fire hazard (flash point = 12.8 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler (and ozone scrubber, if used) in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. The Waters sampler is bi-directional and can be connected at either end.
   NOTE: The sampler does not have a backup section for determination of breakthrough. If high concentrations of aldehydes and ketones are anticipated, connect two samplers in series. The back pressure of the sampling train will be higher and a lower flow rate may be required.
4. Sample 1 to 15 L of air at 0.03 to 1.5 L/min.
   NOTE: To protect from intense light, such as bright sunlight, the sampler can be wrapped with aluminum foil or electrical tape.
5. Place end caps onto the sampler and seal sampler in an envelope. Protect samples from heat.
6. Ship samples on ice (0 °C).

SAMPLE PREPARATION:

NOTE: Check acetonitrile for formaldehyde content by elution and analysis of a blank cartridge; the formaldehyde level should be below the detection limit. Since background levels of formaldehyde on the samplers may change during storage, compare samples with sampler blanks from the same lot. Samples and blanks should be stored under the same conditions.

7. Elute the formaldehyde derivative from the cartridge samplers with 10-mL quantities of acetonitrile.
   a. Collect effluent from each sampler in a 10-mL volumetric flask.
   b. Add acetonitrile to the mark for each sampler.
      NOTE: The silica gel bed of the sampler will retain approximately 0.5 mL of the original 10 mL.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six media working standards over the range of interest.
   a. Prepare a series of aqueous formaldehyde solutions for the fortification of samplers. Suggested concentrations include 1, 4, and 20 µg/mL. See APPENDIX A for standardization of formaldehyde in water.
   b. Connect the outlet of a cartridge sampler to a personal sampling pump with flexible tubing. Turn on the pump and make sure there is a flow of air through the sampler.
   c. Load a 100-µL syringe with a selected volume of aqueous formaldehyde solution in the range of 30 to 90 µL. Suggested quantities of formaldehyde for spiking include 0.04, 0.10, 0.20, 0.30, 0.40, 0.80, 1.0 and 2.0 µg/sample.
   d. Place the tip of the syringe needle against the frit in the inlet of the sampler and eject the formaldehyde solution.
   e. Prepare the media working standard (steps 7.a and 7.b).
   f. Prepare additional working standards (steps 8.b. through 8.e.).
   g. Transfer 3-mL aliquots of working standards to 4-mL vials, and analyze (steps 10, 12 and 13).
   h. Prepare calibration graph, peak area or height vs. µg formaldehyde per sample.
9. Fortify and analyze three quality control spikes and three analyst spikes to ensure that calibration graph is in control.

MEASUREMENT:

10. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2016-1.
11. Transfer a 3-mL aliquot of the sample solution from step 7 to a 4-mL vial. Cap the vial.
12. Inject a 20-µL sample aliquot.
13. Measure peak area or peak height.
    NOTE 1: If sample peak is larger than the largest standard peak, dilute an aliquot of the remaining sample solution, reanalyze, and apply appropriate dilution factor in the calculations.
    NOTE 2: To ensure validity of the samples, identify those samples which contain more than 37 µg of formaldehyde. The capacity of the samplers before breakthrough may have been exceeded for these samples, and collection of smaller samples would be warranted.
    NOTE 3: The size of the 2,4-DNPH peak should be about 2.7 times the size of the formaldehyde-DNPH peak or larger. Otherwise, breakthrough from the sampler may have occurred.

CALCULATIONS:

14. Determine mass, µg, of formaldehyde, W, found in the sample and the average media blank, B, from the calibration graph.

15. Calculate concentration, C, of formaldehyde in the air volume sampled, V (L).

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

Issue 1

This method was originally evaluated with Waters Sep-Pak XPoSure Aldehyde samplers using data produced at NIOSH and at Waters Corporation [2]. Test atmospheres of formaldehyde were generated at Waters Corp. [2]. Overall measurement precision, $\hat{S}_{rT}$, was 0.057 based on NIOSH guidelines [13] including a 5% pump error factor and estimated bias of +4.4%. Sample storage stability was evaluated over the range of 0.5 to 55 µg formaldehyde/sample. Losses for Waters samplers were 4 to 8% when stored up to 14 days at 4 °C. An additional study with Waters samplers found that losses were 5% or less after 4 days of storage at ambient temperature. All calibration standards used at Waters Corporation were liquid standard solutions of formaldehyde-DNPH derivative in acetonitrile [2,14].

The capacity of DNPH-coated silica gel samplers was found to vary with relative humidity (RH) in addition to concentration of formaldehyde. At a formaldehyde concentration of 1.2 mg/m^3 and at 5% breakthrough, the Waters sampler had a capacity at <10% RH of 55 µg, and at >85% RH a capacity of 77 µg. At 2.4 mg/m^3 and <10% RH, the 5% breakthrough capacity of the Waters sampler was 59 µg of formaldehyde. At 2.6 mg/m^3 and >85% RH, the 5% breakthrough capacity was 106 µg. Thus, the smallest capacity at 5% breakthrough was 55 µg of formaldehyde; the upper limit of the range of the method is two thirds of 55 µg, or 37 µg. Capacity information for the Waters sampler is applicable to the Supelco sampler because (a) the Waters and Supelco samplers contain 0.9 and 1 mg of DNPH, respectively, and (b) each sampler contains 350 mg of silica gel.

Issue 2

In subsequent work on this method, additional formaldehyde samplers were evaluated, Supelco S10 LpDNPH cartridges and SKC, Inc. Aldehyde samplers (DNPH-coated silica gel tubes No.226-119) [1]. The sorbent beds of Supelco and Waters cartridges and front sections of SKC samplers were treated with acetonitrile. Formaldehyde was not detected on any blank sampler (LOD = 0.01 µg/mL). The SKC sampler for aldehydes may be used for formaldehyde with modifications of this method (See APPENDIX B). However, evaluation of the SKC sampler at NIOSH has been limited.

Supelco samplers were fortified with known quantities of free formaldehyde in water, and calibration was performed with media standards prepared from Supelco samplers fortified with known quantities of free formaldehyde in water; average recoveries ranged from 96.3% to 99.3% for five levels at 1.00 to 20 µg of formaldehyde per sampler (pooled S_r = 0.0316; n = 6 at each level).

In a storage study, six Supelco samplers were fortified with 4-µg quantities of free formaldehyde in water. Samplers were stored 34 days at 5 °C in the dark; the average recovery based on media standards was 99% (S_r = 0.014).

Eight media standards were prepared by fortification of Supelco samplers with solutions of free formaldehyde in water. The solutions were drawn through the DNPH-coated silica gel beds with an air pump. The resulting LOD and LOQ were 0.07 and 0.23 µg/sample, respectively, according to a least squares calibration graph.

Standard solutions of formaldehyde-DNPH at 0.10 and 1.0 µg/mL (formaldehyde equivalent concentrations) were stored in airtight vials at 5 °C in the dark and were analyzed periodically. The standard solutions were found to be stable (with no detectable loss) for at least 10 weeks and at least 12 weeks, respectively.

It is suggested that the reader see the Backup Data Report for a comparison of media standards with liquid standards for calibration [1]. Air sampling for a 24-hour period can be performed with a single Supelco sampler. Thus, background levels at <1 ppb can be determined.

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METHOD REVISED BY:

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Method originally written by P Iraneta, Waters Corp., MJ Seymour and ER Kennedy, Ph.D., NIOSH/DART.

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

Preparation. Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months when stored at room temperature.

Standardization by pH Titration.
Place 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 3.0 to 12.0 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:

$$Cs = \frac{30.0(N_a V_a - N_b V_b)}{V_s}, mg/mL$$

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 (mL)

Standardization by Colorimetric Titration.
Place 50 mL of freshly prepared 0.1 M sodium sulfite and 3 drops of 0.04% thymophthalein indicator (w/v) in 50:50 ethanol:water into a 250-mL Erlenmeyer flask. Titrate the contents of the flask to a colorless endpoint with 0.1 N sulfuric acid (usually 1 or 2 drops is sufficient). The indicator is blue at pH values above the endpoint and is colorless at pH values below the endpoint. Transfer 3.0 to 12.0 mL of the formaldehyde solution to the same flask and titrate the mixture with 0.1 N sulfuric acid to a colorless endpoint. Calculate the concentration, C (mg/mL), of formaldehyde in solution.

$$C = \frac{30.0(N_a V_a)}{V_s}, mg/mL$$

Where: 30.0 = g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.1 N)
V_a = volume of sulfuric acid used for titration (mL)
V_s = volume of formaldehyde stock solution (mL)

NOTE: Sulfuric acid (0.1 N) is substituted for 0.1 N hydrochloric acid, which is specified in OSHA Method 52, in order to prevent possible formation of bis(chloromethyl)ether, a potent carcinogen, by reaction of formaldehyde with hydrochloric acid [12].

This colorimetric titration was adapted from OSHA Method 52 [5], which was based on the procedure of Walker [15].

APPENDIX B - USE OF SKC SAMPLER FOR FORMALDEHYDE

The SKC, Inc. sampler for aldehydes (DNPH-coated silica gel tube, catalogue No. 226-119) may be used for sampling formaldehyde with modifications of this method. These modifications include the following:

(a) The maximum recommended air volume should be less than 15 L at an air concentration of 2.5 mg/m^3 (indicated on page 2016-1), because the upper limit of the method for the SKC sampler is probably less than 37 µg.

(b) The procedure for recovery of analyte from the sorbent would be modified, i.e., placement of the sorbent sections in vials, addition of solvent, and possible use of an ultrasonic bath.

(c) A volume of solvent much less than 10 mL can be used for recovery. However, the minimum volume should be tested for adequate recovery.

(d) Consequences of using a much smaller volume of solvent for recovery include a lower LOD and LOQ, the need for a different range of calibration standards, and the need for a different range of fortification levels (step 8).

(e) The maximum volume of solution for fortification of the front sorbent bed must be less than 90 µL and should be determined (step 8).

GLYCOL ETHERS

(1) $CH_3OCH_2CHOHCH_3$	MW: 90.1	CAS: 107-98-2	RTECS: UB7700000
(2) $CH_3OC_3H_6OC_3H_6OH$	148.2	34590-94-8	JM1575000
(3) $CH_3OCH_2CH(CH_3)COOCH_3$	132.16	108-65-6	AI8925000

METHOD: 2554 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: See Table I
NIOSH: See Table I
ACGIH: See Table I

PROPERTIES: See Table I

SYNONYMS: (1) propylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxy-1-methylethanol, propylene glycol methyl ether
(2) dipropylene glycol monomethyl ether
(3) propylene glycol monomethyl ether acetate, propylene glycol methyl ether acetate, 1-methoxy-2-propyl acetate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb® 747, 140 mg/70 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 25 L (at lower flow rates)

SHIPMENT: Keep cold, pack securely for shipping

SAMPLE STABILITY: 14 days @ 5°C for analytes 1 and 3; 7 days @ 5°C for analyte 2

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not determined.

BIAS: Not determined.

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: See Table I

DESORPTION: 1 mL of methylene chloride/methanol (85:15) for 30 minutes in ultrasonic bath

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 195°C
-DETECTOR: 240°C
-COLUMN: 90°C (1 min) to 200°C (10°C/min)

CARRIER GAS: Helium, 2.8 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 100% PEG-DA, Stabilwax or equivalent

CALIBRATION: Solutions of analytes in desorption solvent

RANGE: (1) 1.5 to 369 µg[3]
(2) 3.0 to 375 µg[3]
(3) 1.5 to 369 µg[3]

ESTIMATED LOD: (1) 0.5 µg[3]
(2) 1.0 µg[3]
(3) 0.5 µg[3]

PRECISION ($\bar{S}_r$): (1) 0.013[3]
(2) 0.031[3]
(3) 0.016[3]

APPLICABILITY: The working range for propylene glycol monomethyl ether was 0.041 to 10.0 ppm (0.154 to 36.9 mg/m^3), for dipropylene glycol monomethyl ether was 0.050 to 6.19 ppm (0.305 to 37.5 mg/m^3), and propylene glycol monomethyl ether acetate was 0.030 to 6.83 ppm (0.151 to 36.9 mg/m^3) for a 10 L sample . Other methods used for the collection of these analytes used a different solid sorbent and were evaluated at higher analyte concentrations [1,2]. Collection and DE recovery at levels greater than the working range listed should be equal or better than those achieved using charcoal sorbent tubes.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time as the analytes of interest may interfere.

OTHER METHODS: OSHA method 99 [1] and OSHA method 101 [2] can also be used for sampling glycol ethers at or above the REL and PEL. NIOSH Method S69, from the 2nd edition of the NIOSH Manual of Analytical Methods, was used previously for the collection and analysis of dipropylene glycol monomethyl ether and had acceptable recovery at a concentrations at or above the REL/PEL [4].

REAGENTS:

1. Propylene glycol monomethyl ether, reagent grade.*
2. Dipropylene glycol monomethyl ether, reagent grade.*
3. Propylene glycol monomethyl ether acetate, reagent grade.*
4. Methylene chloride, chromatographic grade.*
5. Methanol, chromatographic grade.*
6. Desorbing solution, 15% methanol in 85% methylene chloride (V/V).
7. Propylene glycol monomethyl ether calibration stock solution, 46.2 mg/mL. Dilute 0.5 mL analyte to 10 mL with desorbing solution.
8. Dipropylene glycol monomethyl ether calibration stock solution, 47.5 mg/mL. Dilute 0.5 mL analyte to 10 mL with desorbing solution.
9. Propylene glycol monomethyl ether acetate calibration stock solution, 48.5 mg/mL. Dilute 0.5 mL nitrobenzene to 10 mL with desorbing solution.
10. Air, compressed, purified, and filtered.
11. Helium, purified and filtered.
12. Hydrogen, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of Anasorb® 747 (140mg/70 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section. A urethane foam plug follows the back section. Tubes are commercially available from SKC, Inc.
2. Personal sampling pump, 0.1 to 0.2 L/min, connected with flexible tubing.
3. Gas chromatograph, FID, integrator, and 30-m Stabilwax-DA or equivalent capillary column (page 2554-1).
4. Vials, autosampler, with PTFE-lined caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Volumetric flasks, 10-mL.
7. Refrigerant packs for shipping.

SPECIAL PRECAUTIONS: Methylene chloride is a carcinogen [3]. Methanol is very flammable and toxic. Glycol ethers are irritants and hazardous compounds. Wear appropriate protective clothing and work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately prior to sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size of 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment. Samples should be kept cold.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool preceding the front section into the vial containing the front section. Discard the remaining foam plugs.
6. Add 1.0 mL of the desorbing solution into each vial. Attach crimp caps to each vial.
7. Place the sample vials in an ultrasonic bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to solvent solution in 10-mL volumetric flasks and dilute to the mark. Mix well.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area versus µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb 747 used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each Anasorb 747 tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE versus µg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2554-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

In order to obtain improved analyte collection and recovery results, several procedures were incorporated in the method development. These included the use of a stainless steel inlet liner in the injection port to reduce the possibility of degradation of analytes, lower injection port and detector temperatures to prevent thermal decomposition of analytes, and the use of Anasorb 747 solid sorbent tubes to reduce the possibility of the hydrolysis of the analytes.

This method was developed in support of a field survey to identify and quantitate glycol ether vapors emitted from heat-cured solder mask paints. This method is applicable when levels below the REL/PEL are expected. The average desorption efficiency (DE) recovery for propylene glycol monomethyl ether was 100.6% (RSD = 1.6), for dipropylene glycol monomethyl ether, was 102.4% (RSD = 1.8), and for propylene glycol

monomethyl ether acetate was 102.0% (RSD = 1.7). The average 14-day storage stability recovery at approximately 75x the LOQ for propylene glycol monomethyl ether was 103.1% (RSD = 2.1), for dipropylene glycol monomethyl ether was 77.7% (RSD = 2.3), and propylene glycol monomethyl ether acetate was 95.4% (RSD = 3.7). Samples containing dipropylene glycol monomethyl ether should be analyzed soon after collection to minimize sample loss during storage.

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TABLE 1. EXPOSURE LIMITS AND PHYSICAL PROPERTIES

Analyte	OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH TLV (ppm)	mg/m^3 = 1 ppm @ NTP	Physical Properties
Propylene glycol monomethyl ether	None	100	100	3.75	Liquid; d 0.9234 g/mL @20 °C, BP 120.1 °C, VP 1.6 kPa (12 mm Hg) @ 20°C
Dipropylene glycol monomethyl ether	100	100	100	6.16	Liquid; d 0.9500 g/mL @20 °C, BP 189.6 °C, VP 0.05 kPa (0.5 mm Hg) @ 20°C
Propylene glycol monomethyl ether acetate	None	None	None	5.40	Liquid; d 0.9700 g/mL @20 °C, BP 145.8 °C, VP 0.5 @ 20°C KPa

HIPPURIC and METHYL HIPPURIC ACIDS in urine 8301

(1) hippuric acid	$C_6H_5CONHCH_2CO_2H$	FW: 179.18	CAS: 495-69-2	RTECS: MR815000
(2) 2-methyl hippuric acid	$CH_3C_6H_5CONHCH_2CO_2H$	193.20	42013-20-7	
(3) 3-methyl hippuric acid	$CH_3C_6H_5CONHCH_2CO_2H$	193.20	27115-49-7	
(4) 4-methyl hippuric acid	$CH_3C_6H_5CONHCH_2CO_2H$	193.20	27115-50-7	

METHOD: 8301, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 3: 15 March 2003

BIOLOGICAL INDICATOR OF: Exposure to toluene and xylenes

SYNONYMS: (1) hippuric acid: N-benzoylglycine
(2) 2-methyl hippuric acid: N-(o-Toluoyl) glycine
(3) 3-methyl hippuric acid: N-(m-Toluoyl) glycine
(4) 4-methyl hippuric acid: N-(p-Toluoyl) glycine

SAMPLING		MEASUREMENT	
SPECIMENS:	1. Pre-shift urine 2. End of shift urine after 2 days exposure	**TECHNIQUE:**	HPLC-UV DETECTION
VOLUME:	Complete spot void	**ANALYTES:**	(1) hippuric acid (2) 2-methyl hippuric acid (3) 3- & 4-methyl hippuric acids
PRESERVATIVE:	A few crystals of thymol; store @ 4°C	**EXTRACTANT:**	Ethyl acetate
		INJECTION VOLUME:	10 µL
SHIPMENT:	Pack in styrofoam shipper with bagged refrigerant, ship overnight	**WAVELENGTH:**	254 nm
SAMPLE STABILITY:	Stable 30 days @ 4°C	**COLUMN:**	Reverse phase (C18), run at 37°C
CONTROLS:	Collect samples from unexposed, matched population.	**MOBILE PHASE:**	84/16/0.025% (v / v / v) water / acetonitrile / glacial acetic acid; 1.5 mL/min
		CALIBRATION:	Synthetic urine solutions of analyte.
		RANGE:	10.0 to 1000 µg/mL.
		ESTIMATED LOD:	(1) 4 µg/mL (2) 5 µg/mL (3) 6 µg/mL NOTE: See Method Evalution
		PRECISION ($\bar{S}_r$):	(1) 0.020 (see Table 1) (2) 0.015 (see Table 1) (3) 0.011 (see Table 1)

APPLICABILITY: Hippuric acid and methyl hippuric acids are the principal metabolites of toluene and xylene, respectively. An occupational exposure to either of these organic solvents may be monitored by following the pattern of excretion of these metabolites in urine. Due to overlap in the range of hippuric acid concentration between exposed workers and non-exposed workers, monitoring urinary hippuric acid concentrations are better suited for groups of workers than for individuals [2].

INTERFERENCES: None known; however, para- and meta- isomers elute together in this system. There are other sources of hippuric acid such as food preservatives, ethyl-benzene, and styrene.

OTHER METHODS: This is based on the method of Matsui, et al [3]. Method 8300 can be used for screening. Isotachophoresis has also been used [4]. More recent HPLC methodologies provide better resolution for these compounds [5].

REAGENTS:

1. Thymol, USP.
2. Sodium chloride.
3. Hydrochloric acid (6N).*
4. Ethyl acetate, HPLC grade.
5. Hippuric acid, reagent grade.
6. 2-Methyl hippuric acid, reagent grade.
7. 3-Methyl hippuric acid, reagent grade.
8. 4-Methyl hippuric acid, reagent grade.
9. Combined hippuric acids stock solution, 1 mg/mL per analyte. Add 35 mg each of hippuric acid, 2-methyl hippuric acid, 3-methyl hippuric acid, and 4-methyl hippuric acid to 35 mL synthetic urine in a 40-mL vial. Cap tightly and sonicate for 30 min, then place in 30°C water bath for 5 min. Visually inspect to verify that all compounds are in solution.
   NOTE: The hippuric acid solution will precipitate out at room temperature, so this preparation should be used immediately after removal from the 30°C water bath.
10. Mobile phase. Add 840 mL distilled water to 160 mL acetonitrile (HPLC grade) and 250 µL of glacial acetic acid. Mix and filter.
11. Pre-purified nitrogen, 99.9%.
12. Synthetic urine (Uri sub™ from CST Technologies, Inc., Great Neck, NY).
13. Pooled, unexposed, human urine [1].

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Bottles, polyethylene, 250-mL.
2. Refrigerant, bagged ("Blue Ice," or equivalent).
3. HPLC system consisting of sample injector, pump, ultraviolet detector at 254 nm, strip chart recorder, integrator, RP C-18 column, and column heater (Supelco Discovery #322201-01 or equivalent).
4. Heated water bath purged by nitrogen blow-down apparatus.
5. Centrifuge.
6. Analytical balance.
7. Tubes, 15-mL borosilicate glass with caps.
8. HPLC vials and caps with limited volume inserts (Kimble Glass, Inc., Art. No. 60745N-1232).
9. Micro-syringes: 10-µL, 100-µL, 250-µL, 500-µL, 1-mL and 10-mL.
10. Positive displacement pipette (40-µL).
11. Rotation Mixer (Fisher model 34601 or equivalent).

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. Pre-immunization against Hepatitis C is highly recommended. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.
Acids are extremely corrosive; work with them in a fume hood and wear protective safety equipment.

SAMPLING:

1. Collect pre-shift and post-shift urine in a 250-mL polyethylene bottle containing a few crystals of thymol.
   NOTE: Take the sample at the end of the second day of suspected exposure to toluene or xylene. Also take pre-exposure samples and samples from non-exposed workers as controls.
2. Pack bottles in styrofoam shipper with bagged refrigerant and ship overnight.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of urine [6].
4. Pipette 1.0 mL of well-mixed urine into a 15-mL borosilicate glass tube with cap.
5. Add 80 µL of 6 N Hcl with positive displacement pipette, mix, and add 0.3 grams sodium chloride.

6. Add 4 mL ethyl acetate. Mix for 2 minutes by rotation.
7. Centrifuge at 100 x gravity for 5 minutes.

NOTE: $$RPM = 10^3 \sqrt{RCF / 1.12 r_{max}}$$

r_{max} = rotor radius
Relative Centrifugal Force (RCF) = gravity

8. Transfer 200 µL of the organic (upper) layer to an HPLC vial and evaporate to dryness (~ 30 minutes) using a heated (~30°C) water bath and a gentle stream of nitrogen.
9. Re-dissolve the residue in 200 µL of distilled water.

CALIBRATION AND QUALITY CONTROL:

10. Prepare working standards over the range of 10 to 1000 µg/mL by dilution of combined hippuric acids stock solution using synthetic urine. Working standards are stable for 1 week at room temperature and stable for 30 days at 4°C [1].
11. Include control samples from an unexposed, matched population with each analytical run. If controls were not sent, use pooled, unexposed human urine.
12. Extract and analyze the working standards together with samples, and controls (steps 4 through 9, 14 and 15).
13. Analyze a duplicate field sample injection at a frequency of one replicate per 10 samples to monitor instrument accuracy.

MEASUREMENT:

14. Set up the HPLC according to the manufacturer's recommendations and to conditions on page 8301-1.
15. Inject 10 µL of the standards, samples, and control samples into the HPLC. Determine peak heights.

CALCULATIONS:

16. Calculate the concentration of each analyte in the urine sample, C_u (µg/mL), using the standard curve to correlate the peak height with the concentration amount.
17. Calculate the grams of analyte per grams of creatinine in the urine sample, C (g/g creatinine), using the concentration of analyte in the urine sample, C_u (µg/mL), and the concentration of creatinine in urine determined in step 3, C_R (g creatinine/L urine).

$$C = \frac{C_U}{C_R} \cdot \frac{1000 \mu L}{L}$$

GUIDES TO INTERPRETATION:

1. Typical excretion of hippuric acid in non-exposed individuals is 1.0 g/g creatinine [2]. Methyl hippuric acids are not found in non-exposed humans.
2. The Threshold Limit Value (TLV®) [9] for urine samples collected at the end of a work shift is 1.6 g/g creatinine for hippuric acid and 1.5 g/g creatinine for methyl hippuric acids.

EVALUATION OF METHOD:

LOD/LOQ studies were performed using standards in synthetic urine, standards in pooled urine, and standards in water. Standards dissolved in synthetic urine gave LODs of 4 µg/mL, 5 µg/mL, 6 µg/mL for hippuric acid, 2-methyl hippuric acid, 3-methyl hippuric acid, and 4-methyl hippuric acid, respectively. Water proved to be a poor matrix for hippuric acids, giving a high variability. Pooled urine also gave a high variability due to an initial background. Endogenous hippuric acids in pooled urine will skew the calibration curve.

Recovery study data shows greater than 96% overall recovery for all analytes from spiked synthetic urine. Overall recovery rates were slightly lower (93%) for spiked pooled urine, possibly due to variability in naturally occurring hippuric acids. Precision, Accuracy, and Bias data (Table 1) were obtained for synthetic urine using 7 replicates at 6 different concentration levels from 10 µg/mL to 1000 µg/L. Results using pooled urine were similar.

A 30-day stability study showed that the hippuric acids in synthetic urine were stable for 7 days at 22°C and 30 days at 4°C. In a single synthetic urine sample, hippuric acid was stable through temperature changes from -20°C to 30°C for 24 hours. Sonication did not affect hippuric acid stability in the samples.

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METHOD UPDATED BY:

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Previous Issues

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TABLE 1. OVERALL PRECISION, ACCURACY, AND BIAS

Compound	Range Studied (µg/mL)	Estimated Accuracy (%)	Bias		Overall Precision ($\hat{S}_{rT}$)	Instrument Precision (S_r)
			Average	Range		
Hippuric acid	10-1000	16.0	-0.081	-0.312-0.0237	0.0538	0.020
2-Methyl hippuric acid	10-1000	19.8	-0.099	-0.286-0.0141	0.0672	0.015
3-Methyl and 4-Methyl hippuric acids	10-1000	18.9	-0.097	-0.2959-0.3869	0.0615	0.011

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

METHOD: 1501, Issue 3 **EVALUATION: Full** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

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

PROPERTIES: Table 1

SYNONYMS (Synonyms in Table 1):
Group A: benzene; toluene; ethylbenzene; o-xylene; m-xylene; p-xylene
Group B: cumene; p-tert-butyltoluene; α-methylstyrene; β-methylstyrene; styrene

SAMPLING

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

FLOW RATE: Table 3

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{r,T}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2, stand 30 min with agitation

INJECTION VOLUME: 1 µL (Group A: split 5:1; Group B: split 1:1)

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: Group A: 40 °C (10 min) to 230°C (10 °C/min)
Group B: 35°C (8 min) to 225°C (10°C/min)

CARRIER GAS: He @ 2.6 mL/min

COLUMN: Capillary, fused silica
Group A: 30m x 0.32-mm ID; 1-µm film 100% PEG or equivalent
Group B: 30m x 0.53-mm ID; 3-µm film crossbonded® 35% diphenyl 65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

PRECISION ($\bar{S}_r$): Table 4

APPLICABILITY: This method is for peak, ceiling, and TWA determinations of aromatic hydrocarbons. Interactions between analytes may reduce breakthrough volumes and affect desorption efficiencies. Naphthalene, originally validated in S292 [4], failed to meet acceptable desorption efficiency recovery and storage stability criteria at the levels evaluated in this study. However, the application of this method to naphthalene levels at or near the REL/PEL continues to meet acceptable recovery criteria. Styrene failed to meet acceptable recovery criteria at the two lowest levels evaluated in this study (highest level to meet the criteria was 181 µg/sample).

INTERFERENCES: Under conditions of high humidity, the breakthrough volumes may be reduced. Other volatile organic compounds such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential analytical interferences.

OTHER METHODS: This method updates NMAM 1501 issued on August 15, 1994 [1] which was based upon P&CAM 127 (benzene, styrene, toluene, and xylene) [2]; S22 (p-tert-butyltoluene) [3]; S23 (cumene) [3]; S29 (ethylbenzene) [3] ; S26 (α-methylstyrene) [3]; S30 (styrene); S311 (benzene) [4]; S343 (toluene) [4]; and S318 (xylenes) [4].

REAGENTS:

1. Carbon disulfide*, low benzene, chromatographic quality.
2. Analytes, reagent grade.
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated 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. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and columns (page 1501-1).
4. Autosampler vials, glass, 1.8 mL, with PTFE-lined caps.
5. Pipets, 1-mL, and pipet bulb.
6. Syringes, 10-µL, 25-µL, and 250-µL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C), benzene is a suspect carcinogen. Prepare standards and samples 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 as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Include the glass wool plug in the vial along with the front sorbent section.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 through 12).
   c. Prepare calibration graph (peak area of analyte vs. µg analyte per sample).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of DE stock solution (5 to 25 µL) directly onto front sorbent section of each charcoal tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE vs. µg analyte recovered.
10. Analyze a minimum of three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    Note: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze, and apply the appropriate dilution factor in the calculations.

Analyte	Approximate Retention Time (min)
benzene[a]	3.52
toluene[a]	6.13
ethylbenzene[a]	10.65
o-xylene[a]	12.92
m-xylene[a]	11.33
p-xylene[a]	11.04
cumene[b]	18.61
p-tert-butyltoluene[b]	21.45
α-methylstyrene[b]	19.99
β-methylstyrene[b]	20.82
styrene[b]	18.33

[a] Separation achieved using a 30-m Stabilwax fused silica capillary colum.
[b] Separation achieved using a 30-m Rtx-35 fused silica capillary column.

12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The desorption efficiency, at levels ranging from 5 times the LOQ to 0.1x the REL, was determined for each analyte by spiking known amounts (in CS_2) on coconut shell charcoal tubes. Both groups of analytes (A and B) were spiked together on the charcoal sorbent tubes. All analytes, with the exception of styrene and naphthalene, exhibited acceptable desorption efficiency recovery results at all five levels evaluated. Styrene failed to meet the 75% recovery criteria at the 18.1 µg and 90.6 µg levels. Naphthalene failed to meet the 75% criteria at all levels evaluated ranging from 48.8 µg to 976.0 µg.

Each analyte, at a level approximately 0.05x REL/PEL, was evaluated for its storage stability @ 5°C after 7, 14, and 30 days. All analytes, with the exception of naphthalene, had acceptable recoveries after 30 days storage.

REFERENCES:

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METHOD WRITTEN BY:

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TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	(kPa)	Density @ 20 °C (g/mL)
benzene CAS #71-43-2 RTECS CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 RTECS XS8400000 1-tert-butyl-4-methylbenzene	$C_{11}H_{16}$	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 RTECS GR8575000 isopropylbenzene	C_9H_{12}	120.20	152.4	4.7	0.63	0.862
ethylbenzene CAS #100-41-4 RTECS DA0700000	C_8H_{10}	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 RTECS WL5075300 isopropenylbenzene (1-methylethenyl)-benzene	C_9H_{10}	118.18	165.4	2.5	0.33	0.909
β-methylstyrene CAS #873-66-5 RTECS DA8400500	C_9H_{10}	118.18	175.	—	—	0.911
toluene CAS #108-88-3 RTECS XS5250000 methylbenzene	C_7H_8	92.14	110.6	28.4	3.79	0.867
xylene[c]	C_8H_{10}	106.17				
CAS #1330-20-7	(ortho)		144.4	6.7	0.89	0.880
RTECS ZE2100000	(meta)		139.1	8.4	1.12	0.864
dimethylbenzene (p-xylene)	(para)		138.4	8.8	1.18	0.861
styrene CAS #100-42-5 RTECS WL3675000 vinylbenzene	C_8H_8	104.15	145.2	6.1	0.81	0.906

TABLE 2. PERMISSIBLE EXPOSURE LIMITS, PPM

		NIOSH			ACGIH		
Substance	OSHA TWA	TWA	C	STEL	TLV	STEL	mg/m³ per ppm
benzene	1	0.1[a]	1		10[b]		3.19
p-tert-butyltoluene	10	10		20	1		6.06
cumene	50 (skin)	50 (skin)			50 (skin)		4.91
ethylbenzene	100	100		125	100	125	4.34
α-methylstyrene	100	50		100	50	100	4.83
β-methylstyrene	100	50		100	50	100	4.83
toluene	200	100		150	50 (skin)		3.77
o-xylene	100	100[c]		150	100	150	4.34
m-xylene	100	100			100	150	4.34
p-xylene	100	100			100	150	4.34
styrene	100	50		100	50	100 (skin)	4.26

[a] Potential carcinogen
[b] Suspect carcinogen
[c] Group I Pesticide

TABLE 3. SAMPLING FLOWRATE[a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION

	Sampling			Breakthrough		Range at	Overall		
	Flowrate	Volume[b] (L)		Volume @ Concentration		VOL-MIN	Bias	Precision	Accuracy
Substance	(L/min)	MIN	MAX	(L)	(mg/m³)	(mg/m³)	(%)	($\hat{S}_r$)	(±%)
benzene	≤0.20	5	30	>45	149	42 - 165	-0.4	0.059	11.4
p-tert-butyltoluene	≤0.20	1	29	44	112	29 - 119	-10.3	0.071[c]	20.7
cumene	≤0.20	1	30	>45	480	120 - 480	5.6	0.059	15.2
ethylbenzene	≤0.20	1	24	35	917	222 - 884	-7.6	0.089[c]	17.1
α-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061[c]	16.9
β-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061	16.9
toluene	≤0.20	1	8	12	2294	548 - 2190	1.6	0.052	10.9
xylene (o-,m-,p-)	≤0.20	2	23	35	870	218 - 870	-1.2	0.060	12.2
styrene	≤1.00	1	14	21	1710	426 - 1710	-7.9	0.058[c]	16.7

[a] Minimum recommended flow is 0.01 L/min.
[b] V_{Min} = minimum sample volume @ OSHA TWA;
V_{Max} = maximum sample volume @ OSHA TWA
[c] Corrected value, calculated from data in Reference 5.

TABLE 4. MEASUREMENT RANGE AND PRECISION[a]

Substance	LOD (µg/sample)	Measurement	
		Range (mg)	Precision ($\hat{S}_r$)
benzene	0.5	0.004-0.35	0.013
p-tert-butyltoluene	1.1	0.013-1.09	0.017[a]
cumene	0.6	0.039-3.46	0.017
ethylbenzene	0.5	0.045-8.67	0.015
α-methylstyrene	0.6	0.036-3.57	0.014
β-methylstyrene	0.6	0.036-0.728	0.014
toluene	0.7	0.024-4.51	0.022
o-xylene	0.8	0.044-10.4	0.014
m-xylene	0.8	0.043-0.864	0.013
p-xylene	0.7	0.043-0.861	0.015
styrene	0.4	0.181-8.49	0.014

[a] Corrected value, calculated from data in [5].

HYDROCARBONS, BP 36°-216 °C 1500

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

METHOD: 1500, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

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

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)
cyclohexane, **cyclohexene**, **n-decane**, **n-dodecane**, **n-heptane**, **n-hexane**, **methylcyclohexane**, **n-nonane**, **n-octane**, **n-pentane**, **n-undecane**

SAMPLING

SAMPLER: SOLID SORBENT TUBE [1] (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: Table 3

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5 °C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID [1]

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURES
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (8 min) - 230 °C (1 min) ramp (7.5 °C /min)

CARRIER GAS: Helium, 1 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 3.00-µm film 100% dimethyl polysiloxane

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

PRECISION ($\hat{S}_r$): Table 4

APPLICABILITY: This method may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and alter analyte recovery.

INTERFERENCES: At high humidity, the breakthrough volumes may be reduced. Other volatile organic solvents such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential interferences.

OTHER METHODS: This method is an update for NMAM 1500 issued on August 15, 1994 [2] which was based on methods from the 2nd edition of the NIOSH Manual of Analytical Methods: S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S378, octane [4]; and S379, pentane [4].

REAGENTS:

1. Eluent: Carbon disulfide *, low benzene, chromatographic quality.
2. Analytes, reagent grade.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated 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. Tubes are commercially available.
2. Personal sampling pumps (0.01 to 1.0 L/min, Table 3) with flexible tubing.
3. Gas chromatograph, FID, integrator, and a Rtx-1 or equivalent capillary column (page 1500-1).
4. Glass autosampler vials (2-mL) with PTFE-lined caps.
5. Pipettes (1-mL) and pipette bulb.
6. Syringes (10, 25, 100, and 250 µL).
7. Volumetric flasks (10-mL).

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C). Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach the sampler to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. Additional standards may be added to extend the calibration curve if necessary.
   a. Add known amounts of analytes to carbon disulfide in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph (peak area of analyte vs. µg of analyte per sample).
9. Determine the desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Remove and discard the back sorbent section of a media blank sampler.

c. Inject a known amount of stock solution (5 to 25 µL) directly onto the front sorbent section with a microliter syringe.
d. Allow the tubes to air equilibrate for several minutes, then cap the tubes and allow to stand overnight.
e. Desorb (steps 5 through 7) and analyze with standards and blanks (steps 11and 12).
f. Prepare a graph of DE vs. µg analyte recovered.

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

MEASUREMENT:

11. Set the gas chromatograph according to the manufacturer's recommendations and to the conditions given on page 1500-1. Inject a 1-µL aliquot manually using a solvent flushing technique or with an autosampler.
NOTE: If the peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.

Analyte	Approximate Retention Time (min)
n-pentane	7.5
solvent (CS_2)	9.6
n-hexane	13.0
cyclohexane	16.1
cyclohexene	16.8
n-heptane	17.7
methylcyclohexane	18.9
n-octane	21.6
n-nonane	24.9
n-decane	27.8
n-undecane	30.5
n-dodecane	32.9

NOTE: Retention times may vary slightly due to column manufacturer and age of column, and be influenced by other GC instrumental parameters.

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

Issues 1 and 2:

Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Table 3 does not contain data for n-decane, n-dodecane and n-heptane since they were not evaluated previously. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was assessed at 7, 14, and 30 days. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75% [2,3,4,8].

Issue 3:

The desorption efficiency, at levels ranging from 10 times the LOQ to 0.1 times the REL, was determined by spiking known amounts of analytes (in CS_2) on coconut shell charcoal tubes. All analytes exhibited acceptable desorption efficiency recovery results at six levels evaluated.

Each analyte was evaluated for its storage stability. Sorbent tubes were spiked at approximately 100 µg and stored in a drawer for 7 days, then transferred to a refrigerator at 5° C. Samples were analyzed after 7, 14, and 30 days. All analytes had acceptable recoveries (>90%), except cyclohexene, which had a 30 day recovery of 85% [1].

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[1] Pendergrass SM and May L, Backup Data Report, ACS/CEMB/DART/NIOSH (1999).
[2] NIOSH[1994]. Hydrocarbons, BP 36-136°C. In: Eller PM, ed. NIOSH Manual of Analytical Methods, 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
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[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1989); 29 CFR 1910.1000.
[6] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 92-100 (1992).
[7] 1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati, OH (1993).
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Issues 1 and 2:

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Issue 3:

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TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/ Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25°C (mm Hg)	Vapor Pressure @ 25°C (kPa)	Density @ 25°C (g/mL)
cyclohexane hexahydrobenzene CAS # 110-82-7 RTECS GU6300000	C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene tetrahydrobenzene CAS # 110-83-8 RTECS GW2500000	C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-decane CAS # 124-18-5 RTECS HD6550000	$C_{10}H_{22}$	142.28	174	NA	NA	0.730
n-dodecane CAS # 112-40-3 RTECS JR2125000	$C_{12}H_{26}$	170.34	216.2	NA	NA	0.750
n-heptane CAS # 142-82-5 RTECS MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane CAS # 110-54-3 RTECS MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane CAS # 108-87-2 RTECS GV6125000	C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-nonane CAS # 111-84-2 RTECS RA6115000	C_9H_{20}	128.26	151	NA	NA	0.718
n-octane CAS # 111-65-9 RTECS RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane CAS # 109-66-0 RTECS RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	0.626
n-undecane hendecane CAS # 1120-21-4 RTECS YQ1525000	$C_{11}H_{24}$	156.31	196	NA	NA	0.740

TABLE 2. EXPOSURE LIMITS, PPM [5-7]

	OSHA		NIOSH		ACGIH		mg/m^3
Substance	TWA	PEAK	TWA	C	TLV	STEL	per ppm
cyclohexane	300		300		300		3.44
cyclohexene	300		300		300		3.36
n-decane	none		none		none		5.82
n-dodecane	none		none		none		6.97
n-heptane	500		85	440	400	500	4.10
n-hexane[a]	500		50		50		3.52
methylcyclohexane	500		400		400		4.01
n-nonane	none		200		200		5.25
n-octane	500		75	385	300	375	4.67
n-pentane	1000		120	610	600	750	2.95
n-undecane	none		none		none		6.39

[a] The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.

TABLE 3. SAMPLING FLOWRATE [a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [3, 4, 8]

	Sampling			Breakthrough Volume		Range of	Overall		
	Flowrate	Volume (L)		Vol	Concentration	Generated Samples	Bias	Precision	Accuracy
Substance	(L/min)	MIN	MAX [b]	(L)	(mg/m^3)	(mg/m^3)	(%)	($\hat{S}_{rT}$)	(%)
cyclohexane	0.01- 0.2	2.5	5	7.6	1650	510-2010	1.1	0.060[c]	±11.5
cyclohexene	0.01- 0.2	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-hexane	0.01- 0.2	not	studied	-	-	-	-	-	-
methylcyclohexane	0.01- 0.2	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-nonane	0.01- 0.2	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
n-octane	0.01- 0.2	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-pentane	0.01-0.2	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-undecane	0.01-0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6

[a] Minimum recommended flow is 0.01 L/min.
[b] Approximately two-thirds the breakthrough volume.
[c] Corrected value calculated from data in Ref. 3

TABLE 4. MEASUREMENT RANGE AND PRECISION [1, 3, 4, 8]

		Measurement	
Substance	LOD (µg/sample)	Range (µg)	Precision ($\bar{S}_r$)
cyclohexane [a]	0.1	4 - 5300	0.012
cyclohexene [a]	0.08	3 - 9700	0.014
n-decane	0.06	2 - 584	0.020
n-dodecane	0.05	2 - 600	0.027
n-heptane	0.06	2 - 16300	0.014
n-hexane	0.4	10 - 14500	0.011
methylcyclohexane	0.1	4 - 16100	0.013
n-nonane	0.04	1 - 574	0.018
n-octane	0.3	11 - 18900	0.022
n-pentane	0.6	19 - 11800	0.012
n-undecane	0.05	2 - 592	0.024

[a] Corrected value, calculated from the data in [1,8].

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

METHOD: 1003, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 3: 15 March 2003

OSHA: See TABLE 1
NIOSH: See TABLE 1
ACGIH: See TABLE 1

PROPERTIES: See TABLE 2

COMPOUNDS: See TABLE 1
(synonyms)

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg) (Lot # 2000)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days for all analytes

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: see EVALUATION OF METHOD [1]

OVERALL PRECISION ($\hat{S}_{r_T}$): see EVALUATION OF METHOD [1]

ACCURACY: see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds listed above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE: Group A: Inj = 200°C, Det = 250°C ; 35°C (3 min) to 150°C (8°C/min).
Group B: Inj = 225°C, Det = 250°C ; 35°C (3 min) to 190°C (8°C/min).

CARRIER GAS: He, (Group A: 2.6 mL/min)
(Group B: 4.7 mL/min)

COLUMN: Group A: capillary, fused silica, 30 m x 0.32-mm ID; 1.80-µm film diphenyl/ dimethyl polysiloxane, Rtx® -502.2 or equivalent.
Group B: capillary, fused silica, 30 m x 0.53 - mm ID; 3-µm film 35% diphenyl- 65% dimethyl polysiloxane, Rtx® -35 or equivalent.

CALIBRATION: standard solutions of analytes in CS_2

RANGE: see Evaluation of Method

ESTIMATED LOD: Table 4

PRECISION ($\hat{S}_r$): Table 4

APPLICABILITY: See Table 3 for working ranges. This method can be used for simultaneous determination of two or more of the analytes of interest either by use of both of the capillary columns listed above or by modifying the analytical parameters (i.e., temperature program) of the method. High humidity during sampling will decrease total breakthrough volume.

INTERFERENCES: None identified but as the number of different analytes sampled increases so does the chance for interferences. The choice of capillary column or analytical parameters may be modified to circumvent such interferences.

OTHER METHODS: This method is an update for NMAM Method 1003 (Issue 1, 2/15/84) [2]. Trichloroethylene, NIOSH Method 1022, was included in this method update [3]. Method improvements include higher recoveries at lower sample recovery levels, lower LOD and LOQ values, incorporation of capillary column chromatography, and acceptable recoveries in a 30 day storage stability study.

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Analytes, reagent grade quality.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends 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, Lot# 2000 or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and columns (see page1003-1).
4. Vials, 2-mL, glass, PTFE-lined septum crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringes, 10-µL to 1-mL, readable to 0.1 µL.
7. Pipet, 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). Wear appropriate protection clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break 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. The glass wool plug should be included in the vial containing the front sorbent section. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range from below the LOD to 10x the LOQ or greater if required (see 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. µg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of pure analyte, or calibration stock solution, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot either manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

The current laboratory evaluation of the analytes listed in this method included the incorporation of capillary column chromatography, the improvement of LOD/LOQ values, a desorption efficiency study ranging from approximately 3-5X LOQ to 0.1x the REL/PEL, and the inclusion of a 30 day storage stability study. Most of the analytes evaluated over this range exhibited acceptable recoveries [4]. However four analytes had unacceptable recoveries at the lowest level evaluated [4]. These analytes included benzyl chloride, chloroform, carbon tetrachloride and chlorobenzene. For these compounds the LOQ was adjusted accordingly. All of the analytes evaluated during the storage stability study were determined to be stable after 7, 14, and 30 days storage [4]. Bromoform was marginally stable at 30 days [4].

The initial laboratory evaluation was conducted using spiked samples and generated atmospheres and using SKC Lot 105 coconut shell charcoal as the collection media [1]. Results were:

Compound	Range mg/m³	Sample Size	Bias %	Precision Overall	Precision Measurement	Accuracy ±%	Desorption Efficiency	Ref.
Benzyl chloride	2-8	10 L	8.4	0.096	0.031	25.6	94% @ 96-303 µg	4
Bromoform	3-10	10 L	-1.3	0.071	0.043	14.0	94% @ 35-111 µg	4
Carbon tetrachloride	65-299	15 L	-1.6	0.092	0.037	18.0	93% @ 32-4800 µg	4,5
Chlorobenzene	183-736	10 L	0.3	0.056	0.025	11.0	92% @ 111-7100µg	4,6
Chlorobromomethane	640-2655	5 L	3.4	0.061	0.051	14.0	98% @39-13,000µg	4,7
Chloroform	100-416	15 L	1.3	0.057	0.047	11.6	97% @ 24-7400 µg	4,8
o-Dichlorobenzene	150-629	3 L	-1.9	0.068	0.013	13.7	94% @ 19-1900 µg	4,9
p-Dichlorobenzene	183-777	3 L	-4.3	0.052	0.022	12.5	98% @ 25-2700 µg	4,10
1,1-Dichloroethane	212-838	10 L	2.6	0.057	0.011	12.4	101% @20-8000 µg	4,11
1,2-Dichloroethylene*	475-1915	3 L	-2.9	0.052	0.017	11.3	101% @19-9500 µg	4,12
Ethylene dichloride	195-819	3 L	-2.0	0.079	0.012	15.7	94% @ 2.5-2500 µg	4,13
Hexachloroethane	5-25	10 L	6.6	0.121	0.014	25.4	98% @ 34-756.8 µg	4
1,1,1-Trichloroethane	904-3790	3 L	-0.6	0.054	0.018	10.6	100%@23-11000µg	4,14
Tetrachloroethylene	655-2749	3 L	7.2	0.052	0.013	15.1	95% @ 8-8000 µg	4,15
1,1,2-Trichloroethane	26-111	10 L	9.0	0.057	0.010	17.5	100% @18-1200 µg	4,16
1,2,3-Trichloropropane	163-629	10 L	2.1	0.068	0.027	14.2	99% @ 21-6000 µg	4,17

*mixed isomers used (i.e., cis- and trans-).

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[6] Ibid., S133.

[7] Ibid., S113.

[8] Ibid., Vol 3., S351, (NIOSH) Publication 77-157-C.

[9] Ibid., S135.

[10] Ibid., S281.

[11] Ibid., Vol. 2, S123, (NIOSH) Publication 77-157-A.

[12] Ibid., S110.

[13] Ibid., S122.

[14] Ibid., Vol 3, S328, (NIOSH) Publication 77-157-C.

[15] Ibid., S335.

[16] Ibid., Vol. 2, S134, (NIOSH) Publication 77-157-A.

[17] Ibid., S126.

METHOD REVISED BY:

Stephanie M. Pendergrass, NIOSH/ DART.

TABLE 1. GENERAL INFORMATION.

Compound RTECS	Synonyms	OSHA/NIOSH/ACGIH (ppm)
Group A		
Bromoform ($CHBr_3$); PB5600000	tribromomethane; CAS #75-25-2	0.5 (skin)/0.5 (skin)/0.5 (skin)
Carbon tetrachloride[ab] (CCl_4); FG4900000	tetrachloromethane; CAS #56-23-5	10, C 25/STEL 2 (1 h)/5 (skin)
Chlorobenzene (C_6H_5Cl); CZ0175000	monochlorobenzene; phenyl chloride; CAS #108-90-7	75/--/10
Chloroform[ab] ($CHCl_3$); FS9100000	trichloromethane; CAS #67-66-3	C 50/STEL 2/10
1,1-Dichloroethane (CH_3CHCl_2); KI0175000	ethylidene chloride; CAS #75-34-3	100/100/100
Ethylene dichloride[ab] ($ClCH_2CH_2Cl$); KI0525000	1,2-dichloroethane; CAS #107-06-2	50, C 100/1, STEL 2/10
Tetrachloroethylene[ab] ($Cl_2C=CCl_2$); KX3850000	perchloroethylene; CAS #127-18-4	100, C 200, P 300/0.4 (LOQ)/ 25, STEL 100
Trichloroethylene[a] ($ClCH = CCl_2$); KX4550000	ethylene trichloride; trichloroethene; CAS # 79-01-6	100 ppm (Ca 200 ppm)/Ca 50 ppm
1,1,1-trichloroethane (CH_3CCl_3); KJ297500	methyl chloroform; CAS #71-55-6	350/C 350/350, STEL 450
Group B		
Benzyl chloride[a] ($C_6H_5CH_2Cl$); XS8925000	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1/C 1.0/1
Chlorobromomethane (CH_2BrCl); PA5250000	bromochloromethane; Halon 1011; CAS #74-97-5	200/200/200
o-Dichlorobenzene[c] (1,2-$C_6H_4Cl_2$); CZ4500000	1,2-dichlorobenzene; CAS #95-50-1	50/C 50/25 (skin); STEL 50
p-Dichlorobenzene[ac] (1,4-$C_6H_4Cl_2$); CZ45500000	1,4-dichlorobenzene; CAS #106-46-7	75/1.7 (LOQ)/75, STEL 110
1,2-Dichloroethylene ($ClCH=CHCl$); KV9360000	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200/200/200
Hexachloroethane[ac] (CCl_3CCl_3); KI4025000	perchloroethane; CAS #67-72-1	1 (skin)/1/1 (skin)
1,1,2-Trichloroethane[ad] (Cl_2CHCH_2Cl); KJ3150000	vinyl trichloride; CAS #79-00-5	10 (skin)/10 (skin)/10 (skin)
1,2,3-Trichloropropane[a] ($CH_2ClCHClCH_2Cl$); TZ9275000	allyl trichloride; glycerol trichlorohydrin; CAS #96-18-4	50/10 (skin)/10 (skin)

[a]Suspect carcinogen [20,21,22]; [b]Group I Pesticide; [c]Group II Pesticide; [d]Group III Pesticide

TABLE 2. PHYSICAL PROPERTIES

Compound RTECS	M.W.	mg/m³ = 1 ppm @ NTP	Synonyms	Properties
Group A				
Bromoform ($CHBr_3$)	252.75	10.33	tribromomethane	liquid, d 2.887; BP 148 °C; nonflammable
Carbon tetrachloride (CCl_4)	153.84	6.29	tetrachloromethane	liquid; d 1.585; BP 76.7 °C; FP 23.0 °C; VP 91.3 mm @ 20 °C; vapor density (air = 1) 5.3
Chlorobenzene (C_6H_5Cl)	112.56	4.60	monochlorobenzene; phenyl chloride	liquid; d 1.105 @ 25 °C; BP 131.6 °C; MP 45 °C; flash pt. 29.4 °C (CC)
Chloroform ($CHCl_3$)	119.39	4.88	trichloromethane	liquid, d 1.485 @ 20 °C; BP 61.2 °C; FP -63.5 °C
1,1-Dichloroethane (CH_3CHCl_2)	98.95	4.05	ethylidene chloride	liquid, d 1.174 @ 20 °C; BP 57 to 59 °C; FP 98 °C
Ethylene dichloride ($ClCH_2CH_2Cl$)	98.96	4.05	1,2-dichloroethane	liquid; d 1.2554 @ 20 °C; BP 83.5 °C; FP - 35.5 °C; flash pt. 13 °C; explosive limits in air 6 to 16%
Tetrachloroethylene ($Cl_2C=CCl_2$)	165.83	6.78	perchloroethylene	liquid; d 1.625 @ 20 °C; BP 121 °C; FP - 22.4 °C
1,1,1-trichloroethane (CH_3CCl_3)	133.42	5.45	methyl chloroform	liquid; d 1.325; BP 75 °C; FP 30.4 °C; nonflammable
Trichloroethylene ($ClCH=CCl_2$)	131.40	5.37	ethylene trichloride; trichloroethene	liquid; d 1.459 @ 20°C; BP 87.2°C; FP- 72.8°C; VP 58 mm Hg @ 20°C (9.9 kPa); explosive range 11 to 41% v/v in air
Group B				
Benzyl chloride ($C_6H_5CH_2Cl$)	126.58	5.17	(chloromethyl) benzene; α-chlorotoluene	liquid; BP 179 °C; MP 48 to - 43 °C; d 1.100 @ 20 °C; flash pt. 67 °C
Chlorobromomethane (CH_2BrCl)	129.39	5.29	bromochloromethane; Halon 1011	liquid; d 1.93 @ 20 °C; BP 68 °C; MP - 88 °C; nonflammable
o-Dichlorobenzene (1,2-$C_6H_4Cl_2$)	147.00	6.01	1,2-dichlorobenzene	liquid; d 1.284; BP 172 to 179 °C; FP - 17 °C; flash pt. 65.5 °C
p-Dichlorobenzene (1,4-$C_6H_4Cl_2$)	147.00	6.01	1,4-dichlorobenzene	solid crystals; d 1.458; BP 173.7 °C; MP 53 °C; sublimes; flash pt. 65.5 °C
1,2-Dichloroethylene ($ClCH=CHCl$)	96.94	3.96	acetylene dichloride; 1,2-dichloroethene	liquid; transisomer; d 1.257; BP 47 to 49 °C; MP 57°C; cis-isomer; d 1.282; BP 58 to 60 °C; flash pt. 3.9 °C; FP 80 °C
Hexachloroethane (CCl_3CCl_3)	236.74	9.66	perchloroethane	solid; d 2.091; MP 185 °C; BP sublimes at 187 °C
1,1,2-Trichloroethane (Cl_2CHCH_2Cl)	133.41	5.45	vinyl trichloride	liquid; d 1.4432 @ 20 °C; BP 113.7 °C; FP 36.4 °C; VP 19 mm Hg @ 20 °C
1,2,3-Trichloropropane ($CH_2ClCHClCH_2Cl$)	147.43	6.03	allyl trichloride; glycerol trichlorohydrin	liquid; d 1.3888 @ 20 °C; BP 156.2 °C; FP - 15 °C; flash pt. 82.2 °C (OC)

TABLE 3. SAMPLING LIMITS.

Compound	Air Sample Volume (L)			Working Range, ppm, at Max Sample Volume
	Min	Max	Target	
Bromoform	4 @ 0.5 ppm	70	10	0.2 to 4
Carbon tetrachloride	3 @ 10 ppm	150	15	2 to 105
Chlorobenzene	1.5 @ 75 ppm	40	10	10 to 430
Chloroform	1 @ 50 ppm	50	15	2 to 190
1,1-Dichloroethane	0.5 @ 100 ppm	15	10	4 to 250
Ethylene dichloride	1 @ 50 ppm	50	3	16 to 1320
1,1,1-Trichloroethane	0.1 @ 350 ppm	8	3	18 to 1450
Tetrachloroethylene	1.0 @ 100 ppm	40	3	9 to 1900
Trichloroethylene	0.2 @ 100 ppm	30	10	0.3 to 62.1
Benzyl chloride	6 @ 1 ppm	50	10	0.6 to 5.8
Chlorobromomethane	0.5 @ 200 ppm	60	5	18 to 450
o-Dichlorobenzene	1 @ 50 ppm	10	3	16 to 1100
p-Dichlorobenzene	1 @ 75 ppm	8	3	27 to 330
1,2-Dichloroethylene	0.2 @ 200 ppm	5	3	16 to 560
Hexachloroethane	3 @ 1 ppm	70	10	0.3 to 8.3
1,1,2-Trichloroethane	2 @ 10 ppm	60	10	1.8 to 64
1,2,3-Trichloropropane	0.6 @ 50 ppm	60	10	3 to 310

TABLE 4. MEASUREMENT PARAMETERS.

Compound	Limit of Detection (LOD)	Limit of Quantitation (LOQ)	Precision (S_r)
Bromoform	6.0	19.3	0.051
Carbon tetrachloride	4.0	20.0	0.046
Chlorobenzene	0.6	110.0	0.025
Chloroform	0.8	15.0	0.035
1,1-Dichloroethane	2.0	5.1	0.030
Ethylene dichloride	0.7	2.3	0.026
Tetrachloroethylene	2.0	7.1	0.032
1,1,1-Trichloroethane	1.0	3.0	0.009
Trichlorethylene	0.6	1.9	0.018
Benzyl chloride	1.0	4.5	0.076
Chlorobromomethane	1.5	41.0	0.053
o-Dichlorobenzene	0.8	2.7	0.022
p-Dichlorobenzene	2.0	7.5	0.041
1,2-Dichloroethylene	2.0	5.1	0.041
Hexachloroethane	2.0	6.6	0.021
1,1,2-Trichloroethane	1.0	3.0	0.036
1,2,3-Trichloropropane	1.0	2.7	0.020

Units = µg analyte per sample

Note: For a few of the compounds in this method the LOQ values, when compared to the preceding method development results, may appear higher. This can be explained by the fact that in the initial method development no recovery study was conducted at a level near or above the instrumentally determined LOQ recoveries for each analyte.

HYDROGEN CYANIDE 6017

HCN MW: 27.03 CAS: 74-90-8 RTECS: MW6825000

METHOD: 6017, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: 10 ppm (skim)
NIOSH: STEL 4.7 ppm
ACGIH: C 10 ppm (skin)
(1 ppm = 1.105 mg/m^3)

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) + glass fiber filter, 5-mm

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: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY (IC) / DC AMPEROMETRY

ANALYTE: CN

DESORPTION: 10 mL deionized water; agitate; let stand 60 min

INJECTION LOOP VOLUME: 50 µL

ELUENT: 0.5 M NaAc
0.1 M NaOH
0.5% ethylenediamine

COLUMNS: HPIC-AS7 or equivalent anion separator, HPIC-AG7 or equivalent anion micro guard

DETECTOR: 0.0 V applied Ag° vs. AgCl reference

CALIBRATION: standard solutions of KCN in 0.1 N NaOH

RANGE: 10 to 300 µg CN per sample [2]

ESTIMATED LOD: 1 µg CN per sample [2]

PRECISION ($\hat{S}_r$): 0.041

APPLICABILITY: The working range is 0.3 to 235 ppm (0.3 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 [3].

INTERFERENCES: A high concentration of hydrogen sulfide gives a negative interference. Any component with the same retention time as cyanide will interfere.

OTHER METHODS: This method is based on NIOSH 6010 which uses the same collection procedure with a VISIBLE ABSORPTION detection system [4]. The method has been adapted for use with a Technicon Autoanalyzer [5]. NIOSH Method 7904 uses an ion-specific electrode for measurement and has been used to determine HCN in firefighting environments [6].

REAGENTS:

1. Potassium cyanide, reagent grade.*
2. Sodium acetate trihydrate, A.C.S. grade.
3. Ethylenediamine, 99%.
4. Sodium hydroxide (NaOH), reagent grade.*
5. Sodium lime (CaO + 5 to20% NaOH), reagent grade (Aldrich #26,643-4, or equivalent). Crush and sieve to 10/35 mesh. Store in capped container.*
6. Water, deionized or distilled.
7. Sodium hydroxide solution, 0.1 N.*
8. 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).
9. Eluent, 0.5 M sodium acetate, 0.1 M NaOH, 0.5% ethylenediamine: Dissolve 60 g sodium acetate + 4 g NaOH pellets in 800 mL H_2O. Add 5 mL ethylenediamine. Bring to 1 L with distilled water.

* See SPECIAL PRECAUTIONS

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 the inlet side (SKC, Inc. 226-28, or equivalent).
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. DIONEX DX-500 or equivalent ion chromatograph.
4. DIONEX ED-40 or equivalent electrochemical detector.
5. DIONEX or equivalent amperometry cell with silver working electrode and silver chloride reference.
6. DIONEX AS7 column with AG7 guard column or equivalent.
7. Autosampler.
8. Autosampler vials.
9. Vials, 15- to 20-mL, for sample preparation.
10. In-line filters, 0.45-µm.
11. Micropipettors with disposable tips.
12. Flasks, volumetric, 25-, 50-, 100-, 1000-mL, with stoppers
13. Pipettes, transfer, disposable.

SPECIAL PRECAUTIONS: HCN gas and cyanide particulates are highly toxic and may be fatal if swallowed, inhaled, or absorbed through the skin [7]. Soda lime and NaOH are very caustic [7]. Use gloves and a fume hood when handling these chemicals.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 0.6 to 90 L.
4. Cap tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
6. Transfer front and back sorbent sections to separate vials. Discard glass wool plugs separating and retaining sorbent sections.

   NOTE: An estimate of particulate cyanide may be obtained by analyzing the initial glass fiber filter disk as follows; however, no evaluation data are available for particulate cyanides determined in this manner:

   a. Transfer the glass fiber disk and glass wool plug immediately behind it at the tube inlet to a third vial.
   b. Add 10.0 mL 0.1 N NaOH to each vial.
   c. Proceed with step 8.

7. Add 10.0 mL deionized-distilled water to each vial containing a sorbent section and cap.
8. Allow to stand 60 minutes, with occasional agitation. Transfer to a 10-mL plastic syringe fitted with an in-line 0.45-µm filter. Collect the filtrate in a clean vial. (If samples are allowed to stand for a period of time filtration may not be necessary.)

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 1 to 250 µg CN^- per sample.
   a. Prepare a working standard solution, 1.00 µg/mL CN^-, by diluting 100 µL of calibration stock solution to 100 mL with 0.1 N NaOH.
   b. Pipet 0.5-, 1.00-, 1.50-, 2.00-, and 2.50-mL of the working standard solution into 25-mL volumetric flasks to produce 0.5-, 1.00-, 1.50-, 2.00-, and 2.50-µg CN^- standards
   c. Analyze together with field samples and blanks (steps 12 through 14).
   d. Prepare calibration graph (peak height in nA vs. µg CN^-).
10. Determine desorption efficiency (DE) at least once for each lot of soda lime used for sampling. Prepare at least three tubes at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a blank sampler.
    b. Inject a known amount of calibration stock solution directly onto the soda lime with a microliter syringe.
    c. Cap and allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards and blanks (steps 12 through 14).
    e. Prepare a graph of DE vs. µg CN^- recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set ion chromatograph according to manufacturer's instructions to conditions given on page 6017-1.
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. Calculate the mass, µg, of CN^- in an aliquot analyzed. Apply the appropriate aliquot factor to calculate the mass, µg, of CN^- in the original 10-mL solution.
16. Determine the mass, µg CN^- (corrected for DE), found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections. If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of HCN in the air volume sampled V(L).

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

where 1.039 = conversion factor, CN^- to HCN

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

Only the analytical procedure was evaluated for this method. The sampler, the soda lime tube, was evaluated for NIOSH method 6010 by sampling the test atmospheres of HCN generated from a compressed mixture of HCN in nitrogen [1]. The range of HCN concentration was equivalent to 2 to 15 mg/m^3 for a 3-L air sample. Twenty-two samples collected at 0.2 L/min for 15 minutes indicated overall precision $\hat{S}_{rT}$ of 0.076 with nearly 100% recovery. Breakthrough occurred after 40 minutes of sampling at a flow rate of 0.2 L/min at an HCN concentration of 148 mg/m^3. Sample tubes spiked with solutions of KCN and analyzed after storage indicated that the samples of cyanide ions were stable on the tube for at least 2 weeks. Analysis of 22 tubes which were spiked with KCN standard solutions in the range 10 to 50 µg indicated a recovery of nearly 100% with a pooled precision of 0.041. Desorption efficiency may be poor, below 10 µg CN [6].

This ion chromatographic (IC) procedure for the determination CN^- was developed by Wisconsin Occupational Health Labortory (WOHL) in 1997 [2]. Desorption, quantifiable limit, and linear range were investigated and found comparable to method 6010. WOHL also demonstated that recovery below 10 µg was questionable.

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METHOD WRITTEN BY:

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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.

ISOCYANATES, TOTAL (MAP) 5525

Formula: R-NCO MW: Appendix C CAS: Table 1 RTECS: Table 1

METHOD: 5525, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

NAMES & SYNONYMS: Table 2

SAMPLING

SAMPLER: FILTER (glass fiber, impregnated); or IMPINGER; or IMPINGER + FILTER (see Table 3)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 1 L @ 5 ppb
-MAX: 500 L

SHIPMENT: Cold; impinger solution: vial with PTFE-lined cap; filter: wide-mouth jar with PTFE-lined cap, containing 5.0 mL MAP extraction solution

SAMPLE STABILITY: Extracted filters: store cold and process as soon as possible; prepared samples: at least 3 months at -10° C (freezer) in the dark

REAGENT STABILITY: MAP on filters: 6 months at -10° C (freezer) in dark; MAP solutions: irreversible precipitation occurs within a few weeks in 2 mg/mL solutions

BLANKS: Minimum of 3 field controls, 3 field blanks per set

BULKS: Necessary for oligomer analysis

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC, UV/FLUORESCENCE DETECTION

ANALYTE: MAP derivatives of isocyanates

SAMPLE PREP: Impinger samples: solid-phase extraction (SPE); filter samples: acetylate with acetic anhydride

INJECTION VOLUME: 30 µL

MOBILE PHASE: 65:35 (v/v) acetonitrile:triethylammonium phosphate/formate (100 mM in both), pH gradient 6.0 to 1.6, 1.5 mL/min.

POST-COLUMN SOLUTION: 65:35 (v/v) acetonitrile- 4.4 N phosphoric acid, 0.7 mL/min.

COLUMN: Reversed phase Inertsil™ C 8, 150 x 4.6 mm, 5-µm, titanium frits in a constant temperature column oven set at 30°C.

DETECTORS: UV @ 253 nm; fluorescence (xenon lamp- ex: 368 nm, em: 409 nm; or deuterium lamp- ex: 254 nm, em: 409 nm).

CALIBRATION: MAP derivatives of monomeric isocyanates, with FL or UV for monomer; mandatory use of UV peak area for oligomer.

RANGE: 0.5 nmole NCO per species to 300 nmole total NCO per sample (e.g., 0.04 to 25 µg HDI per sample).

ESTIMATED LOD: 0.2 nmole NCO per species per sample (0.2 nmole NCO equals 0.017 µg HDI per sample).

PRECISION ($\hat{S}_r$): Filters: HDI 0.05; 2,4-TDI 0.06; MDI 0.06 Impingers: not determined.

APPLICABILITY: The useful air concentration range for this method is approx. 1.4 to 840 µg/m^3 NCO total isocyanate group for a 15-L air sample. This is equivalent to 0.4 ppb to 250 ppb for a diisocyanate. The method determines the air concentration of monomeric and oligomeric isocyanates. The applicability of the method depends on the correct choice of sampler for a given environment [1,2].

INTERFERENCES: Any non-isocyanate compound that reacts with MAP. Any compound that elutes at or after the monomer retention time and absorbs at 253 nm may potentially interfere with isocyanate quantification by UV. Interfering compounds that do not fluoresce using 368 nm excitation and 409 nm emission but give an interfering UV signal can be separated by altering the pH gradient.

OTHER METHODS: NIOSH Method 5522 [3] is for monomer and total isocyanate. NIOSH Method 5521 [4] is for monomer and aliphatic oligomeric isocyanate. A chapter in the NIOSH Manual of Analytical Methods, a related journal article, and the references therein describe other methods and method selection criteria [1,2].

REAGENTS:

For Glass-fiber Filter (GFF) Sampling and Analysis

1. 1-(9-anthracenylmethyl)piperazine (MAP) [5,6] impregnated filters.
   a. 37-mm: 1.1 mg MAP/filter.
   b. 25-mm: 0.5 mg MAP /filter.
   c. 13-mm: 0.13 mg MAP/filter.
2. Extracting solution: $1x10^{-4}$ M MAP in acetonitrile (2.76 mg MAP per 100 mL acetonitrile).
3. Acetic anhydride (HPLC grade).*
4. Acetonitrile (HPLC grade).*

For Impinger Sampling and Analysis

5. Impinger solution: $1x10^{-4}$ M MAP [5,6] in butyl benzoate (2.76 mg per 100 mL butyl benzoate).
6. Butyl benzoate: Purified by running through a silica gel column.
7. Methylene chloride (HPLC grade).*
8. Acetonitrile (HPLC grade).
9. Methanol (HPLC grade).*
10. 90:10 acetonitrile-methanol.

Chromatography

11. Phosphoric acid, 85% (99.999%).*
12. Formic acid (ACS reagent grade).*
13. Acetonitrile (HPLC grade).
14. Triethylamine (99.5%).*
15. Hydrochloric acid (concentrated).*
16. 100 mM phosphate-formate buffer, pH 6.0 and pH 1.6, and acetonitrile-buffer mobile phases (APPENDIX A).
17. Post-column phosphoric acid (4.4 N) and acetonitrile-acid post-column addition mobile phase (APPENDIX B).
18. Monomer standards in acetonitrile: MAP-derivatives, $2x10^{-8}$ N to $3x10^{-5}$ N (NCO groups per liter). Synthesis of MAP-derivatives (APPENDIX C).

- See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass-fiber filter, Type A/E Binder-Free, 13- or 37-mm (Gelman or equivalent), coated with appropriate amount of MAP [5,6] (see Reagents) in an opaque cassette filter holder with cellulose backup; or 25-mm glass-fiber filter coated with MAP (see Reagents) in an IOM sampler with stainless steel cassette; or impinger.
2. Personal sampling pump, capable of sampling at 1 to 2 L/min with flexible connecting tubing.
   NOTE: Avoid leaching of plasticizer into solvent during impinger sampling. For impingers, Fluran™ tubing is acceptable, PVC tubing is not.
3. Wide-mouth glass jars (20-mL) with PTFE-lined cap for extraction and transport.
4. Insulated shipping container with ice packs.
5. High performance liquid chromatograph (HPLC) with binary solvent and gradient capabilities, PEEK tubing, and post-column addition pump, interfaced with an autoinjection system, employing 150x4.6-mm Inertsil™ C8, 5-µm column with titanium frits, in a column oven set to 30 °C (or a minimum of 5 degrees above ambient). Adaption of method to a narrower bore column is acceptable.
6. UV detector set to 253 nm.
7. Fluorescence (FL) detector with either (a) Xenon source: excitation 368 nm, emission 409 nm; or (b) Deuterium source: excitation 254 nm, emission 409 nm.
8. Volumetric flasks, glass, various sizes.
9. Visiprep™ or equivalent solid phase extraction (SPE) manifold with drying attachment and disposable valve liners.
10. Supelclean™ LC-Si or equivalent SPE tubes (0.5g) with 6-mL reservoir.
11. Disposable 20-mL glass vials with PTFE-lined caps.
12. Microsyringes.
13. HPLC vials.
14. Pipets, disposable glass.
15. PTFE syringe filters (0.45-µm pore size).
16. Forceps for handling filters.
17. Sealing bands.
18. Top-loading balance , 2 to 3 decimal place.
19. Analytical balance, 5 place.

SPECIAL PRECAUTIONS: Diisocyanates are highly toxic and known respiratory irritants. Follow manufacturer's guidelines when handling pure products. Follow hazardous material shipping requirements when transporting. Preparation of urea derivatives, samples, and standards should be done in a hood to avoid exposure to isocyanate and solvent vapors. Toxicity of MAP is unknown. Acetic anhydride is a severe irritant; acetonitrile is flammable and an irritant. Methylene chloride is an irritant and suspected carcinogen. Methanol is toxic and flammable. Strong acids are toxic and corrosive. Triethylamine is toxic and corrosive.

SAMPLING:

NOTE 1: Use sampling conditions listed below for the sampler selected: glass fiber filter (1); impinger (2); impinger followed by glass fiber filter (3). See Table 3 for examples of exposure scenarios and which sampler to choose. Refer to the chapter on isocyanates [1] for more detailed information on how to choose the appropriate sampler.

NOTE 2: Field controls are made by sampling in an area near the analyte sampling location but where one would not expect to find analyte. These samplers are then treated exactly like the samples from this point on.

NOTE 3: Field blanks are samplers handled exactly the same as samples except that no air is drawn through them.

1. Filter sampling
   a. Calibrate each sampling pump with a representative sampler in line.
      NOTE: When sampling aerosol with aerodynamic diameter >20 µm, an IOM sampler with stainless steel cassette or other suitable inhalable sampler should be used [1,2].
   b. Attach filter cassette to sampling pump with flexible tubing.
   c. Sample at a rate of 1 to 2 L/min (2 L/min for the IOM) for a total sample of at least 1 L.
   d. Immediately after sampling, place filter in a wide-mouth jar with a PTFE-lined screw cap containing 5.0 mL of 1×10^{-4} M MAP in acetonitrile. Secure screw cap with a sealing band.
      NOTE 1: If an IOM sampler is used, place entire stainless steel cassette and filter in the jar with 10.0 mL of extracting solution instead of 5.0 mL, recap and swirl to wet all surfaces of the IOM sampler.
      NOTE 2: If collecting vapor-only samples, since in-field extraction is not necessary, ship the unextracted samplers with ice packs to the lab for analysis.
   e. Store samples in a refrigerator and ship the samples with ice packs.
   f. Obtain a bulk sample (at least 3 mL) and a Material Safety Data Sheet (MSDS) for products used in the process giving rise to exposure (e.g., for a two-part polyurethane coating system, a sample of both the isocyanate product and the polyol product). These bulk samples are necessary for oligomer analysis. Ship bulks in a separate container from the air samples.
   g. Obtain a minimum of three field controls and three field blanks per sample set or at least one field control and one field blank for every ten samples. These controls and blanks are necessary for distinguishing between artifacts and isocyanates.

2. Impinger sampling
   a. Calibrate each sampling pump with a representative sampler in line.
   b. Transfer 15.0 mL of 1×10^{-4} M MAP in purified butyl benzoate to each impinger and connect impinger to sampling pump with flexible tubing that is free of phthalate plasticizer (Fluran™ tubing is acceptable, PVC tubing is not.)
   c. Sample at 1 L/min for a total sample of at least 1 L.
   d. Using a disposable pipet, transfer the entire contents of the impinger to a 20-mL vial with a PTFE-lined screw cap. Secure screw cap with sealing band.
   e. Store samples in a refrigerator and ship the samples with ice packs.
   f. Obtain bulk samples and MSDSs as described in step 1.f.
   g. Obtain a minimum of three field controls and three field blanks per sample set or at least one field control and one field blank for every ten samples. These controls and blanks are necessary for distinguishing between artifacts and isocyanates.

3. Impinger + filter sampling
   a. Sample with an impinger followed by a MAP-coated filter when impinger sampling is desired (e.g., a highly reactive aerosol) but particles < 2 µm are suspected to be present (e.g., condensation or combustion aerosol). Particles < 2 µm are not collected efficiently by impingers [1,2].
   b. Attach the inlet of the filter cassette to the outlet of the impinger and the outlet of the filter cassette to the pump with flexible tubing. The portion of the tubing connecting the impinger to the filter should be free of phthalate plasticizer (Fluran™ tubing is acceptable, PVC tubing is not.)
   c. Sample at a rate of 1 L/min for a total sample size of at least 1 L.
   d. After sampling, treat the impinger solution as described in step 1.d. If a combined measure of the total isocyanate from the two stages is desired, place the filter in the impinger sample vial. If separate measurements of the two stages are desired, place the filter in a separate jar containing MAP-acetonitrile extraction solution as in step 1.d.
   e. Store samples in a refrigerator and ship the samples with ice packs.
   f. Obtain bulk samples and MSDSs as in step 1.f.
   g. Obtain a minimum of three field controls and three field blanks as described in steps 1.g. and 2.g.

SAMPLE PREPARATION:

NOTE 1: For correct sample preparation, follow directions below for type of sampler used: glass fiber filter (4); impinger (5); impinger followed by glass fiber filter (6).
NOTE 2: Refrigerate all samples immediately upon receipt.

4. Filter and filter extract
   a. For vapor-only samples received without in-field extraction, follow the procedure in step 1.d. of filter sampling and allow the samples to extract overnight in a refrigerator before proceeding.
   b. For samples that are extracted in-field, acetylate with 5 µL of acetic anhydride upon receipt of samples. For samples that are extracted in the lab, acetylate with 5 µL of acetic anhydride after overnight extraction. Let these react at least two hours at room temperature or overnight in the refrigerator before proceeding.
   c. Attach the outlet of a 0.45-µm PTFE Luer-lock syringe filter to the SPE vacuum manifold with disposable liner. Place an empty polypropylene syringe barrel in the inlet of the syringe filter. Add the entire extraction solution into the syringe barrel.
   d. Force the sample through the PTFE filter using either positive or negative pressure and collect in a glass vial with a PTFE-lined cap.

5. Impinger
   a. Attach a 6-mL SPE cartridge containing 500 mg silica gel to a solid-phase extraction (SPE) vacuum manifold with disposable liners.
   b. Condition the SPE cartridge with 2 mL butyl benzoate, bringing the liquid level down to the top of the sorbent bed.
   c. Add a 5.0-mL aliquot of sample solution to the SPE cartridge, adjusting the vacuum of the SPE manifold to obtain a flow of approx. 1 to 2 mL/min and stopping when the liquid level reaches the top of the sorbent.
   d. Add 6 mL methylene chloride to the SPE cartridge. Elute the cartridge at 1 to 2 mL/min until the liquid level reaches the top of the sorbent. Discard all eluate collected up to this point.
   e. Add 3 mL of 9:1 acetonitrile-methanol to the SPE cartridge. Elute at approx.1-2 mL/min until the liquid level reaches the top of the sorbent. Collect the eluate in a pre-weighed glass vial.
   f. Add 3 mL of methanol to the SPE cartridge. Elute and collect the eluate in the same vial as in step 5.g.
   g. Use a stream of nitrogen to reduce the volume to exactly 1.0 mL. Reconstitute to volume if necessary by addition of acetonitrile. Determine exact volume using the sample weight and the density of acetonitrile (0.786 g/mL).

6. Impinger + Filter
   a. Follow steps under Sample Preparation step 5 for the impinger part of the sample.
   b. Follow steps under Sample Preparation step 4 for the filter part of the sample.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate with six working standards in the range of interest. Prepare liquid standards with concentrations in terms of moles isocyanate group per liter (normality) in the range 3 x 10^{-5} N to 2 x 10^{-8} N. Intersperse standards among samples. For filter samples and impingers, liquid standards should consist of the MAP derivative(s) of the appropriate diisocyanate monomer(s) in acetonitrile. A concentrated stock solution of the MAP derivatives of isocyanate monomers can be made in methylene chloride (Solubility: 1x10^{-3}N to 5x10^{-3}N). See APPENDIX C for synthesis of MAP derivatives to be used as standards. For filter samples only, to mimic samples in artifact content, a MAP impregnated filter similar to the filter used for the sample can be placed in 5.0 mL of each level of standard, and then treated the same as the samples starting at step 4.
8. Prepare calibration graphs (response vs. normality of standard solution) for both the UV and fluorescence detectors.
   a. The calibration curve prepared from either the UV or the FL detector may be used to quantify the monomer. A quadratic fit may be used for the fluorescence calibration curve if curvature is seen at the low end.
   b. A linear calibration curve using UV peak area **must be** used to quantify the oligomer because the UV response for monomer and oligomer is the same while the FL response is not.
9. Analyze two solvent blanks at the beginning of each sample set. Using the second blank chromatogram, subtract this chromatogram electronically from sample chromatograms. This improves the UV baseline of sample chromatograms and facilitates accurate integration of peaks in low level samples. Analyze one additional solvent blank within the sample set.
10. Analyze a minimum of three field controls and three field blanks or at least one field control and one field blank for every ten samples. Use the field controls and field blanks to identify non-isocyanate peaks (generally reagent artifact peaks) that are likely to appear in the samples. If the blanks are consistent and the sample set is analyzed soon after sampling, subtraction of a field blank instead of the solvent blank from the sample data may make interpretation of the data simpler.
11. Analyze bulk isocyanate products whenever available, but if oligomer is to be quantified, analysis of the bulk products used at the worksite **must** be done. Bulk isocyanate chromatograms are useful for qualitative confirmation of peaks observed in the sample chromatograms. It is also advisable to analyze bulk non-isocyanate products (such as the polyol portion of a two-part spray system) in the same manner to ensure that they give rise to no interfering compounds that may be mistaken for isocyanates. Bulk products must be derivatized with MAP prior to analysis. An appropriate dilution of the bulk in methylene chloride based on the manufacturer's NCO content, followed by immediate derivatization of an aliquot of this diluted bulk in 5 x 10^{-4} M MAP in acetonitrile must be done. After reacting overnight, acetylate this bulk-MAP reaction mixture with acetic anhydride as in step 4.b. APPENDIX D is a protocol for a bulk dilution/derivatization with MAP that works well for most representative bulks. This bulk-MAP sample can then be analyzed on the HPLC.
12. Analyze three quality control blind spikes per sample set.

MEASUREMENT:

13. Set HPLC and detectors to conditions and settings given on pages 5525-1 and 5525-2. Note that in addition to a mobile phase flow of 1.5 mL/min, there is also a post column addition of 0.7 mL/min of 65:35 (v/v) acetonitrile-4.4 N phosphoric acid. Keep the column at constant temperature in an oven at 30°C. Equilibrate the entire system for at least forty minutes before the start of the daily analysis, using mobile phase B (65:35 (v/v) acetonitrile-pH 1.6 buffer), running post-column acid mobile phase also.
14. The HPLC gradient program can be customized to optimize the separation of the particular isocyanate species. An example of a gradient program to start with is:

    0 - 4 min: 100% mobile phase A (65:35 (v/v) acetonitrile-pH 6 buffer)
    4 - 17 min: Linear gradient from 100% mobile phase A to 100% mobile phase B (65:35 (v/v) acetonitrile-pH 1.6 buffer)
    17 - 30 min: Hold 100% mobile phase B
    30 - 36 min: Re-equilibrate at 100% mobile phase A

    NOTE 1: A gradient that provides better resolution for aliphatic isocyanate products is given in Bello et al. [7].

NOTE 2: For isocyanate products that essentially contain only monomer, the gradient can be truncated after the monomer elutes. After truncation, a two minute hold using pH 1.6 mobile phase before returning to initial conditions will ensure baseline stability for the next sample run.

NOTE 3: If there is an interfering peak in the area of interest that is not influenced by pH, changing the length of hold at the beginning of the run should move the interference peak away from the area of interest.

NOTE 4: For multi-component monomers such as TDI and HMDI and for multi-component isocyanate products that contain monomer and oligomer, changing the hold at the beginning, changing the gradient ramp, placing a hold in the middle of the ramp, or a combination of all of the above may help in separation of the individual components for a specific product.

15. Inject a 30-µL sample aliquot.
16. Monomer measurement:
    Isocyanate species for which pure analytical standards are available, such as diisocyanate monomers, can be measured by comparing the response of the peak at the correct retention time with the calibration curve generated by analyzing standards. Either UV peak height or area or fluorescence peak height or area can be used for quantification of monomer. The fluorescence detector is more sensitive, so it is usually better for measuring monomers at low levels. Peak height is usually preferable to peak area, especially in the presence of closely-eluting interfering peaks. Confirmation of the identity of the monomer is achieved by comparing the FL/UV response ratio of the sample peak to that of the standard giving similar response.
    NOTE: The FL/UV ratio may change somewhat at low levels. The sample peak should give a FL/UV response ratio within 15% of the ratio for the standard peak of comparable size.
17. Oligomer measurement (total isocyanate):
    Isocyanate species for which pure analytical standards are not available, such as oligomeric isocyanates, must be measured by using the UV area of the sample peak(s) and the slope of the linear portion of the calibration curve generated by analyzing monomer standards. Frequently, numerous isocyanate species elute as an envelope of poorly resolved peaks. In this case, rather than attempting to integrate peaks individually, the entire chromatogram is integrated over the area of interest. Because the fluorescence baseline is not disturbed by the gradient and the fluorescence detector is selective for MAP-derivatized compounds, the sample fluorescence chromatogram can be very useful for determining when to begin and end integration of peaks in the UV chromatogram. The fluorescence chromatogram is used qualitatively to confirm the presence of MAP groups in the eluting species. The fluorescence response varies too much from compound to compound to quantify isocyanate species for which standards are unavailable. However, the excitation and emission wavelengths that have been chosen make the detection very selective for MAP derivatives. Experience has shown that MAP-derivatized isocyanates will have a FL/UV ratio of approximately 0.33 to 2 times that of the MAP-derivatized monomer.

CALCULATIONS:

18. Monomers:
    Generate a calibration graph usually using fluorescence, plotting peak area or peak height as a function of concentration (normality, isocyanate milliequivalents per milliliter) of monomer standards. Determine the normality of the analyzed sample aliquot from the calibration graph.

a. For impinger samples use the following formula:

$$M = N \cdot Wt_{eq} \cdot V_f \cdot \left(V_t / V_{al}\right) \cdot 1000, \mu g / sample$$

where:

M = mass of isocyanate species (µg/sample),
N = the normality (isocyanate milliequivalents per milliliter) of the analyzed sample solution as taken from the calibration curve,
Wt_{eq} = the equivalent weight of the monomeric isocyanate in milligrams per isocyanate milliequivalent,
V_f = the final volume of SPE solution in milliliters,
V_t = the 15-mL volume of the total sample, and
V_{al} = the volume of the aliquot analyzed.

b. For filter samples use the following formula:

$$M = N \cdot Wt_{eq} \cdot V_f \cdot 1000, \mu g / sample$$

where:

M = mass of isocyanate species (µg/sample)
N = the normality (isocyanate milliequivalents per milliliter) of the analyzed sample solution as taken from the calibration curve,
Wt_{eq} = the equivalent weight of the monomeric isocyanate in milligrams per isocyanate milliequivalent, and
V_f = the final volume of the sample solution in milliliters.

19. Oligomers (total isocyanate):
Identification of oligomers is best done by following the flow chart presented in Appendix E. The bulk chromatogram is used as the comparison standard when identifying which peaks to include in the quantification. Quantification of oligomers must be accomplished using a UV area calibration curve generated from analyzing monomer standards, preferably using the monomer on which the oligomer is based. Generate a calibration curve, plotting UV peak area as a function of concentration (normality, isocyanate milliequivalents per milliliter) of monomer standards. Use the slope of the linear portion of the calibration curve to determine the normality of a single component, a group of components, or all isocyanate components in the analyzed sample aliquot.

$$N = \frac{UV}{slope_{cal}}$$

where:

N = the normality of sample component(s),
UV = the UV area of sample component(s), and
$slope_{cal}$ = the slope of the calibration curve in units of UV area per normality.

The method measures normality of oligomeric isocyanate group in the analyzed sample. It cannot measure µg per sample unless the molecular weight of the component is known. Generally, there is a mixture of compounds of different and unknown molecular weights. To deal in micrograms per sample, use the formulae given above for monomer quantification and the equivalent weight of the particular monomer of interest. This value is the monomer mass equivalent - the mass of the monomer that would contain the same number of isocyanate groups as was found in the sample. Alternatively, the micrograms of isocyanate group per sample can be calculated using the formulae and entering 42 for the equivalent weight.

EVALUATION OF METHOD:

Shelf Life of MAP, MAP Solutions and MAP-Coated Filters:

Pure, solid MAP is stable for years when stored in a freezer. Concentrated solutions of MAP (concentrated stocks or filter-spiking solutions) are not very stable and should be kept in the freezer for a maximum of one week [7,8]. MAP-coated glass-fiber and quartz-fiber filters are stable for 1 week at room temperature and 6 months in the freezer [7,8]. Artifacts derived from MAP are present in the chromatogram of MAP-coated filter samples. Although the levels are low, these impurities dictate the method LOD when they coelute with an analyte. The level of artifacts observed is not correlated well with storage time. Room temperature storage results in greater artifact levels than storage in the freezer. MAP is known to be light sensitive. It is not clear what role exposure to light plays in the formation of the chromatographic interferences. It is recommended that exposure to light be minimized when handling MAP solutions and MAP-coated filters. No formal study has been conducted regarding the shelf life of impinger solutions of MAP in butyl benzoate. However, no problems have been observed when the impinger solutions are used within one week of being made. Impinger samples are noted to have fewer artifacts than filter samples. Although this may be due in part to greater stability of the dilute MAP solutions versus MAP on filters, it may also be attributable to the generally lower amount of reagent used in impinger samples as well as the solid-phase extraction procedure to which impinger samples are subjected.

Stability of MAP-Isocyanate Derivatives:

Pure, solid MAP-derivatized isocyanate monomers are stable for years when stored in the freezer. MAP-derivatized monomers and oligomers of aliphatic isocyanates are very stable in acetonitrile (the sample solvent) for at least one year [7]. Samples containing TDI-MAP gave results 16-24% lower than the original values when reanalyzed after storage for nine months in the freezer [8].

Filter Materials:

Comparison of quartz-fiber and glass-fiber filters showed no significant differences in recovery of MAP-derivatized monomers from the filters. Comparison of stainless steel and cellulose backup pads showed no significant reagent loss with either. Neither backup material contributed to the artifact production in the filter sample [8].

Filter Versus Impinger Sampling:

A side-by-side comparison of MAP-coated IOM filters and MAP impingers, conducted in autobody shops using aliphatic isocyanate products [9], showed no significant difference in the performance of these two samplers. It can be concluded from this study that losses of relatively slow-curing aliphatic isocyanates collected on filters due to curing reactions are minimal when filters are extracted in the field immediately after sampling. It also appears from this study that the IOM's better aspiration efficiency for relatively large aerosol did not result in increased collection efficiency compared to the midget impinger. This suggests that an inhalable sampler is not necessary in this type of environment. In general, the appropriate choice of sampler - filter, impinger, or impinger and filter in series - is dictated by the particular exposure scenario [1,2].

PEEK Versus Stainless Steel HPLC Columns:

PEEK and stainless steel HPLC columns were compared with respect to efficiency, tailing, and carryover. No significant differences in performance were observed [8]. Therefore, stainless steel columns are considered acceptable. However, because MAP derivatives are known to adsorb onto stainless steel surfaces, it is recommended that the frits of the column be constructed of more inert material, i.e., PEEK or titanium.

pH Gradient:

Method 5525 uses pH-gradient HPLC to enable measurement of relatively weakly retained monofunctional isocyanates and diisocyanate monomers as well as relatively strongly retained oligomeric isocyanates in the same analysis. Several characteristics of the pH gradient have been evaluated [10]. The pH gradient is selective, only accelerating strongly basic compounds (all compounds containing a MAP group are strongly basic). The strength of the pH gradient was evaluated by comparing the degree to which retention is

shortened in the strong mobile phase relative to the weak mobile phase. A model monofunctional isocyanate (octyl isocyanate) eluted 14 times faster and a model diisocyanate (MDI) eluted several hundred times faster using the strong mobile phase. Re-equilibration time is only a few minutes when switching from the strong mobile phase back to the weak mobile phase. Detector baselines are very stable during the gradient. The fluorescence baseline is unchanged and the UV_{253} baseline is disturbed less than 1 mV. The UV response of MAP derivatives has been found to be independent of the pH gradient. However, the fluorescence response is highly dependent on the pH of the mobile phase. This is corrected by post-column addition of acid to the mobile phase prior to detection.

Compound-to-Compound UV Response Variability:

Evaluation of UV response for several MAP-derivatized isocyanates, including monofunctional isocyanates and diisocyanates [5,7] showed a compound-to-compound RSD of 3.0-3.5% at the maximum 254-256 nm and an RSD of 1.0-2.2% at the less intense but more selective wavelengths of 352 nm, 368 nm, and 388 nm. In other studies, the UV response of MDI triisocyanate oligomer varied from 6% higher than the mean of several monomers [7] to about 10% lower than the MDI monomer [8]. The overwhelming majority of the data suggests very little variability in UV response among MAP-derivatized isocyanate compounds, supporting the validity of quantifying non-monomeric isocyanate species by using the UV area of the monomer standard.

Recovery of MAP-Derivatized Monomers:

Quartz-fiber and glass fiber filters were spiked with HDI-MAP, 2,4-TDI-MAP, and MDI-MAP at 630 ng NCO group per component per filter along with 500 µg MAP. Recovery ranged from 97-98% for the quartz-fiber filters and 97-99% for the glass-fiber filters [8]. In another study, MAP-coated quartz-fiber filters were spiked with a mixture of HDI, 2,4-TDI, and MDI at nominal levels of 21, 63, 210, 630, and 2100 ng NCO group per component. Recoveries averaged 93% for HDI, 91% for 2,4-TDI, and 92% for MDI with no correlation between recovery and spiking level over the range studied. As part of an International Organization for Standardization (ISO) intercomparison study, two commercial products containing only monomeric isocyanates were studied [8]. Levels spiked on filters were 2100, 1050, 525, and 105 ng NCO group per filter, corresponding to 2X, 1X, 0.5X, and 0.1X the U.K STEL level. For Desmodur H (HDI monomer), the mean recoveries were 104% at 2X, 103% at 1X, 102% at 0.5X, and 99% at 0.1X. For Desmodur T-80 (a mixture of 2,6-TDI and 2,4-TDI), the mean recoveries were 101% at 2X, 104% at 1X, 103% at 0.5X, and 108% at 0.1X. Bello et al. found HDI monomer recovery averaging 108% in the range of 0.45 to 42 ng NCO per filter and, in a separate study, a mean recovery of 100% in the range of 8 to 250 ng NCO per filter [7].

Recovery of Total Isocyanate Group:

Losses of isocyanates can occur at several stages in the sampling and analytical process [1,2]. Bello et al. evaluated total reactive isocyanate group (TRIG) recoveries from spiked filters and impingers as well as recoveries from HPLC analysis [7]. Desmodur N3300 (HDI isocyanurate) was derivatized with MAP and spiked onto quartz-fiber filters. Extraction and analysis found recovery ranging from 91-93% compared to directly analyzed product for spiking levels ranging from 90 ng to 2.34 µg NCO per filter. Similarly, a bulk product containing HDI isocyanurate and IPDI oligomers was derivatized with MAP, spiked into MAP-containing impingers, processed by solid-phase extraction, and analyzed by HPLC. The recovery of the TRIG varied from 92-106% for the HDI isocyanurate in the range 18-2500 ng NCO/mL and 76-89% for the IPDI oligomer in the range of 16-1900 ng NCO/mL. Recoveries from HPLC analysis were determined by comparison with isocyanate content obtained by bulk product titration. The products investigated and their respective recoveries were Bayer N100 (HDI biuret) 75%, Bayer N3300 (HDI isocyanurate) 94%, Bayer N3400 (HDI isocyanurate + uretidinedione) 95%, Bayer Z4470 (IPDI oligomers) 100%, and B26-2 (HDI isocyanurate + IPDI oligomers) 96%. These HPLC recoveries were conducted at high analyte levels. It is recognized that quantitative recoveries of complex products are not possible at low levels because many components fall below the limit of detection [7]. As part of an International Organization for Standardization (ISO) intercomparison study, two commercial products containing oligomeric isocyanates were studied [8]. Levels spiked on filters were 2100, 1050, 525, and 105 ng NCO group per filter, corresponding to 2X, 1X, 0.5X, and 0.1X the U.K. STEL level. For Desmodur N3300 (HDI isocyanurate), the mean recoveries were 52% at 2X, 43% at 1X, 35% at 0.5X, and 28% at 0.1X. These results are very different than those obtained by Bello et al. [7] and require re-examination. For Suprasec 5030 (polymeric MDI), the mean recoveries were 65% at 2X, 62% at 1X, 59% at 0.5X, and 54% at 0.1X. Studies are underway to account for missing isocyanate in oligomeric products.

Limit of Detection/Limit of Quantification:

The limit of detection (LOD) and limit of quantification (LOQ) were determined by spiking several MAP-derivatized monomers onto MAP filters in the range of 0.01 to 3.0 nanoequivalents, extracting the filters with acetonitrile, acetylating and analyzing by HPLC. The method LOD is estimated to be about 0.2 nanoequivalents NCO per sample and the LOQ 0.5 nanoequivalents NCO per sample for both fluorescence height and UV area [8]. As an example, these are equivalent to an LOD of 17 ng per sample and an LOQ of 42 ng per sample for HDI monomer. Bello et al. estimated the method detection limit to be 8 ng per sample for HDI monomer [9]. The instrumental LOD is substantially lower than the method detection limit, but is not achievable because of low levels of reagent-derived artifacts that are present in the chromatogram. Occasionally an analyte peak will coelute with a relatively large artifact peak, raising the LOD and LOQ substantially. Our experience is that IPDI monomer isomers coelute with some HDI oligomers when both are present in a sample. This makes the IPDI monomers, which are typically present at very low levels, unmeasurable.

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TABLE 1. EXPOSURE LIMITS, PROPERTIES, CAS AND RTECS NUMBERS

Isocyanates	Exposure Limits µg/m³*			Properties [11]	CAS #	RTECS #
	OSHA (PEL)	NIOSH (REL)	ACGIH (TLV)			
Toluene 2,6-diisocyanate (2,6-TDI)	no PEL	lowest feasible (Ca)	no TLV	liquid; d 1.225 g/mL @ 25°C; MP 19.5-21.5°C; VP 3.33 Pa (0.025 mm Hg) @ 25°C [12]	91-08-7	CZ6310000
Toluene 2,4-diisocyanate (2,4-TDI)	140 (ceiling)	lowest feasible (Ca)	36 140 STEL	liquid; d 1.214 g/mL @ 25°C; MP 20-22°C, VP 3.33 Pa (0.025 mm Hg) @ 25°C [12]	584-84-9	CZ6300000
4,4'-Methylene-bis(phenyl isocyanate) (MDI)	200 (ceiling)	50; 200 (10 min ceiling)	51	solid (fused); d 1.180g/mL @ 25°C; MP 42-44°C; VP $6x10^{-4}$ Pa ($4.5x10^{-6}$ mm Hg) @ 25°C [12]	101-68-8	NQ9350000
1,6-Hexamethylene diisocyanate (HDI)	no PEL	35; 140 (10 min ceiling)	34	liquid; d 1.04 g/mL @ 25°C; BP 255°C; 7 Pa (0.05 mm Hg) @ 25°C [13]	822-06-0	MO1740000
Isophorone diisocyanate (IPDI)	no PEL	45; 180 (10 min ceiling)	45	liquid; mixture of isomers, d 1.049 @ 25°C; MP -60°C [14]; VP 0.04 Pa @ 20°C (0.0003 mm Hg) [12]	4098-71-9	NQ9370000
4,4'-Methylene-bis(cyclohexyl isocyanate) (HMDI)	no PEL	No REL, 110 (10 min ceiling)	54	liquid; mixture of isomers, d 1.066 g/mL @ 25°C; VP 0.13 Pa @ 20°C (0.001 mm Hg) [15]	5124-30-1	NQ9250000
1,5-Naphthalene diisocyanate (NDI)	no PEL	40;70 (10 min ceiling)	no TLV	solid flakes; MP 129-131°C [12]; VP 0.4 Pa @ 25°C (0.003 mm Hg) [12]	3173-72-6	NQ9600000

* 1 ppb = 7.12 µg/m³ TDI, 10.24 µg/m³ MDI, 6.88 µg/m³ HDI, 9.09 µg/m³ IPDI, 10.73 µg/m³ HMDI, 8.60 µg/m³ NDI

TABLE 2. SYNONYMS OF COMMON ISOCYANATES

Isocyanate Acronym	Common Chemical Name	Synonyms
2,4-TDI	Toluene 2,4-diisocyanate	2,4-Diisocyanatotoluene; 2,4-diisocyanato-1-methylbenzene; isocyanic acid, 4-methyl-m-phenylene ester; methyl-m-phenylene isocyanate; 4-methyl-1,3-phenylene diisocyanate; tolylene 2,4-diisocyanate
2,6-TDI	Toluene 2,6-diisocyanate	2,6-Diisocyanatotoluene; 2,6-diisocyanato-1-methylbenzene; 2-methyl-1,3-phenylene diisocyanate; tolylene 2,6-diisocyanate
MDI	Methylenebis-(phenyl isocyanate)	4,4'-Diisocyanatodiphenylmethane; 4,4'-diphenylmethane diisocyanate; isocyanic acid, methylene di-p-phenylene ester; 1,1'-methylenebis(4-isocyanatobenzene); 4,4'-methylenebis(phenyl isocyanate); methylenebis(4-phenyl isocyanate); methylenediphenyl diisocyanate; methylenedi-p-phenylene diisocyanate
HDI	Hexamethylene diisocyanate	1,6-Diisocyanatohexane; 1,6-Hexanediol diisocyanate; HMDI; hexane-1,6-diisocyanate ; 1,6-hexylene diisocyanate; isocyanic acid, hexamethylene ester
IPDI	Isophorone diisocyanate	5-Isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane; 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate; isocyanic acid, methylene(3,5,5-trimethyl-3,1-cyclohexylene) ester; isophorone diamine diisocyanate
HMDI	4,4'-Methylenebis-(cyclohexyl isocyanate)	Hydrogenated MDI

TABLE 3. EXAMPLES OF EXPOSURE SCENERIOS AND WHICH SAMPLER TO CHOOSE

Sampler	Sampling Section in Method	Exposure Scenario
GFF: 0.1 mg MAP/cm^2	1	Vapor only (e.g., flexible foam manufacture using TDI monomer) Aerosols of aliphatic isocyanates (e.g., autobody refinishing using HDI- and IPDI-based polyisocyanates) Aerosols of aromatic isocyanates <2 µm (e.g., condensation aerosol from heating MDI)
Impinger: 1x10^{-4} M MAP in butyl benzoate (2.76 mg MAP per 100 mL)	2	Aerosols of aromatic isocyanates >2 µm (e.g., spraying of MDI polyisocyanate or cutting partially-cured MDI-based product)
Impinger + GFF: MAP impinger followed by MAP on GFF	3	Aerosols of aromatic isocyanates both <2 µm and >2 µm (mixture of mechanically generated aerosol and condensation aerosol, e.g., heating and cutting partially-cured MDI-based product)

APPENDIX A: PREPARATION OF PHOSPHATE-FORMATE BUFFER AND MOBILE PHASE

100 mM PHOSPHATE - 100 mM FORMATE BUFFER

Add 46.12 g 85% Phosphoric Acid (~27 mL) and 15.08 mL Formic Acid to 3700 mL deionized hi-pure water. The initial pH should be ~1.56. Titrate with Triethylamine (TEA) to a pH of 6.0 using a standardized pH meter. This will take between 115 and 120 mL of TEA. After the pH adjustment to pH 6.0, add additional deionized hi-pure water to bring the final volume to 4.0 L.

Split into two 2L-portions. The first portion is adjusted to pH 1.6 with concentrated HCl, monitoring the pH by pH meter. This should take between 30 and 35 mL of concentrated HCl.

The second portion remains at pH 6.0, but must have a volume of hi-pure water added that is equal to the volume of HCl added to the first portion. This will ensure that the concentration of salts in the two different pH buffers are the same resulting in less baseline change during the gradient run.

Store all buffers in the refrigerator until mixed with acetonitrile.

MOBILE PHASE: 65:35 ACETONITRILE-PHOSPHATE/FORMATE BUFFER (For both pH 6.0 and pH 1.6)

Mix 650 mL acetonitrile and 350 mL buffer. Total volume will be less than 1000 mL. The mobile phase made from pH 6.0 buffer is designated mobile phase A. The mobile phase made from pH 1.6 buffer is designated mobile phase B.

APPENDIX B: PREPARATION OF PHOSPHORIC ACID AND MOBILE PHASE FOR POST-COLUMN ADDITION

4.4 N PHOSPHORIC ACID
Add 50 mL phosphoric acid (85%) to 400 mL deionized hi-pure water and adjust to 500 mL.

65:35 ACETONITRILE-(4.4 N PHOSPHORIC ACID) MOBILE PHASE
Mix 650 mL acetonitrile with 350 mL of 4.4 N phosphoric acid.

APPENDIX C: SYNTHESIS OF MAP DERIVATIVES

Chemical	MW	EQ. WT.	MAP Derivative MW	MAP Derivative EQ. WT.
MAP: 1-(9-Anthracenylmethyl)piperazine	276.4	276.4		
HDI: Hexamethylene diisocyanate	168.2	84.1	721.0	360.5
TDI: Tolylene diisocyanate (toluene diisocyanate)	174.2	87.1	727.0	363.5
MDI: 4,4'-Methylenebis(phenyl isocyanate)	250.3	125.2	803.1	401.6
HMDI: 4,4'-Methylene-bis(cyclohexyl isocyanate)	262.4	131.2	815.2	407.6
MDI Trimer (MDI Triiso)	381.4	127.1	1210.6	403.5
IPDI: Isophorone diisocyanate	222.3	111.2	775.1	387.5
PhICN: Phenyl isocyanate	119.1	119.1	395.5	395.5
BuICN: Butyl isocyanate	99.1	99.1	375.5	375.5
AcMAP: Acetylated MAP			318.4	318.4

2 MAP + 1 diisocyanate yields 1 MAP-diisocyanate derivative

1. Theoretical yield 1 meq: range from 360-408 mg.
2. Weigh 1 meq of diisocyanate to four decimal places. Dissolve in 10 mL of toluene.
3. Weigh 1.2 meq of MAP (20% excess) to four decimal places. Dissolve in 20 mL of toluene.
4. While stirring the MAP solution, add the diisocyanate solution dropwise over a 10 to 15 minute period. Continue to stir for at least one hour.
5. Tightly cover the solution and store overnight in the freezer to promote maximum precipitation.
6. Using a Buechner funnel with filter paper, filter the solution to collect the precipitate.
7. Wash several times with small amounts of cold toluene to remove any remaining MAP.
8. Wash several times with small amounts of cold hexane to displace the toluene. Continue to pull air through the solid for several minutes to dry.
9. Transfer the solid derivative into a preweighed vial with Teflon cap.
10. Using the vacuum pump, apply vacuum until a stable weight is obtained.

APPENDIX D: PREPARATION OF BULK DERIVATIVES

1. Dilute bulk 1/10 in methylene chloride by wt/wt. Quickly proceed to step 2.
   a. Weigh disposable 7 mL vial empty.
   b. Add about 0.5 g bulk, weigh vial again.
   c. Add 4.5 g (3.4 mL) methylene chloride by volume addition, weigh vial again. Use this total weight of 1:10 dilution in calculating final concentration of bulk solution. Density of methylene chloride is 1.325 g/mL.

2. Weigh 1.0 mL of the 1:10 dilution of bulk to determine density. Use this density in calculating the final concentration of bulk solution.

3. Dilute the solution resulting from Step 1 1:100 (10 µL into 990 µL) in methylene chloride by vol/vol. Immediately proceed to step 4.

4. Add 25 µL of the solution resulting from Step 3 to 975 µL acetonitrile containing $5X10^{-4}$ N MAP (1:40 dilution).

5. Let react overnight in dark.

6. Add 5 µL acetic anhydride. Allow to react at least two hours at room temperature or overnight in the refrigerator before proceeding.

7. Analyze by HPLC, injecting 30 µL.

8. Total dilution is about 1:40,000.

9. Final bulk solution concentration (C_B, g/mL):

$$C_B = \frac{Wt_{bulk}}{Wt_{tot}} \cdot Dens_{\cdot 1:10} \cdot DF, g / mL$$

where:

Wt_{bulk} = the weight of sample (Step 1)
Wt_{tot} = the combined weight of sample and methylene chloride (Step 1)
$Dens_{1:10}$ = the density of the initial sample preparation (Steps 1 and 2)
DF = the dilution factor (Steps 3 and 4) (as presented above, DF = 0.00025)

ISOPHORONE 2556

$C_9H_{14}O$ MW: 138.21 CAS: 78-59-1 RTECS: GW7700000

METHOD: 2556, Issue 1 **EVALUATION:** PARTIAL **Issue 1:** 15 March 2003

OSHA : 25 ppm
NIOSH: 4 ppm; Group III Pesticide
ACGIH: C 5 ppm (animal carcinogen)

PROPERTIES: liquid; d 0.923 g/mL @ 25 °C; BP 213 °C; VP 26 kPa (0.2 mm Hg 260 ppm) @ 20 °C

SYNONYMS: 3,5,5-trimethyl-2-cyclohexen-1-one

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-4, 80 mg/40 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L @ 25 ppm
-MAX: 25 L

SHIPMENT: Ship cold.

SAMPLE STABILITY: At least 14 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not Determined.

ACCURACY: Not Determined.

BIAS: Not Determined.

OVERALL PRECISION ($S_{r,T}$): Not Determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Isophorone

EXTRACTION: 1 mL diethyl ether; stand 30 min and rotate 1.5 hours

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTOR: 240 °C
-DETECTOR: 300 °C
-COLUMN: 50 °C (0.5 min) to 225°C (10 °C/min)

CARRIER GAS: He, 3.0 mL/min

COLUMN: Capillary, fused silica 30-m x 0.32-mm ID; 1 µm film crossbond carbowax- PEG for acidic compounds

CALIBRATION: isophorone in diethyl ether

RANGE: 6 to 831 µg per sample [1]

ESTIMATED LOD: 1.0 µg per sample [1]

PRECISION ($\bar{s}_r$): 0.01 [1]

APPLICABILITY: The working range for this method is 0.042 to 5.88 ppm (0.24 to 33.2 mg/m³) for a 25-L air sample. High humidity may greatly decrease breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This method was developed for air sampling at lower concentrations of isophorone. NMAM Method 2508, for isophorone, is based on the 2nd edition method S367 [2,3]. This older method uses a petroleum-based charcoal sorbent tube and packed-column gas chromatography.

REAGENTS:

1. Diethyl Ether, chromatographic grade.*
2. Isophorone.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4- mm ID, flame-sealed ends, containing two sections of 20/40 mesh XAD-4 (80 mg front/40 mg back) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, base-deactivated inlet liner, and column Stabilwax-DA or equivalent (see page 2556-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 250-, 25-, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 3- and 5-mL, with pipet bulb.
8. Cold packs for shipping.
9. Mechanical rotary mixer.

SPECIAL PRECAUTIONS: Diethyl ether is highly volatile and an acute fire and explosion hazard. Work with it only in a hood. Isophorone is a lachrymator [2]. Work with it should be done in a hood and caution should be taken while it is being used.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1.0 L/min for a total sample size of 2 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (and glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard the foam plugs.
6. Add 1.0 mL diethyl ether to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation and place on a rotary mixer for 1.5 hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 6 to 831µg isophorone per sample.
   a. Add known amounts of isophorone to a 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg isophorone).

9. Determine desorption efficiency (DE) at least once for each batch of XAD-4 used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of isophorone directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg isophorone recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2556-1. 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 diethyl ether, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

$$C = \frac{(Wf + Wb - Bf = Bb)}{V}, mg / m^3$$

EVALUATION OF METHOD:

NIOSH method NMAM 2508 for isophorone reported an average DE recovery of 86% over the high concentration range of 849 to 3400 µg [1]. While the results are considered acceptable, at the lower levels encountered in current analyses, the recoveries would most likely fall below those considered acceptable. Therefore, a method development effort was initiated to improve the recovery and analysis of isophorone at these lower levels.

In 1987, Levin and Carleborg reported that isophorone was quantitatively recovered from XAD polymer using diethyl ether as the desorption solvent at the 750 µg level [4]. Initial results using this approach were plagued by varying recoveries and poor peak resolution which was solved by using a Stabilwax-DA fused silica capillary column and a base-deactivated inlet liner in the gc injection port. The base-deactivated inlet liner should be replaced after 35-40 injections. Additionally, the samples were placed on a rotary mixer for 1.5 hours after the addition of the diethyl ether. These changes resulted in an average recovery of 94.1% over the range of 55 to 831µg and the LOD being lowered to 1 µg/sample. Isophorone samples, when spiked at levels 0.15 times the REL, were stable (89% recovery) for 30 days when stored at 5°C.

REFERENCES:

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[2] NIOSH [1994]. NMAM Method 2508: Isophorone. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th edition. Cincinnati, OH: U.S. Deptartment of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS(NIOSH) Publication No. 94-113.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S367, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C.
[4] Levin JO, Carleborg L [1987]. Evaluation of Solid Sorbents for Sampling Ketones in Work-Room Air, Ann. Occup. Hyg., Vol. 21(1):31-38.

METHOD WRITTEN BY:

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ISOPROPYL ACETATE 1460

$CH_3COOCH(CH_3)_2$ MW: 102.14 CAS: 108-21-4 RTECS: AI4930000

METHOD: 1454, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : 250 ppm
NIOSH: no REL
ACGIH: 250 ppm; STEL 310 ppm

(1 ppm = 4.18 mg/m^3 @ NTP)

PROPERTIES: Colorless liquid; BP 89.4 °C; d 0.87 g/mL @20 °C; miscible in most organic solvents; VP 6.33 kPa (47.5 mm Hg)

SYNONYMS: 2-Propyl Acetate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg, Lot 2000)

FLOW RATE: 0.02 to 0.2 L/min

VOL -MIN: 0.1 L @ 250 ppm
-MAX: 9 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 Days @ 5°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: GAS CHROMATOGRAPHY, FID

ANALYTE: Isopropyl acetate

DESORPTION: 1 mL of carbon disulfide containing 1% methanol

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 40°C (1 min) to 200°C (10°C/min)

CARRIER GAS: Helium, 2.8 mL/min

COLUMN: Capillary, fused silica, 30-m x 0.32-mm ID, 1.00 µm film crossbonded® 100% dimethyl polysiloxane or equivalent

CALIBRATION: Standard solutions of isopropyl acetate in carbon disulfide/ methanol (99:1)

RANGE: 0.6 to 697.6 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION ($\hat{S}_r$): 0.013

APPLICABILITY: The working range is 0.018 to 20.9 ppm (0.075 to 87.2 mg/m^3) for an 8-L air sample [3].

INTERFERENCES: None identified.

OTHER METHODS: This method was developed as an update for NMAM 1454, Issue 1 which was based upon NIOSH Method S50 from the 2nd edition of the NIOSH Manual of Analytical Methods [1,2].

REAGENTS:

1. Isopropyl acetate, ACS reagent grade.
2. Eluent: carbon disulfide, chromatographic grade.*
3. Methanol, chromatographic grade.*
4. Standard solutions: Isopropyl acetate in carbon disulfide/methanol (99:1) in the range of 0.2 to 700 µg per sample.
5. Helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube must be less than 3.4 kPa at 1 L/min. Tubes are commercially available.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and Rtx-1® or equivalent capillary column (page 1460-1).
4. Vials, 2-mL glass, PTFE-lined caps.
5. Syringe, 10-, 25-µL, readable to 0.1 µL.
6. Syringe, 1-mL, readable to 0.1 mL.
7. Pipets, 3-, 5-mL, readable to 0.1 mL.
8. Volumetric flasks, 10-mL.

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

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.02 and 0.2 L/min for a total sample size of 0.1 to 9 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION

5. Place the front (and glass wool) and back sorbent sections of the sampler tube in separate vials. Discard the foam plugs.
6. Add 1.0 mL CS_2 / methanol (99:1) to each container and cap tightly.
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 below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of isopropyl acetate to solvent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg isopropyl acetate).
9. Determine desorption efficiency (DE) at least once per year for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.

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

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1460-1. 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 solvent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

NOTE: µg/L=mg/m^3

EVALUATION OF METHOD:

The current method development effort was the result of requests to evaluate and improve problematic gas chromatography methods as part of the NMAM methods update project. Initial evaluations confirmed that Anasorb CSC (coconut shell charcoal) tubes were still the most suitable media for the sampling and analysis of isopropyl acetate. The average DE recoveries for isopropyl acetate, at substantially lower analyte concentration ranges (17 to 698 µg versus 3.75 to 15.4 mg [1,2]) were improved over the previous method (98.4% [3] versus 86.2%[1,2]) when CS_2/methanol (99:1) was used as the desorption solvent. The LOD for isopropyl acetate was lowered to 0.6 µg/sample [3] from the 10 µg/sample [1,2] reported in the previous method. A 30-day storage stability study was completed for isopropyl acetate with an average recovery of 99.9% [3].

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[1] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S50, U.S. Department of Health and Human Services. DHEW (NIOSH) Publication No. 77-157-B.
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METHOD WRITTEN BY:

Stephanie Pendergrass, NIOSH / DART

ISOPROPYL ETHER 1618

$((CH_3)_2CH)_2O$ MW: 102.18 CAS: 108-20-3 RTECS: TZ425000

METHOD: 1618, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1994**
Issue 2: 15 March 2003

OSHA: 500 ppm
NIOSH: 500 ppm
ACGIH: 250 ppm; STEL 310 ppm

(1 ppm = 4.18 mg/m³ @ NTP)

PROPERTIES: liquid; 0.725 g/mL @ 20°C; BP 67.5°C; VP 15.9 kPa (119 mm Hg, 15.7% v/v) @ 20°C; explosive range 1.4 to 7.9% v/v in air

Synonyms: diisopropyl ether; 2-isopropoxypropane; 2,2'-oxybispropane

SAMPLING

SAMPLER: Solid Sorbent Tube (coconut shell charcoal; 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 500 ppm
-MAX: 3 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 992 to 4260 mg/m³ [2] (3-L samples)

BIAS: 2.2%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056

ACCURACY: ±12.0%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Isopropyl ether

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURES
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (1 min) - 150 °C ramp (10 °C /min)

CARRIER GAS: Helium (1-2 mL/min)

COLUMN: Capillary, fused silica, 30-m x 0.32-mm ID; 3µm film 100% dimethyl siloxane

CALIBRATION: Solutions of analyte in CS_2

RANGE: 2 to 651 µg per sample (capillary column); 1000 to 12000 µg per sample (packed column)

ESTIMATED LOD: 0.2 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.014 [1]

APPLICABILITY: The working range is 3 to 1170 ppm (16 to 4900 mg/m³) for a 3-L air sample [1]. The sorbent's capacity for the analyte has not been determined under conditions of high relative humidity [2].

INTERFERENCES: Any compound that has a similar retention time under these analytical conditions.

OTHER METHODS: This method is based on and supercedes S368 [3] and NMAM 1618 (Issue 1) [5].

REAGENTS:

1. Eluent: Carbon disulfide* (CS_2), chromatographic quality.
2. Isopropyl ether*, reagent grade.
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silanized glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Tubes are commercially available.
2. Personal sampling pumps (0.01 to 0.05 L/min) with flexible tubing.
3. Gas chromatograph, FID, integrator, and Rtx®-1 or equivalent capillary column (see page 1618-1).
4. Glass autosampler vials (2-mL) with PTFE-lined caps.
5. Pipettes (1-mL) and pipette bulb.
6. Microliter syringes, 10-µL and convenient sizes for making dilutions .
7. Volumetric flasks (10-mL).

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and highly flammable (flash point = -30°C); isopropyl ether is flammable and tends to form explosive peroxides [4]. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach the sampler to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.1 to 3 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. Additional standards may be added to extend the calibration curve if necessary.
   a. Add known amounts of isopropyl ether to eluent in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph (peak area of analyte vs. mg of analyte per sample).
9. Determine the desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8).

a. Prepare three tubes at each of five levels plus three media blanks.
b. Remove and discard the back sorbent section of a blank sampler.
c. Inject a known amount of stock solution (1 to 20 µL) directly onto the front sorbent section with a microliter syringe.
d. Allow the tubes to air equilibrate for several minutes, then cap the tubes and allow to stand overnight.
e. Desorb (steps 5 through 7) and analyze with standards and blanks (steps 11and 12).
f. Prepare a graph of DE vs. µg analyte recovered.
g. Analyze a minimum of three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.
h. Analyze at least three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

10. Set the gas chromatograph according to the manufacturer's recommendations and to the conditions given on page 1618-1. Inject a 1-µL aliquot manually using a solvent flushing technique or with an autosampler.
    NOTE: If the peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
11. Measure the peak area.

CALCULATIONS:

12. 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 $W_b > Wf / 10$, report breakthrough and possible sample loss.
13. Calculate the concentration, C, of analyte in the air volume, V(L), sampled:

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

EVALUATION OF METHOD:

Issue 1

S368 was issued on April 21, 1976 [3] and validated over the range 992 to 4260 mg/m^3 for 3-L air samples from dynamically generated test atmospheres [2]. The isopropyl ether concentrations were verified by GC/FID analysis. Breakthrough (5% on the backup section) occurred at 26 min when sampling a test atmosphere containing 4260 mg/m^3 of isopropyl ether in dry air at a flow rate of 0.198 L/min.

Issue 2

The desorption efficiency, at levels ranging from 10 times the LOQ to 0.1 times the REL, was determined by spiking known amounts of isopropyl ether (in CS_2) on coconut shell charcoal tubes. The isopropyl ether exhibited acceptable desorption efficiency recovery results (97.1% - 103.4%) over the 20 to 651 µg range evaluated [1]. Isopropyl ether was evaluated for its storage stability. Sorbent tubes were spiked at approximately 615 µg and stored at ambient temperature for 7 days, then transferred to a refrigerator at 5° C. Samples were analyzed after 7, 14, and 30 days. Average recovery was 101.1%, 98.7%, and 94.8% respectively [1]. For this issue, the analytical range is lowered due to increased sensitivity and resolution with capillary column chromatography.

REFERENCES:

[1] Pendergrass SM, May LR [2002]. NMAM 1618 Backup Data Report, Cincinnati, OH: National Institute for Occupational Safety & Health, DART, February.
[2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S368. U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185. Available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S368, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C. Method S368 was originally validated under NIOSH Contract CDC-99-74-45.
[4] NIOSH/OSHA [1981]. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services and U.S. Department of Labor, Publ. (NIOSH) 81-123, January. Available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
[5] NIOSH [1994]. NIOSH Manual of Analytical Methods, 4th ed., supplement, NMAM 1618, Depart. of Health and Human Services, DHHS (NIOSH) Publication No. 94-113.

METHOD UPDATED BY:

Stephanie M. Pendergrass, NIOSH/DART.
Leroy R. May, NIOSH/ PRL.

Method originally written by Charles V. Cooper, NIOSH/DPSE.

KETONES I 2555

Formulas: See Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 2555, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: See Table 3

SYNONYMS: (1) Acetone: dimethyl ketone, ketone propane, 2-propanone.
(2) Methyl ethyl ketone: methyl acetone, 2-butanone, MEK.
(3) 2-Pentanone: ethyl acetone, methyl propyl ketone, MPK.
(4) Methyl isobutyl ketone: hexone, 4-methyl-2-pentanone, MIBK.
(5) 2-Hexanone: methyl n-butyl ketone, methyl butyl ketone, MBK.
(6) Di-isobutyl ketone: sym-diisopropyl acetone, 2,6-dimethyl-4-heptanone, isovalerone, valerone, DIBK.
(7) Cyclohexanone: anone, cyclohexyl ketone, pimelic ketone.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb CMS, 150 mg/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

	Acetone	Others
VOL-MIN:	0.5 L	1 L
-MAX:	3.0 L	10 L

SHIPMENT: Refrigerate samples.

SAMPLE STABILITY: All analytes 30 days @ 5°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: GAS CHROMATOGRAPHY, FID

ANALYTE: See Table 1

DESORPTION: 1 mL CS_2 for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 40°C (1 min) to 200°C (8°C/min)

CARRIER GAS: Helium, 1mL/min

COLUMN: Capillary, fused silica, 30 m x 0.53-mm ID, 3.00-µm film crossbonded® 35% diphenyl - 65% dimethyl polysiloxane

CALIBRATION: Standard solutions of analytes in CS_2

RANGE: See Table 4.

ESTIMATED LOD: See Table 4.

PRECISION ($\bar{S}_r$): See Table 4.

APPLICABILITY: For three-liter sample, the working range for acetone was 0.378 to 41.4 ppm (0.92 to 100.2 mg/m³). For a 10-L sample the working range for methyl ethyl ketone was 0.092 to 10.2 ppm (0.275 to 30.5 mg/m³), for 2-pentanone was 0.077 to 8.67 ppm (0.276 to 31.1 mg/m³), for methyl isobutyl ketone was 0.066 to 6.83 ppm (0.275 to 28.5 mg/m³), for 2-hexanone was 0.066 to 7.45 ppm (0.275 to 31.1 mg/m³), for diisobutyl ketone was 0.052 to 5.07 ppm (0.308 to 30.1 mg/m³), and for cyclohexanone was 0.075 to 9.79 ppm (0.300 to 39.2 mg/m³).

INTERFERENCES: Any compounds with similar retention times as the analytes of interest. Alternate columns include Rtx-1 and Rtx-5 or equivalent capillary columns.

OTHER METHODS: This method was developed as part of an update for NMAM 1300, issue 2 (dated 15 August 1994) [1]. NMAM 1300, issue 2 was based on NIOSH Manual of Analytical Methods, 2nd edition methods S1, S18, S19, S20, S178, and S358. This method includes: lower LOD/LOQ values for each analyte, improved DE recovery results for each analyte (at lower levels), inclusion of methyl ethyl ketone and methyl isobutyl ketone in the method by the use of a different sorbent tube (Anasorb CMS), a 30-day storage stability study, and replacement of the packed column with a Rtx-35 fused silica capillary column.

REAGENTS:

1. Carbon disulfide (GC grade).*
2. Analytes, reagent grade.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, compressed, purified, filtered.
6. Calibration stock solution: Add known amounts of analytes to carbon disulfide in 10-mL volumetric flask.

* 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 Anasorb CMS (150 mg/ 75 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, connected with flexible tubing.
3. Gas chromatograph equipped with FID, integrator and capillary column (page 2555-1).
4. Autosampler vials, 2-mL, glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipettes, 3-mL and 5-mL.
7. Volumetric flasks, 10-mL.
8. Bagged refrigerant, Blue-ice or equivalent.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic, explosive, and a fire hazard (FP = -30°C). Work with carbon disulfide in a well ventilated hood. Analytes should be handled in a fume hood. Use protective clothing and eyewear.

SAMPLING:

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

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool preceding the front section into the vial containing the front sorbent section. Discard the urethane foam plugs.
6. Add 1.0 mL of carbon disulfide into each vial. Attach crimp caps to each vial.
7. Allow to stand for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in a 10-mL volumetric flask and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.

b. Inject a known amount (5 to 25 µL) of DE stock solution directly onto the front sorbent section of each Anasorb CMS tube with a microliter syringe.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs µg analyte recovered.

10. Analyze a minimum of 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 2555-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method development was based upon a prioritized list of problematic gas chromatographic methods identified in a survey of external users of the NIOSH Manual of Analytical Methods. Method improvements include the use of capillary column chromatography, lower LOD/LOQ values, improved desorption efficiency (DE) at lower quantitative levels, and a storage stability study conducted at 7, 14, and 30 days. The method also incorporates the use of an improved solid sorbent tube sampler (Anasorb CMS) resulting in improved sample recovery and allowing methyl ethyl ketone and methyl isobutyl ketone to be included in the method without loss of sample recovered from the sorbent tube. Table 4 lists the method evaluation data, the LOD/LOQ values, the range of measurements, and the precisions for each analyte. [2]

The average DE determined for acetone was 98.2% (RSD = 0.019), for methyl ethyl ketone was 98.6% (RSD = 0.017), for 2-pentanone was 99.3% (RSD = 0.011), for methyl isobutyl ketone was 96.4% (RSD = 0.011), for 2-hexanone was 100.6% (RSD = 0.013), for diisobutyl ketone was 102.4% (RSD = 0.013), and for cyclohexanone was 95.4% (RSD = 0.015).

The average 30-day storage stability recovery for acetone was 100.7% (RSD = 0.017), for methyl ethyl ketone was 101.7% (RSD = 0.018), for 2-pentanone was 101.5% (RSD = 0.028), for methyl isobutyl ketone was 103.8% (RSD = 0.018), for 2-hexanone was 101.4% (RSD = 0.029), for diisobutyl ketone was 103.5% (RSD = 0.019), and for cyclohexanone was 87.4% (RSD = 0.009).

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 4th ed., V. 2, U.S. Dept. of Health and Human Services, Publ. (NIOSH) 94-113 (1994).
[2] Pendergrass SM [1998]. Backup data for Ketones I, NIOSH Method 2555, Issue 1. Cincinnati, Oh: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, (unpublished, February).

METHOD WRITTEN BY:

Stephanie M. Pendergrass, NIOSH/DART

TABLE 1. GENERAL INFORMATION

Analyte	Formula	MW	CAS #	RTECS #
Acetone	$(CH_3)_2CO$	58.1	67-64-1	AL3150000
MEK	$CH_3COCH_2CH_3$	72.1	78-93-3	EL6475000
2-Pentanone	$CH_3CO(CH_2)_2CH_3$	86.1	107-87-9	SA7875000
MIBK	$CH_3COCH_2CH(CH_3)_2$	100.2	108-10-1	SA9275000
2-Hexanone	$CH_3CO(CH_2)_3CH_3$	100.2	591-78-6	MP1400000
Diisobutyl ketone	$[(CH_3)_2CHCH_2]_2CO$	142.3	108-83-8	MJ5775000
Cyclohexanone	$C_6H_{10}O$	98.2	108-94-1	GW1050000

TABLE 2. ANALYTE EXPOSURE LIMITS

Analyte	OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH TLV (ppm)	Conversion ppm to mg/m^3
Acetone	1000	250	500	1 ppm = 2.42 mg/m^3
MEK	200	200	200	1 ppm = 3.00 mg/m^3
2-Pentanone	200	150	200	1 ppm = 3.58 mg/m^3
MIBK	100	50	50	1 ppm = 4.17 mg/m^3
2-Hexanone	100	1	5	1 ppm = 4.17 mg/m^3
Diisobutyl ketone	50	25	25	1 ppm = 5.92 mg/m^3
Cyclohexanone	50	25	25 (A3 - unclassified carcinogen)	1 ppm = 4.00 mg/m^3

TABLE 3. PHYSICAL PROPERTIES.

Analyte	State	Density @ 20°C (g/mL)	BP (°C)	Vapor Pressure (@ 20°C) kPa(mm Hg)
Acetone	liquid	0.7915	56.2	35.5 (266)
MEK	liquid	0.8050	79.6	13.0 (100)
2-Pentanone	liquid	0.8120	101.7	3.6 (27)
MIBK	liquid	0.8042	115.8	2.0 (15)
2-Hexanone	liquid	0.8120	127.2	0.4 (3)
Diisobutyl ketone	liquid	0.8089	168.2	0.23 (1.7)
Cyclohexanone	liquid	0.9470	156.7	0.3 (2)

TABLE 4. METHOD EVALUATION

Analyte	LOD (µg/sample)	LOQ (µg/sample)	Range (µg/sample)	Precision (S_r)
Acetone	0.9	2.7	2.7 - 295.0	0.021
Methyl Ethyl Ketone	0.9	2.7	2.7 - 300.0	0.008
2-Pentanone	0.9	2.7	2.7 - 305.0	0.009
Methyl Isobutyl Ketone	0.9	2.7	2.7 - 280.0	0.013
2-Hexanone	0.9	2.7	2.7 - 305.0	0.010
Diisobutyl Ketone	1.0	3.0	3.0 - 295.0	0.010
Cyclohexanone	1.0	3.0	3.0 - 273.0	0.006

FORMULAS: TABLE 1 MW: TABLE 1 CAS: TABLE 1 RTECS: TABLE 1

METHOD: 2553, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

COMPOUNDS/ SYNONYMS:
(1) 2-Heptanone: Methyl-n-amyl ketone
(2) 3-Heptanone: Ethyl butyl ketone
(3) Mesityl oxide: 4-Methyl-3-penten-2-one
(4) 5-Methyl-3-heptanone: Ethyl amyl ketone
(5) Camphor: 2-Camphanone, Gum Camphor

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb CMS, 150/75 mg) [1]

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L
-MAX: 25 L

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C [1]

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Not Determined.

BIAS: Not Determined.

OVERALL PRECISION ($\hat{S}_{r_T}$): Not Determined.

ACCURACY: Not Determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Table 1

DESORPTION: 1 mL of 2% isopropanol in CS_2 with agitation [1]

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 225°C [1]
-DETECTOR: 300°C [1]
-COLUMN: 55°C (3 min hold) to 190°C (8°C/min) [1]

CARRIER GAS: Helium (4.8 mL/min) [1]

COLUMN: Capillary, fused silica, 30-m x 0.32-mm ID; 1.00 µm film crossbond trifluoro-propylmethyl polysiloxane or equivalent [1]

CALIBRATION: Solutions of analytes in desorption solvent

RANGE: See Table 2 [1]

ESTIMATED LOD: See Table 2 [1]

PRECISION ($\bar{S}_r$): See Table 2 [1]

APPLICABILITY: For a 10-L air sample, the working range for 2-heptanone is 0.86 to 24.8 ppm (4.0 to 121 mg/m^3); for 3-heptanone is 0.43 to 12.9 ppm (2.0 to 60.3 mg/m^3); for mesityl oxide is 0.22 to 6.89 ppm (0.9 to 22.6 mg/m^3); for 5-methyl-3-heptanone is 0.21 to 6.29 ppm (1.1 to 33.0 mg/m^3); and for camphor is 0.14 to 4.84 ppm (0.9 to 30.2 mg/m^3) [1].

INTERFERENCES: Any compound having the same retention times as the analytes of interest.

OTHER METHODS: This method was developed as part of an update of NIOSH Method 1301 (Issue 2, 15 August 1994) [2] which combined the NIOSH Methods: S10, S12, S13, S15, and S16 from the 2nd edition of the NIOSH Manual of Analytical Methods [3,4]. Improvements included: lower LOD/LOQ values, improved DE recovery results (at lower levels) by using Anasorb CMS and 2% IPA in CS_2, a 30 day storage stability study, and the replacement of the packed column with a Rtx-200 fused silica capillary column.

REAGENTS:

1. 2-Heptanone, reagent grade (98%).
2. 3-Heptanone, reagent grade (98%).
3. Mesityl oxide, reagent grade (98%).
4. 5-Methyl-3-heptanone, reagent grade (97%).
5. Camphor, reagent grade (99%).
6. Carbon disulfide, low benzene grade.*
7. Isopropanol.
8. Helium, prepurified and filtered.
9. Hydrogen, prepurified and filtered.
10. Air, compressed and filtered.
11. Desorption solvent: 2% isopropanol in carbon disulfide (v/v).
12. DE stock solution: Add known amount of analyte to desorption solvent in 10-mL volumetric flask.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of Anasorb CMS (front = 150 mg; back = 75 mg) separated by a 2-mm urethane plug. A silylated glass wool plug precedes the front section and a 3-mm urethane plug follows the back section. Tubes are commercially available (SKC # 226-121).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and Rtx-200 fused silica capillary column.
4. GC autosampler vials, 2-mL glass, with PTFE-lined crimp caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Pipets, 3-mL and 5-mL, with pipet bulb.
7. Volumetric flasks, 250-mL and 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a fire/explosion hazard (flash point = -30°C). Isopropanol is flammable. All work should be performed in a ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately prior to sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at a known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 25 L.
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (include the initial glass wool plug) and back sorbent sections of the sampler in separate vials. Discard the foam plugs.
6. Add 1.0 mL of the 2% isopropanol/carbon disulfide desorption solvent to each vial. Securely attach crimp caps to each vial.
7. Allow to desorb for 30 minutes with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of each analyte to the desorption solvent solution in 10-mL volumetric flasks and dilute to the mark. Mix well.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area versus µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.

b. Inject a known amount of DE stock solution directly onto the front sorbent section of each Anasorb CMS with a microliter syringe.
c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE versus µg analyte recovered.

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

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2553-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L= mg/m^3

EVALUATION OF METHOD:

This method updates NMAM 1301, which was identified as a problematic gas chromatographic method from a survey of external users of the NIOSH Manual of Analytical Methods. This new method, by use of capillary column chromatography coupled with an improved solid sorbent sampler and modified desorption solvent, resulted in improvements in LOD/LOQ, sample recovery and storage stability compared to NMAM 1301. The average DE recovery was improved for all analytes at levels lower than those reported in NMAM 1301, ranging from 95% for mesityl oxide to 100% for 3-heptanone. All samples were stable for 30 days with recoveries ranging from 94% for camphor to 99% for 2-heptanone. The complete summary of results is in Table 2.

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METHOD WRITTEN BY:

Stephanie M. Pendergrass, NIOSH/DART

TABLE 1. GENERAL INFORMATION

Compound/ (Synonyms) CAS # RTECS	Formula (M.W.)	Exposure Limits			mg/m^3= 1 ppm	Properties
		NIOSH REL (ppm)	OSHA PEL (ppm)	ACGIH TLV (ppm)	@ NTP	
Methyl-n-amyl-ketone (2-Heptanone) (CAS # 110-43-0) RTECS MJ5075000	$C_7H_{14}O$ (114.19)	100	100	50	4.67	liquid; d 0.820 g/mL; BP 151 °C; VP 0.27 kPa (2 mm Hg)
Ethyl butyl ketone (3-Heptanone) (CAS # 106-35-4) RTECS MJ5250000	$C_7H_{14}O$ (114.19)	50	50	50	4.67	liquid; d 0.818 g/mL; BP 148 °C; VP 0.53 kPa (4 mm Hg)
Mesityl oxide (4-methyl-3-penten-2-one) (CAS # 141-79-7) RTECS SB4200000	$C_6H_{10}O$ (98.15)	10	25	15	4.01	liquid; d 0.822 g/mL; BP 129 °C; VP 1.1 kPa (8 mm Hg)
5-Methyl-3-heptanone (Ethyl amyl ketone) (CAS # 541-85-5) RTECS MJ7350000	$C_8H_{16}O$ (128.21)	25	25	25	5.00	liquid; d 0.822 g/mL; BP 159 °C; VP 0.27 kPa (2 mm Hg)
Camphor (CAS # 76-22-2) RTECS EX1225000	$C_{10}H_{16}O$ (152.24)	2	2	2	6.22	solid; spec. gr. 0.992 @ 25 °C; MP 174 °C; VP 0.024 kPa (0.18 mm Hg, 1470 mg/m3); sublimes

Note: All densities and vapor pressures are at 20°C unless otherwise stated.

TABLE 2. ANALYTICAL RESULTS [1]

Analyte	LOD (µg)	Precision (S_r)	Range (µg)	DE (Avg)	Storage Stability (at 5 °C after 30 Days)
2-heptanone	0.5	0.025	40-1206	0.970	0.994
3-heptanone	0.7	0.031	20-603	1.004	0.984
mesityl oxide	0.3	0.014	9-276	0.950	0.993
5-methyl-3-heptanone	0.7	0.032	11-330	0.987	0.990
camphor	0.7	0.043	9-302	0.970	0.939

LEAD BY PORTABLE ULTRASONIC EXTRACTION/ASV 7701

Pb MW: 207.19 (Pb), 223.19 (PbO) CAS: 7439-92-1 (Pb), 1317-36-8 (PbO) RTECS: OF7525000 (Pb), OG1750000 (PbO)

METHOD: 7701, Issue 2 **EVALUATION: FULL** **Issue 1: 15 January 1998**
Issue 2: 15 March 2003

OSHA: 0.05 mg/m³
NIOSH: 0.05 mg/m³
ACGIH: 0.05 mg/m³

PROPERTIES: soft metal: d 11.3 g/cm³@ 20 °C; MP 327.5 °C, BP1740 °C; valences 2+, 4+ in salts

SYNONYMS: elemental lead, lead compounds (except alkyl lead)

SAMPLING

SAMPLER: FILTER (37-mm, 0.8-µm pore, mixed cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 20 L @ 0.05 mg/m³
-MAX: 1500 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

FIELD BLANKS: Minimum of 2 field blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 0.150 mg/m³ (as Pb) (based on Pb mass loadings) [4]

BIAS: None identified in laboratory studies[3-5] <10% in field study [6]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 (screen-printed electrodes); 0.094 (Hg film on glassy carbon electrodes) [4]

ACCURACY: ± 17.2 % (disposable electrodes); ± 19.3 % (renewable electrodes) [4]

MEASUREMENT

TECHNIQUE: PORTABLE ANODIC STRIPPING VOLTAMMETRY

ANALYTE: Lead

EXTRACTION: 10% HNO_3, 10 mL; ultrasonication

ANALYSIS ALIQUOT VOL.: 0.1 to 5 mL

DEPOSITION POTENTIAL: -0.8 V to -1.0 V vs. Ag/AgCl

ANODIC SWEEP: Deposition potential to 0.0 V vs. Ag/AgCl sweep rate variable [1,2]

REFERENCE ELECTRODE: Ag/AgCl or calomel

WORKING ELECTRODE: Mercury film on glassy carbon or screen-printed

SUPPORTING ELECTROLYTE: Mixture of NaCl/NaOH or KCl/KOH, L-ascorbic acid

CALIBRATION: Pb^{2+} in 5% HNO_3

RANGE: 0.31 to >1000 µg Pb per sample [3,4]

ESTIMATED LOD: 0.09 µg per sample [3]

PRECISION ($\hat{S}_r$): 0.068 @ 60 µg (as Pb) per sample [3]

APPLICABILITY: The working range is (at least) 0.20 to 5.00 mg/m³ (as Pb) for a 120-L air sample. Lead determination by ultrasonic extraction/ASV method is applicable to the on-site, field-based determination of lead in air filter samples, and also may be used for laboratory-based air filter sample preparation and analysis.

INTERFERENCES: Thallium is a known interference, but its presence is unlikely in the vast majority of samples. Extremely high concentrations of copper may cause a positive bias. Surfactants can poison electrode surfaces, so if the presence of surfactants is suspected they must be eliminated during sample preparation [7,8]

OTHER METHODS: Laboratory-based methods include atomic spectrometric methods following concentrated acid hotplate digestion: NIOSH methods 7082 (flame AAS), 7105 (graphite furnace AAS), and 7300 (ICP-AES). ASTM standards based on NIOSH methods for sample collection, preparation and analysis have been published [9].

REAGENTS:

1. Nitric acid,* 10% (v/v) (Prepared from concentrated nitric acid, reagent grade; spectroscopic grade if trace analysis).
2. Distilled or deionized water (ASTM Type I or better [10]).
3. Calibration stock solution, 1000 µg/mL Pb. Commercial standard, or dissolve 1.00 g Pb metal in minimum of 10 mL of 50% HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable for at least one year.
4. Supporting electrolyte: Aqueous inert salt mixture such as 2.5 M NaCl and 0.25 M NaOH* (reagent grade or equivalent) [3,4].
5. Dissolved oxygen scavenger such as 0.25 M L-ascorbic acid (tissue culture grade or equivalent) [3,4].
6. Mercuric nitrate (reagent grade), if required (for Hg film electrodes).
7. Certified Reference Materials (CRMs) for lead, primary or secondary.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Mixed cellulose ester filter, 0.8-µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Field-portable anodic stripping voltammeter.
4. Disposable or renewable voltammetry electrodes.
5. Ultrasonic bath, 50 watts minimum power.
6. Power source for ultrasonic bath.
7. Plastic centrifuge tubes, 50-mL, with screw caps.
8. Test tube rack (size to fit in ultrasonic bath).
9. Plastic sample cell container.
10. Mechanical pipets (class A equivalent), 0.1-mL to 10-mL, as needed.
11. Pipet tips for mechanical pipets.
12. Forceps
13. Bottles, polyethylene, 100- to 1000-mL.
14. Volumetric flasks, 100-mL (for preparatory lab work).
15. Plastic rods.

NOTE: Clean all glassware and reusable plasticware with diluted nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Nitric acid and sodium hydroxide are irritants and may burn skin. Perform extractions in a well-ventilated area. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in the line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 20 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and, with forceps, transfer the samples and blanks to separate 50-mL centrifuge tubes. Push the filters to the bottom of the tubes with plastic rods.
4. Add 10 mL of 10% HNO_3 and cap the centrifuge tubes.
5. Place centrifuge tubes in ultrasonic bath, and agitate at room temperature for at least 30 min.
   NOTE 1: The water level in the bath should be above the level of liquid within the centrifuge tubes.
   NOTE 2: Proper performance of the ultrasonic bath should be demonstrated before use. This can be accomplished by checking recoveries of lead from performance evaluation materials.
6. Shake tubes for 5 to 10 sec, and allow to settle.

CALIBRATION AND QUALITY CONTROL:

7. Prior to field work, prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb.
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks, and dilute to volume with 10% HNO_3. Store and transport the working standards in polyethylene bottles, and prepare fresh weekly.
   b. Analyze the working standards together with the blanks and samples (steps 11 through 14).
   c. Prepare a calibration graph of instrumental response vs. lead concentration (µg/mL Pb).
      NOTE: Some portable instruments read concentration directly. Calibrate according to manufacturer's directions.
8. Analyze at least one standard for every 20 samples to check for instrument drift (steps 11 through 14).
9. Check recoveries with at least one spiked media blank per 20 samples (one per batch minimum). Use certified reference materials to substantiate recoveries. Use method of standard additions to check for matrix effects or interferences.
10. Check for lead contamination by analyzing at least one reagent and one media blank per 20 samples (minimum of one per batch)(steps 11 through 14).

MEASUREMENT:

11. Set instrument parameters as specified by the manufacturer, or use conditions specified on page 7701-1.
    NOTE: If renewable electrodes are used, clean the glassy carbon electrode and deposit a fresh mercury film prior to conducting analyses.
12. Transfer sample aliquot (1 to 5 mL) to analytical cell, and dilute with 10% HNO_3, if necessary.
    NOTE: High concentrations of lead may require analysis of diluted analyte solutions.
13. Add supporting electrolyte and oxygen scavenger to sample cell. Ensure final volume of the cell is 5 mL (disposable electrodes) or 10 mL (renewable electrodes) by diluting with distilled or deionized water.
14. Measure lead content of the sample aliquot (µg/sample or µg/mL), and record the result.
    NOTE 1: For renewable electrodes, rinse and drain electrochemical sample cell at least three times with distilled or deionized water between sample runs. For disposable electrodes, use a fresh plastic sample cell container for each sample analyzed.
    NOTE 2: If the measured value is above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Using measured lead contents, calculate the corresponding concentrations (µg/mL) of lead in the original extracted sample, C_s, and average media blank, C_b, from the calibration graph.
    NOTE: Be sure to account for dilution factors.
16. Using solution volumes (mL) of the samples, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_S V_S - C_b V_b}{V}, mg / m^3$$

NOTE: µg/mL ≡ mg/m^3

EVALUATION OF METHOD:

This method was evaluated with lead aerosol samples generated in the laboratory (40 to 80 µg Pb per filter) [3], and with air particulate samples collected from workplaces where abrasive blasting of leaded paint on highway bridges was being conducted [4]. For the latter, lead loadings cover the range from below the detection limit of 0.09 µg Pb per filter to loadings in excess of 1500 µg Pb per filter [4]. The method also has been evaluated with performance evaluation materials and by interlaboratory testing [3-5]. Lead recoveries from Certified Reference Materials (CRMs) were found to be quantitative (≥90%) and equivalent to recoveries obtained using confirmatory analytical methods (NIOSH 7082, 7105, and 7300 [11]).

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METHOD REVISED BY:

Kevin Ashley, Ph.D., NIOSH/DART.

LEAD in DUST WIPES by Chemical Spot Test (Colorimetric Screening Method)

9105

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

METHOD: 9105, Issue1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no PEL
NIOSH: no REL
ACGIH: no TLV

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: WIPE, meeting the specifications of ASTM E1792 [1].

SAMPLE: Human skin (e.g., hands) or non-dermal surfaces (e.g., floors, walls, furniture)

SAMPLE STABILITY: Stable

BLANKS: At least 5% of samples, min. of 2 per batch

ACCURACY

RANGE STUDIED: <0.01 to >1,000 µg Pb per wipe

BIAS: Not applicable

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

ACCURACY: Response may differ for different wipe materials, different matrices and different rhodizonate solutions.

MEASUREMENT

TECHNIQUE: CHEMICAL SPOT TEST, Rhodizonate-based solution or spot test kit applied to wipe sample [2]

ANALYTE: Rhodizonate complex of lead

POSITIVE INDICATOR: Observed color change on wipe from yellow/orange to pink/red (under acidic conditions) [2,3]

RESPONSE: The method is ordinarily positive for the presence of lead in the range of 5 - 15 µg/sample, upwards to and exceeding milligram amounts [3,4].

APPLICABILITY: This is a qualitative, colorimetric screening method, designed for field use. The method was designed as a handwipe method for human skin, but is also applicable to various non-dermal surfaces including floors, walls, furniture, etc. A characteristic color change on the wipe (i.e., from yellow/ orange to pink/ red hues) indicates the presence of lead. By estimating the performance parameters for a given wipe/rhodizonate solution combination, the performance characteristics can be evaluated [5]. If quantitative results are needed, lead in the wipe samples can be measured on-site using a modification of NIOSH method 7701, or in a fixed-site laboratory using NIOSH methods 7082, 7105, 7300, or equivalent.

INTERFERENCES: Tl^+, Ag^+, Cd^{2+}, Ba^{2+}, and Sn^{2+} also form colored compounds with rhodizonate ion, but with less sensitivity than that of Pb^{2+}, and only the lead-rhodizonate complex gives the characteristic pink or red color [3]. Interferences from the wipe medium, e.g., surfactants, are possible.

OTHER METHODS: Laboratory methods for the determination of lead in dust wipes include modifications of NIOSH methods 7082 (Lead by Flame AAS), 7105 (Lead by Graphite Furnace AAS), 7300 (Elements by ACP), and 7701 (Lead by Portable ASV).

REAGENTS:

1. Vinegar (e.g., 5% acetic acid as white vinegar) or 1% nitric acid (v/v).*
2. Sodium or potassium rhodizonate salt (rhodizonic acid).
   NOTE: Rhodizonate solutions may degrade quickly over time. Solutions should be prepared fresh daily and kept refrigerated.
3. Distilled or deionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Plastic pump spray bottles (fine spray preferred) with a capacity of at least 125 mL.
2. Wipes for sample collection, meeting the specifications of ASTM E1792 [1].
3. Safety glasses or goggles.
4. Gloves, vinyl disposable or powderless latex gloves.
5. Scintillation vials, plastic screw top containers or plastic centrifuge tubes.

   NOTE: Commercial kits are available.

SPECIAL PRECAUTIONS: If 1% nitric acid is used, use common sense safety precautions when handling the solution (e.g., wear vinyl gloves, safety glasses/goggles, and avoid contact with clothing and exposed skin).

SAMPLING:

Dermal surfaces (e.g., hands):

1. For workplace dermal sampling, tear open a wipe packet and without touching the wipe, offer the wipe to the employee to be evaluated.
2. Instruct the employee to remove the wipe from the packet, and unfold it.
3. Instruct the person to wipe the palms first, then the top surfaces of both sides of his or her hands (using normal hand washing pressure). Tell the employee to wipe using the same side of the wipe, and to continue wiping his/her hands for a period of not less than 30 seconds.

Other (non-dermal) surfaces:

4. Obtain wipe samples in accordance with ASTM E1728 [6], or use the following modification.
   a. With gloved hands, open a wipe packet and unfold the wipe.
   b. Wipe a delineated (known) area of the surface, being sure to cover the entire area thoroughly. Wipe across the surface using repeated horizontal motions.
   c. Then wipe the same surface again using the same side of the wipe for sampling, and wipe at a right angle to the first wiping motion.
   d. Don a new pair of clean gloves for successive wipe samples.

SAMPLE PREPARATION:

NOTE: The following procedure is written for sodium rhodizonate, and can be amended using potassium rhodizonate. Also, commercial spot test kits may be used to test for lead on wipe samples in lieu of the procedure described below, but skin contact with the reagents should be avoided.

5. Prepare a solution of rhodizonic acid using the sodium rhodizonate powder. Dissolve a pre-weighed portion of 0.135 grams (135 mg) in 105 cc of very cold water (~2 °C). This is the indicator solution. The indicator solution should turn an orange color when mixed.
6. Place a quantity of the indicator solution into one of the spray bottles, label the bottle: #2 or lead indicator solution. Refrigerate the remaining solution.
7. Fill another spray bottle with household vinegar or make up a 1% (v/v) nitric acid solution, label that bottle #1 or lead extraction solution.
   NOTE 1: The indicator solution will remain active for 2-3 days (if kept cold). After a time the indicator solution will begin to turn color (pale yellow) and lose viability, at which time a new solution

must be mixed. A new indicator solution should be prepared at least daily, especially if not refrigerated at a very low temperature (approaching 0 °C). The lead disclosing solution should be kept cold where possible (e.g., recommend to use a small cooler for field storage of indicator solution).

NOTE 2: Alternative solutions and test indicators may be used, and this can alter the sensitivity and selectivity of the test for lead.

8. Place sample (wipe) on clean surface.
9. Spray with 3 pumps of bottle #1 (vinegar) extraction solution.
10. Spray wipe with 2 pumps of bottle #2 (indicator solution).
11. If sample turns red, lead is present. If no color change, sample is considered negative.
    NOTE 3: For quantitative analysis, see Method 7300 for ICP.

EVALUATION OF METHOD:

The method has been evaluated preliminarily using ASTM E1792 [1] wipes spiked with certified reference materials (CRMs), and has been found to give a positive response for at least ten micrograms of lead per wipe. The method has also been subjected to limited field testing, and shows a positive response for at least a few tens of micrograms of lead per wipe. Extremely heavy soiling on the wipe could interfere with visualization of the red color change due to darkening of the wipe, but the pink or red hues should still be visible around the area of the heaviest soiling, provided lead is present. Difficult matrices (e.g., dust wipes containing paint chips) may require leaching in dilute nitric acid before spot testing.

Persons with color blindness may not be able to detect the pink or red hues characteristic of this spot test method.

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METHOD WRITTEN BY:

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MANEB 3600
Dermal Patch

$C_4H_6N_2S_4Mn$ MW: 265.2 CAS: 12427-38-2 RTECS: OP07000

METHOD: 3600, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: not applicable
NIOSH: not applicable
ACGIH: not applicable

PROPERTIES: powder, yellow, wettable; sparingly soluble in water and organic solvents; vp not significant

NAMES & SYNONYMS: manganous ethylenebis(dithiocarbamic acid), Manzate; Dithane M-22

SAMPLING

SAMPLER: PATCH
Dry NuGauze®, spun polyester gauze patch (see Figure 1)

FLOW RATE: not applicable

VOL-MIN: not applicable
-MAX: not applicable

SHIPMENT: desorb immediately in shipping bottles, pack in blue ice, cool to 4 °C, ship via overnight express

SAMPLE STABILITY: at least 1 week at 4 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not applicable

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV detection

ANALYTE: ethylenebisdithiocarbamate anion

EXTRACTION: 40 mL desorbing solution (1% L-cysteine, 3% $Na_4EDTA \cdot 2H_2O$ in water) in 50 to 65-mL wide-mouth bottles with Teflon®-lined screw caps

INJECTION VOLUME: 100 µL

MOBILE PHASE: 0.0675 M phosphate, 0.0525 M $NaClO_4$, pH 6.9, 1 g/L $Na_2EDTA \cdot 2H_2O$, 2 mL/min

COLUMN: Dionex AS7 anion exchange column or equivalent, GS7 guard column

DETECTOR: UV, 285 nm (λ max) or 254 nm

CALIBRATION: solutions of Maneb in 1% L-cysteine, 3% Na_2EDTA

RANGE: 0.02 to 4 mg/sample [1]

ESTIMATED LOD: 0.02 mg/sample (0.5 µg/mL) [1]

PRECISION ($\bar{S}_r$): 0.015 [1]

APPLICABILITY: This method determines Maneb collected on dry Nu Gauze® (spun polyester gauze) dermal patches attached to clothing on the arm(s), leg(s), or torso of agricultural workers. It is applicable to the determination of Zineb, Mancozeb, and Nabam since these all convert to the same analyte when dissolved in EDTA solution.

INTERFERENCES: Not thoroughly investigated. No interferences have been found during method development.

OTHER METHODS: Maneb may also be determined by first methylating followed by HPLC analysis with a C18 column [2-5].

REAGENTS:

1. Maneb,* purity >90%
2. Water, deionized
3. Mobile Phase, 0.0675 M phosphate buffer, 0.0525 M $NaClO_4$, 1 g/L $Na_2EDTA•2H_2O$: In a 1-L volumetric flask, dissolve 4.79 g dibasic sodium phosphate; 4.59 g monobasic potassium phosphate; 6.43 g sodium chlorate; 1 g ethylenediaminetetraacetic acid, disodium salt, dihydrate in 500 mL of deionized water. Bring to volume with deionized water. Adjust pH to 6.9.
4. L-cysteine, reagent grade.
5. Ethylenediaminetetraacetic acid, disodium salt, dihydrate ($Na_2EDTA•2H_2O$), reagent grade.
6. Sodium phosphate, dibasic, anhydrous (Na_2HPO_4), reagent grade.
7. Potassium phosphate, monobasic, anhydrous (H_2PO_4), reagent grade.
8. Sodium Chlorate ($NaClO_3$), reagent grade.
9. Ethylenediaminetetraacetic acid, tetrasodium salt, dihydrate ($Na_4EDTA•2H_2O$)*
10. Desorbing solution, 1% L-cysteine, 3% Na_4EDTA in water: In a 1-L volumetric flask, dissolve 10 g L-cystene and 30 g $Na_4EDTA•2H_2O$ in 500 mL water. Dilute to volume with deionized water. (The pH will be approximately 8.6.*)
11. Calibration stock solution*, 1 mg/mL: Dissolve 10 mg Maneb in 10 mL desorbing solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Polyester gauze, Johnson & Johnson Nu Gauze® 10-cm x 10-cm (4" x 4"), 4-ply or equivalent.
2. Patch holders, aluminized cardboard (see Figure 1).
3. High performance liquid chromatograph (HPLC) with UV detector, 254 nm (or 285 nm if a variable-wavelength UV detector is available), and autosampler. Set chromatograph to conditions on page 1.
4. Columns: Dionex AS7 anion exchange column, AG7 guard column or equivalent.
5. Ultrasonic bath.
6. Forceps.
7. Bottles, wide-mouth, amber, 50- to 65-mL, with PTFE-lined screw caps.
8. Volumetric flasks, 10-mL, 100-mL, 1-L.
9. Graduated cylinder, 50-mL.
10. Vials, autosampler.
11. Pipets, glass, various sizes.
12. Syringes, 100-µL with large bore needle (≥19-gauge).

SPECIAL PRECAUTIONS: Maneb has degradation products which are known to be carcinogenic, mutagenic, and teratogenic [6-9]. Avoid contact with Maneb. Wear appropriate protective equipment. Na_4EDTA is very alkaline. Avoid contact with skin or eyes of either the dry powder or aqueous solutions.

SAMPLING:

NOTE: The sampling procedure has not been thoroughly investigated. This is a prototype method only.

1. Place Nu Gauze® patches in the patch holders.
2. Label each patch holder with name, date, body location, and time of attachment; then attach to clothing on the arm(s), leg(s), or torso of the human subject(s) at location noted on patch label.
3. Label amber wide-mouth glass shipping bottles with the same information.
4. After a 4- to 8-hour time period for the human subject(s) working in the field or with Maneb application equipment, remove the patch holders and record the time.
5. Using forceps, remove the Nu Gauze® patches from the patch holders by folding the corners into the middle. Place patches in shipping bottles with as little disturbance of the collected Maneb as possible.

6. Prepare sufficient desorbing solution for all samples and blanks: 4 g L-cysteine and 12 g $Na_4EDTA•2H_2O$ in 400 mL of deionized water for every 10 samples (40 mL per sample). Prepare this solution in the field to prevent premature oxidation of the L-cysteine preservative.
   NOTE: The EDTA here must be the tetrasodium form, not the disodium form. See SPECIAL PRECAUTIONS.
7. Add 40 mL of desorbing solution to each shipping bottle, cap, and shake well to wet the Nu Gauze® and dissolve the Maneb.
8. Prepare 2 to 10 blank samples by adding 40 mL to clean Nu Gauze® patches in shipping bottles.
9. Pack shipping bottles securely in blue ice or other means to keep at 4 °C, and ship via overnight express.

SAMPLE PREPARATION:

NOTE: Desorption of samples is done on site.

10. On arrival at laboratory, store samples at 4 °C.
11. Ultrasonicate capped sample bottles for 5 to 10 minutes.
12. Transfer 1 to 2 mL of each desorbed sample solution, standards, and blanks to autosampler vials for analysis. Analyze within 24 hours.

CALIBRATION AND QUALITY CONTROL:

13. Calibrate daily with at least six working standards over the range of 0.1 to 100 µg/mL.
    a. Pipet aliquots of calibration stock solution into 10-mL volumetric flasks, and bring to volume with desorbing solution.
    b. Include a calibration blank of unspiked working solution.
    c. Analyze together with field samples, field blanks, and laboratory control samples (steps15 through 17).
    d. Prepare a calibration graph (peak area vs. concentration, µg/mL).
       NOTE: To prepare media standards, prepare a slurry of Maneb in methanol, 1 mg/mL. Ultrasonicate for approximately 2 minutes to pulverize and disperse the particles of Maneb. Shake slurry periodically to keep the Maneb suspended. Up to 20% ethylene glycol can be included to help keep the particles in suspension. Withdraw a measured amount using a 100-µL syringe with a large bore (≥ 19-gauge needle) and spike onto a dry Nu Gauze® patch within a 50- to 65-mL amber wide-mouth bottle. After drying, desorb the Maneb-spiked Nu Gauze® with 40 mL of desorbing solution and ultrasonicate.
14. Prepare laboratory control samples (LCS), in duplicate, with each sample set.
    a. Spike Maneb in methanol onto 10-cm x 10-cm Nu Gauze® patches placed in 50- to 65-mL amber glass bottles in concentrations within the analytical range.
    b. Desorb with 40 mL of desorbing solution.
    c. Analyze along with field samples, standards, and blanks (steps 15 through 17).

MEASUREMENT:

15. Set liquid chromatograph to manufacturer's recommendations and conditions given on page 3600-1.
16. Transfer sample aliquots to injection vials. Inject 100-µL aliquots manually or with an autosampler. Rinse and dry syringe after each injection.
17. Measure peak areas. If sample peak area exceeds the linear calibration range, dilute with aqueous 1% L-cysteine, 3% $Na_4EDTA•2H_2O$ solution, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18. From the calibration graph, read the concentration, C (µg/mL), of Maneb found in the sample.
19. Calculate the mass, M, of Maneb in the sample (µg/sample).

$$M(\mu g) = C(\mu g / mL) x 40 mL$$

CONFIRMATION:

No confirmation method has been tested. Possible alternatives are ion-pairing chromatography with a C-18 column [5], or analysis of methylated derivatives on a C-18 column [3,4].

EVALUATION OF METHOD:

This method has been evaluated in the laboratory only. No field samples have been analyzed to date.

LOD/LOQ

A series of media standards (See Note above under step 13.d.) from 0.1 to 100 µg/mL were prepared in duplicate, analyzed, and fitted with a linear curve. The Limit of Detection (LOD), 0.02 mg/sample for a 40-mL desorbing volume, and Limit of Quantitation (LOQ), 0.066 mg/sample, were estimated using NIOSH SOP 018 [10].

PRECISION AND ACCURACY

Twenty-four media standards were prepared, six at each of four levels: 3xLOQ, 10xLOQ, 30xLOQ, and 100xLOQ, as described above in Note under step 13.d. The media standards were desorbed with 40 mL of desorbing solution and analyzed. Levels 3xLOQ, 10xLOQ, and 100xLOQ were used to obtain a pooled relative standard deviation. One of the six samples at the 100xLOQ level was shown to be an outlier by Grubbs' test and was not included in the calculations. Bias, Accuracy, and Overall Precision were not determined. The recoveries were all greater than 90% except for Level 3xLOQ, which was 88% [1].

STABILITY

Stability studies were performed at 528 µg Maneb per dermal patch. At room temperature (24 °C), Maneb on dry Nu Gauze® patches was not stable, with less than 60% recovery on Day 2. At 4 °C, however, Maneb was stable on dry Nu Gauze® to at least Day 8. Maneb which was spiked onto Nu Gauze® and allowed to stand approximately two hours while the solvent dried and was then desorbed in a 1% L-cysteine, 3% Na_4EDTA solution, was stable to Day 22 with recoveries greater than 90%. At Day 30 the recovery was 87% [1].

COMMENTS:

Most ethylene-bis-dithiocarbamates (EBDC) containing divalent (or higher) metals (*e.g.*, Maneb, Mancozeb, and Zineb) dissolve with difficulty in almost every solvent. If the metal ion is removed by complexation with EDTA (at high pH), the EBDC will dissolve but will begin to degrade rapidly, presumably by oxidation, to disulfides or other products. Adding an antioxidant such as L-cysteine greatly inhibits this oxidative degradation. Excluding headspace air has been shown to assist in reducing oxidation; however, cooling to 4 °C is one of the most important factors in sample preservation.

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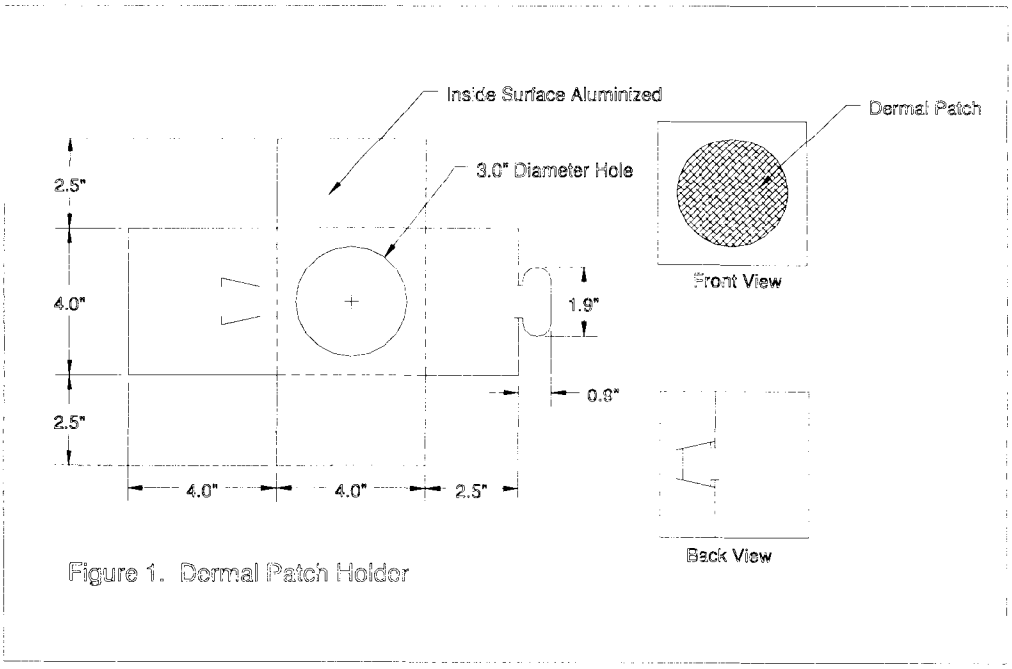

Figure 1. Dermal Patch Holder

MANEB
Hand Wash

3601

$C_4H_6N_2S_4Mn$ MW: 265.2 CAS: 124-38-2 RTECS: OP07000

METHOD: 3601, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: not applicable
NIOSH: not applicable
ACGIH: not applicable

PROPERTIES: powder, yellow, wettable; sparingly soluble in water and organic solvents; vp not significant

NAMES & SYNONYMS: manganous ethylenebis(dithiocarbamic acid), Manzate; Dithane M-22

SAMPLING

SAMPLER: PLASTIC BAG containing hand-wash solution,150 mL

SHIPMENT: add 1 g L-cysteine, 3 g $Na_4EDTA \cdot H_2O$ to each sample, ship in refrigerant packs, 4 °C, via overnight express

SAMPLE STABILITY: at least 1 week at 4 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV detection

ANALYTE: ethylenebisdithiocarbamate anion

INJECTION VOLUME: 100 µL

MOBILE PHASE: 0.0675 M phosphate, 0.0525 M $NaClO_4$, pH 6.9, 1 g/L $Na_2EDTA \cdot 2H_2O$, 2 mL/min

COLUMN: Dionex AS7 anion exchange column, GS7 guard column or equivalent

DETECTOR: UV, 285 nm (λ max) or 254 nm

CALIBRATION: solutions of Maneb in 1% L-cysteine, 3% Na_2EDTA

RANGE: 0.03 to 15 mg/sample [1]

ESTIMATED LOD: 0.2 µg/mL or 0.03 mg/sample [1]

PRECISION ($\hat{S}_r$): 0.015 [1]

APPLICABILITY: This method determines Maneb washed from the hands of workers. It is applicable to the determination of Zineb, Mancozeb, and Nabam since these all convert to the same analyte when dissolved in EDTA solution.

INTERFERENCES: Not thoroughly investigated. No interferences have been found during method development.

OTHER METHODS: Maneb can also be determined by first methylating followed by HPLC analysis with a C18 column [2-5].

REAGENTS:

1. Maneb*, purity > 90%
2. Water, deionized
3. Mobile Phase, 0.0675 *M* phosphate buffer, 0.0525 *M* $NaClO_4$, 1 g/L $Na_2EDTA{\bullet}2H_2O$: In a 1-L volumetric flask, dissolve 4.79 g dibasic sodium phosphate; 4.59 g monobasic potassium phosphate; 6.43 g sodium chlorate; 1 g ethylenediaminetetraacetic acid, disodium salt, dihydrate in 500 mL of deionized water. Bring to volume with deionized water. Adjust pH to 6.9.
4. L-cysteine, reagent grade.
5. Ethylenediaminetetraacetic acid, disodium salt, dihydrate ($Na_2EDTA{\bullet}2H_2O$), reagent grade.
6. Sodium phosphate, dibasic, anhydrous (Na_2HPO_4), reagent grade.
7. Potassium phosphate, monobasic, anhydrous (H_2PO_4), reagent grade.
8. Sodium chlorate ($NaClO_3$), reagent grade.
9. Ethylenediaminetetraacetic acid, tetrasodium salt, dihydrate ($Na_4EDTA{\bullet}2H_2O$)*.
10. Triton-X-100 solution: 1 mL Triton-X-100 plus 50 mL water.
11. Diluting solution: 1% L-cysteine, 3% $Na_4EDTA\ 2H_2O$ in water. Prepare as follows: Dissolve 10 g of L-cysteine and 30 g of $Na_4EDTA\ 2H_2O$ in 50 mL of deionized water in a 1-L volumetric flask. Dilute to volume with deionized water. (The pH will be approximately 8.6*.)
12. Calibration stock solution*: Dissolve 10 mg of Maneb in 10 mL diluting solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Plastic bags, polyethylene, 2 quart size, freezer bag type, containing 150-mL hand wash solution.
2. High performance liquid chromatograph (HPLC) with UV detector, 254 nm (or 285 nm if a variable-wavelength UV detector is available). Set chromatograph to conditions on page 3601-1.
3. Ultrasonic water bath.
4. Graduated cylinder to measure water for hand wash 150 mL.
5. Bottles, glass, amber, wide-mouth, 75- to 125-mL, with PTFE-lined screw caps.

SPECIAL PRECAUTIONS: Maneb has degradation products which are known to be carcinogenic, mutagenic, and teratogenic [6-9]. Avoid contact with Maneb by wearing appropriate protective equipment. Na_4EDTA is very alkaline; avoid contact with skin or eyes of either the dry powder or aqueous solutions.

SAMPLING:

NOTE: The sampling procedure has not been thoroughly investigated; this is a prototype method only.

1. Pour 150 mL of water into a plastic bag. Record the total volume of water in the bag.
2. Add 5 drops of Triton-X-100 solution to the water in the bag.
3. Ask the worker to insert his hand into the water and, while holding the bag closed around his arm, shake his hand in the water for approximately 30 seconds.
4. After removing the hand from the bag, add 1 g L-cysteine and 3 g $Na_4EDTA\ 2H_2O$ to the bag.
   NOTE 1: The EDTA here must be the tetrasodium form, not the disodium form. See SPECIAL PRECAUTIONS.

NOTE 2: Preweighing the L-cysteine and the EDTA into small vials is a convenient way of dispensing these chemicals in the field.

NOTE 3: The addition of EDTA and L-cysteine to the hand-wash solution before washing the hand is not recommended, because these chemicals will make the hand-wash solution very alkaline, slippery, and have an unpleasant odor (from the L-cysteine).

5. Shake the bag until all the L-cysteine and EDTA dissolve.
6. Pour the hand-wash solution from the bag into a 75- to 125-mL amber wide-mouth bottle to overflowing and cap with no headspace.
7. Prepare a blank sample by following all steps above, except step 3.
8. Pack securely for shipment in refrigerant packs to keep at approximately 4 °C, and ship via overnight express.

SAMPLE PREPARATION:

9. On arrival at the laboratory, store the samples at 4 °C.
10. Put capped sample bottles in the ultrasonic bath for 5 to 10 minutes.
11. Transfer 1 to 2 mL of each hand-wash solution, standard, and blank to an autosampler vial for analysis. Analyze within 24 hours. No further sample preparation is necessary.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least six working standards over the range of 0.1 to 100 µg/mL.
    a. Pipet aliquots of calibration stock solution into 10-mL volumetric flasks, and bring to volume with diluting solution.
    b. Include a calibration blank of unspiked diluting solution.
    c. Analyze together with field samples, field blanks, and laboratory control samples (steps 14 through 16).
    d. Prepare a calibration graph (peak area vs. concentration, µg/mL).
13. Prepare Laboratory Control Samples (LCS), in duplicate, with each sample set.
    a. Independently prepare quality control Maneb LCS solutions in aqueous 1% L-cysteine, 3% $Na_4EDTA•2H_2O$ at concentrations within the analytical range.
    b. Analyze along with the field samples, blanks, and liquid standards (steps 14 through 16).

MEASUREMENT:

14. Set liquid chromatograph to manufacturer's recommendations and the parameters given on page 3601-1.
15. Inject sample aliquots (100 µL) manually or with an autosampler. Rinse and dry syringe after each injection.
16. Measure peak areas. If sample peak area exceeds the linear calibration range, dilute with an aqueous 1% L-cysteine, 3% $Na_4EDTA•2H_2O$ solution, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

17. From the calibration graph, read the concentration, C (µg/mL), of Maneb found in the sample.
18. Calculate the mass of Maneb, M (µg), in the hand wash sample volume, V (mL).

$$M = CxV, \mu g / sample$$

CONFIRMATION:

No confirmation method has been tested. There are several possible alternatives, such as ion-pairing chromatography with a C-18 column [5], or analysis of methylated derivatives on a C-18 column [3,4].

EVALUATION OF METHOD:

This method has been evaluated in the laboratory only. No field samples have been analyzed to date.

LOD/LOQ

A series of liquid standards from 0.1 to 100 µg/mL was prepared in duplicate, analyzed, and fitted with a linear curve. The Limit of Detection (LOD), 0.2 µg/mL, and Limit of Quantitation (LOQ), 0.66 µg/mL, were estimated with the NIOSH SOP 018 method [10].

PRECISION AND ACCURACY

Twenty-four liquid standards were prepared, six at each of four levels: 3xLOQ, 10xLOQ, 30xLOQ, and 100xLOQ. The relative standard deviation of the 100xLOQ level was considerably lower than that of the other three levels and, therefore, was not used to compute the pooled relative standard deviation. The pooled relative standard deviation for the first three levels was 0.015. Since all samples were spiked liquid standards, accuracy and bias were not determined. Since no samples were generated, overall precision was not calculated.

STABILITY

Stability studies were performed on solutions at 6.6 µg/mL Maneb concentration. It was determined that it is necessary to store the samples at 4 °C in a solution of 1% L-cysteine, 3% $Na_4EDTA\ 2H_2O$. Samples stored at 4 °C were stable to 30 days with greater than 90% recovery with or without headspace. At 24 °C, however, samples with headspace deteriorated more rapidly. Therefore, as a precaution against the possibility of elevated temperatures during shipping, samples should be stored and shipped with no headspace.

COMMENTS:

Most ethylene-bis-dithiocarbamates (EBDC) containing divalent (or higher) metals, (*e.g.*, Maneb, Mancozeb, and Zineb) dissolve with difficulty in almost every solvent. If the metal ion is removed by complexation with EDTA (at high pH), the EBDC will dissolve but will begin to degrade rapidly, presumably by oxidation, to disulfides or other products. Adding an antioxidant such as L-cysteine greatly inhibits this oxidative degradation. Excluding headspace air has been shown to assist in reducing oxidation; however, cooling to 4 °C is one of the most important factors in sample preservation.

REFERENCES:

[1] DataChem Laboratories [1995]. Backup Data Report for Maneb, dermal patch and hand wash. Unpublished report, DataChem Laboratories, Salt Lake City, UT.

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METALWORKING FLUIDS (MWF) ALL CATEGORIES 5524

DEFINITION: Metal-working fluids CAS: NONE RTECS: NONE

METHOD: 5524, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no PEL
NIOSH: 0.4 mg/m^3 as thoracic particulate (0.5 mg/m^3 as total particulate)
ACGIH: no TLV

PROPERTIES: not defined: Fluids contain varying amounts of mineral oil, emulsifiers, water, alkanolamines, polyethoxyethanols, biocides, surfactants, pressure additives and boron compounds.

SYNONYMS: metalworking fluids (MWF), metal removal fluids, machining fluids, mineral oils, straight fluids, soluble fluids, synthetic fluids and semi-synthetic fluids

SAMPLING

SAMPLER: Thoracic particulate: FILTER + CYCLONE (tared 37-mm, 2-µm PTFE filter, + thoracic cyclone).
Total particulate: (tared 37-mm, 2-µm PTFE filter

FLOW RATE: thoracic- 1.6 L/min)
total- 2 L/min

VOL-MIN: 1000 L @ 0.4 mg/m^3 or 0.5 mg/m^3
-MAX: Not determined

SHIPMENT: routine

SAMPLE STABILITY: Refrigerate upon receipt at laboratory; analyze within 2 wks of collection

BLANKS: at least 5 field blanks per set

BULK SAMPLE: one for each fluid at each site for solubility testing

ACCURACY

RANGE STUDIED: 0.05 to 0.9 mg/sample

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): total weight 0.06
extracted weight 0.07

ACCURACY (Estimated): total weight 0.12
extracted weight 0.14

MEASUREMENT

TECHNIQUE: GRAVIMETRIC

ANALYTE: airborne metal working fluid

EXTRACTION: ternary Solvent: Dichloromethane: methanol: toluene (1:1:1)
binary Solvent: methanol:water (1:1)

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights

RANGE: 0.05 to 2 mg per sample

ESTIMATED LOD: total weight- 0.03 mg per sample [7]
extractable - 0.03 mg per sample weight [7]

PRECISION ($\hat{S}_r$): total weight- 0.04 (≥0.2mg/sample) [1]
extracted - 0.05 (≥0.2mg/sample) weight [1]

APPLICABILITY: The working range is 0.050 to 2 mg/sample for a 1000-L air sample. The total weight procedure permits an estimate of the total particulate aerosol, including nuisance dust, airborne metal particulate and metal working fluid. If the extraction procedure is used, the technique permits an estimate of the total metal working fluid to which the worker is exposed. The method is applicable to all metal working fluids- straight, soluble, synthetic, and semi-synthetic as long as they are soluble in the extraction solvent [1,2]. Only one MWF (Glacier, Solutia Inc.) has thus far been found to be insoluble in the ternary extraction solvent. However, that MWF is soluble in the binary blend. Tests have shown that the binary solvent in combination with the ternary solvent is effective in extracting this fluid. [8].

INTERFERENCES: None identified. However, any material collected on the filter and soluble in the extraction solvents may interfere with the analysis.

OTHER METHODS: This method is similar to Method 0500 for Particulates Not Otherwise Regulated [3]. This method replaces Method 5026 which employs infrared analysis for mineral oil mist [4].

REAGENTS:

1. Dichloromethane, distilled-in-glass.
2. Methanol, distilled-in-glass.
3. Toluene, distilled-in-glass.
4. Water, filtered, double deionized
5. Calcium sulfate, desiccant.
6. Ternary solvent blend*: Mix equal volumes of dichloromethane, methanol, and toluene in a clean dust-free container. Use a bottle with a screw cap (e.g. a clean, empty solvent bottle): Mix the solvents by gentle swirling, not by violent shaking.
7. Binary solvent blend* : Mix equal volumes of methanol, and water in a clean dust-free container. Use a bottle with a screw cap (e.g. a clean, empty solvent bottle): Mix the solvents by gentle swirling, not by violent shaking

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 37-mm PTFE, 2-µm pore size membrane filter and supporting pad in 37-mm cassette filter holder. Use a 2-piece (closed-face) cassette for sampling total particulate; For sampling thoracic particulate, use a 3-piece cassette with thoracic cyclone (BGI, Inc. Cat. No. GK2.69 or equivalent).
2. Personal sampling pump, 1.6 to 2 L/min, with flexible connecting tubing.
3. Microbalance, capable of weighing to 0.001 mg.
4. Static neutralizer: e.g., ^{210}Po; replace nine months after the production date.
5. Forceps (preferably nylon or chrome-plated steel).
6. Extraction funnel (SKC.,Inc., Cat. No. 225-605 or equivalent).
7. Desiccator.
8. Wash Bottle, PTFE, for containing wash solvent.
9. Vials 20-mL, with leakproof PTFE-lined caps, for transporting bulk fluid samples and solubility testing.
10. Syringe, gas-tight with large bore needle, e.g.16-gauge needle.
11. Graduated cylinder 20 mL
12. Paper towels.
13. Metal screen for drying filters following extraction, approx. 1.5 ft square or other convenient size, (Pre-wash screen with ternary blend solvent and allow to dry.)

SPECIAL PRECAUTIONS: Dichloromethane is a suspect carcinogen. Handle all solvents in a fume hood. Use extreme caution when blending the solvents together. The heat of mixing can cause pressure to develop as the solvents are blended, e.g., blowing a stopper from a glass-stoppered container. Use a clean container sealed with a PTFE-lined screwcap.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Number the backup pads with a ballpoint pen and place them, numbered side down, in the filter cassette bottom sections.
2. Preweigh the filters by the weighing procedure given in step 3. Record the mean tare weight of sample filters, W_1 and field blanks, B_1 (mg).
3. Weighing procedure:
   a. Equilibrate the filters in an environmentally controlled weighing area or chamber for 1 hour.
   b. Zero the balance before each weighing.
   c. Using forceps, pass each filter over a static neutralizer. Repeat this step if the filter does not release easily from the forceps or attracts the balance pan. Static electricity can cause erroneous weight readings.
   d. Weigh each filter until a constant weight is obtained (two successive weighings within 10 µg). Record the mean of the last two weighings to the nearest microgram.
4. Assemble the filter in the 2- or 3- piece 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. For collection of a thoracic sample, insert the cyclone at the inlet to the 3-piece cassette.
6. Calibrate each personal sampling pump with a representative sampler in line.
7. For thoracic measurements, sample at 1.6 L/min for 8-hrs.
   For total particulate measurements, sample at 2 L/min for 8 hrs.
   Do not exceed a total filter loading of approximately 2 mg.
   NOTE: In order to test the extraction step of the analytical procedure, obtain a sample of the pure uncut bulk metal-working fluid (MWF) for solubility testing. Place this sample in a small (10-mL) leakproof container that is sealed with a leakproof PTFE-lined screwcap.
7. Submit at least five blank filter samples as field blanks for each set of samples collected per day. Handle these in the same way as the field samples; i.e., open each in a non-contaminated environment, then close the sampler and ship it to the lab along with the rest of the samples.
9. Refrigerate all samples that are to be stored overnight (or longer) prior to shipment to the laboratory. Ship all samples to the laboratory via overnight express delivery service.
10. Refrigerate the samples immediately upon receipt at the lab until ready for analysis.
11. Analyze the samples within two weeks of receipt at the laboratory.

SAMPLE PREPARATION AND MEASUREMENT:

10. Solubility test of bulk MWF:
    a. Shake the container of bulk MWF to assure that a homogeneous sample is obtained.
    b. Place 10-mL of the ternary solvent blend in a 20-mL scintillation vial.
    c. Using a large-bore gas-tight syringe; inject 50 µL of the bulk MWF into the ternary solvent blend. Cap the vial and shake as necessary to dissolve the MWF. The fluid is soluble if the resulting solution is clear and free of precipitates and phase separation.
    d. If the MWF is soluble in the ternary blend, the samples can be extracted with the ternary blend . A list of MWF evaluated for solubility thus far is given as an APPENDIX to this method and also at the NIOSH Manual of Analytical Methods website: (http://www.cdc.gov/niosh/nmam/nmampub.html)
11. Wipe dust from the external surface of each filter cassette (containing either samples or blanks) with a moist paper towel to minimize contamination. Discard the paper towel.
12. Remove the top and bottom plugs from the filter cassette. Equilibrate the filters (in the cassettes) for no more than 2 hrs in a desiccator that employs calcium sulfate.
13. Remove from the desiccator. Equilibrate for 1 hr in the balance room.
14. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of sample.
    NOTE: If the filter adheres to the underside of the cassette top, very gently lift it away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.
15. Weigh and record (steps 3 b-d)the post-sampling weight of each filter, W_2 (mg) and blanks B_2 (mg). Record anything remarkable about the filter (e.g., overload, leakage, wet, torn, etc.)

CALIBRATION AND QUALITY CONTROL:

16. 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.
17. Process three tared media blanks through the measurement process for total particulate and the extractables.

EXTRACTION:

18. General guidelines (see NOTE below):
    If the weights of samples exceed the amount expected to be collected at the REL, e.g. 0.4 mg (thoracic) or 0.5 mg (total particulate) for a 1 m^3 air sample, extract the samples and blanks as follows:

NOTE: Samples weighing < 0.4 to 0.5 mg (for a 1 m^3 sample) may be extracted as desired. The reason that the cutoffs of 0.4 and 0.5 mg (per 1000 L sample) have been specified is to assure simple compliance with the standard. If the gross sample weight indicates that the standard has not been exceeded, there may be no reason to extract the sample. Otherwise, the usefulness of any extraction data obtained at levels < 0.4 to 0.5 mg per sample is guided by the quantitation limit (LOQ) of the extraction procedure. Extraction data obtained at levels between the LOD and the LOQ of the extraction procedure should be used with appropriate caution.

a. Place each filter (membrane side up) in the filter funnel assembly connected to the vacuum source.
b. Pour one 10-mL aliquot of the ***ternary solvent*** down the inside of the funnel over the filter. Allow solvent to drain by gravity.
c. Pour one 10-mL aliquot of the ***binary solvent*** down the inside of the funnel over the filter. Allow solvent to drain by gravity.
d. Pour a second 10-mL aliquot of the ***ternary solvent*** down the inside of the funnel over the filter. Allow at least 30 seconds of contact time. Remove the solvent under slight vacuum. Wash the inner wall of the filter funnel with 1-2 mL of the ternary blend contained in a PTFE wash bottle. Remove the solvent under slight vacuum.
e. Turn off the vacuum to the filter funnel.
f. Carefully, remove the filter from the filter funnel, place it on the clean metal screen, and allow to dry on the metal screen for 2 hours in a fume hood. Do not remove the filter from the funnel while vacuum is applied or the filter may delaminate.

NOTE: One fluid, Glacier (Solutia Chemical, St Louis), was insoluble in the ternary blend but was soluble in the binary blend. Tests have shown that this fluid is efficiently extracted from the filters using steps 18 a - e.

19. Weigh each filter, including field blanks (using steps 3 a-d). Record the post-extraction weight, W_3 (mg) of the extracted sample filters and B_3 (mg) for the extracted blank filters. Record anything remarkable about the extracted filter (e.g, torn, wet, delamination etc.)

CALCULATIONS:

20. Calculate the concentration of total- or thoracic particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1) \cdot 10^3 \, L/m^3}{V}, (mg/m^3)$$

where: W_1 = mean tare weight of filter before sampling (mg)(step 3)
W_2 = mean post-sampling weight of sample-containing filter (mg)(step 15)
B_1 = mean tare weight of blank filters (mg) (step 3)
B_2 = mean post-sampling weight of blank filters (mg) (step 15)

21. Calculate the concentration of extracted MWF aerosol C_{MWF} (mg/m^3), in the air volume sampled, V (L):

$$C_{MWF} = \frac{(W_2 - W_3) - (B_2 - B_3) \cdot 10^3 \, L/m^3}{V}, (mg/m^3)$$

where: W_2 = mean post-sampling weight (pre-extraction weight) of sample-containing filter (mg)(Step 15)
W_3 = mean post-extraction weight of sample-containing filter (mg) (step 19)
B_2 = mean post-sampling weight of blank filters (mg) (step 15)
B_3 = mean post-extraction weight of blank filters (mg) (step 19)

22. Report the concentration C as total- or thoracic particulate weight; report the concentration C_{MWF} as the weight of the MWF aerosol.

EVALUATION OF METHOD:

The development of the ternary solvent used in this method is described in reference [1]. This method was initially tested with representative samples of straight, soluble, semi-synthetic, and synthetic metalworking fluids (MWF). Samples were spiked onto tared polytetrafluoroethylene (PTFE) membrane filters, stored overnight, and analyzed the following day. The samples were weighed, then the MWF was extracted from the filter with a 1:1:1 blend of dichloromethane:methanol: toluene. The extraction of all fluids from the filters was quantitative over the range 200 µg to 815 µg for the straight fluid, from 223 µg to 878 µg for the soluble fluid, from 51 µg to 189 µg for the semi-synthetic fluid, and from 102 µg to 420 µg for the synthetic fluid. For those weights of all four fluids spiked at levels ≥ 200 µg, the relative standard deviation was estimated to be 4% for the total weight procedure and 5% for the extraction procedure. If the sampling imprecision of 5% is included, these estimates become 6% and 7% respectively for the total weight and extraction procedures. Limits of quantitation, estimated from blanks carried through the entire analytical procedure, were 30 µg for the weighing technique and 60 µg for the extraction technique. No estimate of the bias was available. [2] The filters are dessicated to remove excess water, especially from water-based MWF samples.

In a more rigorous test of the method for a 79-plant survey [7], the average limits of quantitation were estimated to be 0.1 mg for both the total- and extracted- weight procedures. However, there was high variability in these estimates for the sites sampled. The upper 95% confidence limit for the LOQs for both the total weight- and extractable weight- measurements was 0.3 mg. In order to assess the effectiveness of the extraction step, a secondary extraction of the most heavily-loaded filters obtained in this survey was conducted; On average, < 5% of the sample weight was removed during the 2nd extraction, indicating that the majority of extractable material had been removed during the first extraction. Samples were refrigerated upon receipt at the laboratory [6, 7].

The fractions extracted (FE or weight extracted/weight of sample) were studied as a function of the four metalworking fluid types and three main work operations grinding, milling, and turning. This evaluation indicated that FE generally decreased in the order: straight > semisynthetic or soluble > synthetic; the differences in the fractions extracted for the straight and the synthetic fluids were statistically significant only for the grinding operation at two sample levels tested.

During the 79-plant survey, the stability of quality assurance (QA) samples, spiked separately with a straight, a soluble, a semisynthetic, and a synthetic fluid indicated that the QA samples all lost weight according to simple linear decay equations. These decay equations were used to estimate the amounts expected to be reported for QA filters by the performing laboratory. For storage periods ranging from 17 to 26 days, the total weight of samples recovered for all QA samples were ≥80% of those expected from the decay equations. For these QA samples, the fractions extracted of all four fluid types were ≥ 0.90.

The binary solvent extraction step has been added to assure complete extraction of MWF components that may be incompletely removed by the ternary blend. In addition, the binary solvent extends the procedure to samples that contain ternary blend-soluble fluids co-mingled with ternary blend-insoluble fluids, e.g. Glacier. Tests of the extraction of five MWF (including Glacier) showed that extraction efficiencies using the ternary blend in combination with the binary blend were comparable to those reported in reference 1 using the ternary blend alone (FE > 90 % ;CV < 0.10) . The binary solvent extractant liquor obtained from the Glacier samples generally contained potassium and phosphorous at levels approximately expected for the mass spiked onto the filters. The binary solvent extracts of the four other test fluids were analyzed for sodium, potassium or boron marker elements. Sodium was present in the extract of the soluble fluid at > background levels. The boron marker was not detected in the extract from the semisynthetic fluid. The potassium marker was not detected in the extract from the synthetic fluid [8].

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METHOD WRITTEN BY:

R. Glaser, NIOSH/DART.

APPENDIX

List of Metalworking Fluids that have been found to be soluble in the ternary blend. The individual fluids have been identified by type and manufacturer [6,7].

MANUFACTURER	TRADENAME	TYPE	SOLUBLE
All Power	KOOLMIST 77	Semi-synthetic	Yes
American Lubricants	All Purpose Cutting Oil	Straight	Yes
Americhem Corp	AM Cutting 2506 Oil	Straight	Yes
Angler Industries	Draw LT-1R	Synthetic	Yes
	Angler OIL Cut 121-M straight oil	Straight	Yes
Aqueous Cleaning Tech Inc	ACT 486 Cutting Coolant	Soluble	Yes
	ACT 734 Synthetic Coolant	Synthetic	Yes
Associated Chemists	ACI Templex 5950	Semi-synthetic	Yes
	ACI 4926 Carbide Grinding Fluid	Synthetic	Yes
	ACI 4920 Grinding Fluid	Synthetic	Yes
	ACI Templex 4966	Semi-synthetic	Yes
	ACI Templex 4929 Low Foam Grinding Fluid	Synthetic	Yes
	ACI 4931 Mach and Tap Fluid	Straight	Yes

Blaser Swisslube	BLASOCUT 4000 STRONG	Soluble	Yes
	Blasocut 2000 Universal	Soluble	Yes
Castrol	Castrol Meqqem Cob	Synthetic	Yes
	Clearedge 6519	Semi-synthetic	Yes
	Clearedge 6584	Semi-synthetic	Yes
	Drawfree 811 (Previously Iloform)	Soluble	Yes
	N100 Pale oil (Brass Oil)	Straight	Yes
	Safety Cool 407	Soluble	Yes
	Safety Cool 800	Semi-synthetic	Yes
	Syntilo 9951	Synthetic	Yes
	Syntilo 9954	Synthetic	Yes
Chemtrol Inc	CT-345-J	Semi-synthetic	Yes
Chevron	Chevron Met Working Fluid #503	Straight	Yes
Citgo Petroleum	Citgo Cutting Oil 205	Soluble	Yes
	Citgo Cutting Oil 425	Straight	Yes
	Citicool 22	Synthetic	Yes
	Citcool 33	Synthetic	Yes
CLC Lubricants	CLC Cut PX2 NS	Straight	Yes
	CLC Chem Finish 605	Straight	Yes
	CLC Chem Cut MX-CG	Straight	Yes
	Coolant 2224 Plus	Synthetic	Yes
	Chem Finish 605	Straight	Yes
Commonwealth Oil	Comminac 32 MAX	Straight	Yes
Cutting & Grinding Fluids Inc	CG 650 D	Soluble	Yes
	CG 5352 R	Straight	Yes
	CG 5352 RR	Straight	Yes
	Kool Kut 692	Soluble	Yes
DA Stuart Co	Dascool LN 231-78	Semi-synthetic	Yes
	Dascool 2223	Semi-synthetic	Yes
	Superkool 25 straight	Straight	Yes
	Surgrind 86	Synthetic	Yes
Die-Casting ID Corp	ID DUA Chem 202	Semi-synthetic	Yes
Diversy Corp	LUBRICOOLANT AC	Soluble	Yes
	LUBRICOOLANT 4D	Soluble	Yes
DoALL Co.	DoAll 80	Straight	Yes
	Kool All 940	Semi-synthetic	Yes
	Kool All 948	Semi-synthetic	Yes
ELF Lubricants North America Inc	Elfdraw S 13	Synthetic	Yes
Enterprise Oil Co	Duracut 130	Straight	Yes

ETNA Products	Master Draw B 942/I	Soluble	Yes
Fuchs Lubricants	Fuchs Velvesol 96	Soluble	Yes
	Lus-Co-Cut 570ST	Straight	Yes
	Lus-Co-Cut 514 CMP Straight oil	Straight	Yes
	Lus-Co-Cut 400 Straight oil	Straight	Yes
	Renodraw 419NC	Soluble	Yes
	Renocut 471 straight oil	Straight	Yes
	Shamrock LF	Soluble	Yes
	Ultracool 430	Synthetic	Yes
Hangsterfer's Lab Co	Hangsterfer's Hard Cut # 531	Straight	Yes
Houghton Intl	CUTMAX 570	Straight	Yes
	Cut Max TPO-46	Straight	Yes
	Hocut 787 H	Soluble	Yes
Intercon Enterprises	Jokisch W2-OP	Semi-synthetic	Yes
ITW Fluid Prod Group	Accu-Lube LB-2000	Straight	Yes
	Accu-Lube LB 3000	Straight	Yes
	Rustlick PB-10 Soluble	Soluble	Yes
	Rustlick WS 5050	Soluble	Yes
Lillyblad	DB BROMUS B water souble	Soluble	Yes
	DB Water Soluble oil D	Soluble	Yes
Lyondell Petrochemical	Transkut HD 200	Straight	Yes
Master Chemical	Trim E 190	Soluble	Yes
	Trim CE/CE	Soluble	Yes
	Trim O M287	Straight	Yes
	TRIMSOL	Soluble	Yes
	Trim Microsol 265	Soluble	Yes
	TRIMSOL Silicone Free	Soluble	Yes
Metalworking Lubricants	METKUT 20546-TX-40	Straight	Yes
Milacron	Cimstarr 60-LF	Semi-synthetic	Yes
	Cimstar 3700	Semi-synthetic	Yes
	Cimtech 100	Synthetic	Yes
	Cimstar Qual Star	Semi-synthetic	Yes
	Cimtap II		Yes
	Cimperial 1010	Soluble	Yes
	Cimperial 1011	Soluble	Yes
	Cimstar 55	Semi-synthetic	Yes
	Cimstar 540	Semi-synthetic	Yes
	Cimtech 400	Synthetic	Yes
	C10 TX	Soluble	Yes
Mobil Oil Corp	Mobil Mobilmet Omicron	Straight	Yes
	Mobil Mobilmet Nu oil	Straight	Yes
	Mobil Vascul 18F	Straight	Yes
	Mobilmet Alpha Straight Oil	Straight	Yes

	Mobilmet Omega	Straight	Yes
	Vacmul 281	Straight	Yes
	Mobil Hydraulic AW 68 Straight Oil	Straight	Yes
	Mobilmet Upsilon	Straight	Yes
	Vacmul 3A Honing oil/EDM	Straight	Yes
Monroe Fluid Tech Co	Prime Cut Soluble Oil	Soluble	Yes
Motor Oil Inc	Thredkut 99 cutting oil	Straight	Yes
	Kleercut CF	Straight	Yes
National Oil Products	National Oil Products 3115 cutting oil	Straight	Yes
	National Oil Products Supreme Soluble HD	Soluble	Yes
Oakite Products Inc	Oakite Controlant 650 NS	Synthetic	Yes
Ocean State Oil	Hycut 4 Straight Oil	Straight	Yes
	Neil Cut 570 Cutting straight oil	Straight	Yes
Perkins Products	Perkut 296-H	Straight	Yes
	Perkool 5005- EP	Semi-synthetic	Yes
Relton Corp	Relton A-9 Aluminum Cutting Fluid	Soluble	Yes
Rex Oil & Chemical Co	Titan Cutting Straight Oil	Straight	Yes
	Magic Cutting Oil	Straight	Yes
Richards Apex Prod. formerly G Whitefield Richards Co	Near-a-Lard # 62	Straight	Yes
Rock Valley Oil & Chemical Co	Rockpin Straight Oil	Straight	Yes
Solar Chem Co	Solar Cut	Synthetic	Yes
Solutia	**Glacier**	Synthetic	**No**
Spartan Chem Co.	COOLSPAR	Synthetic	Yes
Steco Corp	TAP Magic Aluminum	Semi-synthetic	Yes
	Tapmagic Extra Cuttng Fluid	Straight	Yes
Stirling Industries Division	Tufcut 316	Straight	Yes
	Raecut A-1	Straight	Yes
	16228 HONING OIL	Straight	Yes
Sunnen Products	Sunnen Honnig Oil MB 30-55	Straight	Yes
Tapmatic Corp	LPS Tapmatic Plus 2	Synthetic	Yes
Texaco	Texaco Sulfur Oil (Sultex)	Straight	Yes
	Texaco SultexF	Straight	Yes
	Texaco 2731 Almag Special	Straight	Yes
	Texaco 01659 rando HD 68 brass st oil	Straight	Yes

Trico Mfg	TriCool	Synthetic	Yes
Union Butterfield	Union Butterfield Tapping & Cutting Oil	Straight	Yes
Unocal Refining	Unocal Kooper Kut 11HD	Straight	Yes
US Oil Co Inc	Blanking Oil 250	Straight	Yes
	Alkut 810	Straight	Yes
	US Drawlube 1517	Straight	Yes
	Vanishing Oil 300	Straight	Yes
	Gem Soluble CP	Soluble	Yes
	US Cut 6040	Straight	Yes
	Spindle Oil ISO 10 Al st oil	Straight	Yes
	321-SS Cutting Straight Oil	Straight	Yes
Valenite Inc	ValCool Turntech	Semi-synthetic	Yes
	Valcool VNT 800	Soluble	Yes
Varoum Chemical	Gauge Sterling Brass Cutting Oil	Straight	Yes
	Metacut MS Steel Cutting Oil	Straight	Yes
	GM 465	Straight	Yes
Viking Chemical Co	Cut Rite 305 CFX	Straight	Yes
Vulcan Oil & Chem	Ultrasol Soluble Oil	Soluble	Yes
	J-Cut 931 Cutting Oil	Straight	Yes
	Poseidon R&O HD	Straight	Yes
WS Dodge Oil Co	Pale oil (all Viscosity grades)	Straight	Yes
	Combo base 82 Additive	Straight	Yes
	Deosol 202	Soluble	Yes
	Pale Straight Oil 55	Straight	Yes
	Superkut Cutting Oil 72/200	Straight	Yes
ZEP Products	ZEP Lubeze 14	Straight	Yes

METHYL ACRYLATE 2552

$C_4H_6O_2$ MW: 86.1 CAS: 96-33-3 RTECS: AT2800000

METHOD: 2552, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: 10 ppm
NIOSH: 10 ppm
ACGIH: 2 ppm (skin notation)
(1 ppm = 3.52 mg/m³)

PROPERTIES: flammable liquid; den = 0.9574 g/mL @ 20°C; BP = 80.5°C; VP = 65 mm Hg @ 20°C; Flash Point = -3°C; FP = -76.7°C; Vapor Density = 2.95.

SYNONYMS: Methoxycarbonylethylene, Methyl ester of acrylic acid, Methyl propenoate, 2-propenoic acid methyl ester.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb CMS, 150/75 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 10 ppm
-MAX: 5 L

SHIPMENT: Keep cold; pack securely for shipment.

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 2 - 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied.

BIAS: Not determined.

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined.

ACCURACY: Not determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl acrylate

DESORPTION: 1 mL of carbon disulfide with agitation.

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (hold 3 min) to 150 °C (8°C/min)

CARRIER GAS: He (2.6 mL/min)

COLUMN: Capillary, fused silica, 30-m x 0.53-mm ID; 3µm film crossbonded® 35% diphenyl-65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of methyl acrylate in CS_2

RANGE: 1.9 to 172.3 µg per sample [1]

ESTIMATED LOD: 0.5 ug per sample [1]

PRECISION ($\hat{S}_r$): 0.007 [1]

APPLICABILITY: The working range is 0.11 to 9.79 ppm (0.39 to 34.5 mg/m³) for a 5 L air sample [1]. Method is applicable to any sampling environment where methyl acrylate is present in the vapor state.

INTERFERENCES: Any compound eluting during the analysis and having a similar retention time.

OTHER METHODS: This method udates NMAM 1459 [2] which is Method S38 from the 2nd edition of the NIOSH Manual of Analytical Methods [3]. Improvements include but are not limited to the following: smaller volume of desorption solvent required, desorption efficiency (DE) results were improved by using a different solid sorbent tube, and a lower LOD/LOQ was established [1]. A storage stability study was completed and was found acceptable with a 105.3% recovery after 4 weeks at 5°C [1].

REAGENTS:

1. Methyl acrylate, reagent grade (99.9+).*
2. Carbon disulfide, chromatographic grade*.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, prefiltered and purified.
6. Calibration stock: Dilute 3 µL of Methyl acrylate in 10 mL solvent. Prepare remaining standards by serial dilution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long x 6-mm ID, containing two sections of Anasorb CMS separated by a 3-mm section of polyurethane foam. Silanized glass wool plugs hold each section in place. Tubes are commercially available (SKC # 226-121 or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator, and Rtx-35 fused silica capillary column.
4. Autosampler vials, glass, 12-mm crimp caps.
5. Syringes, 10-µL to 1-mL.
6. Volumetric flasks, 10-mL.
7. Pipets, various sizes.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable and should be handled in a well ventilated fume hood. Methyl acrylate reacts violently with strong oxidants resulting in an explosion and fire hazard. Methyl acrylate polymerizes easily under the effects of heat, light, and peroxides.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sample tube in line.
2. Break open the ends of the sample tube immediately prior to sampling. Attach sample tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap both ends of the sample tubes with plastic caps and pack cold for shipment.

SAMPLE PREPARATION:

5. Place the initial glass wool plug and front sorbent section of the sample tube into autosampler vial. Place the back sorbent section of the sample tube in separate autosampler vial. Discard the polyurethane foam separator and the remaining glass wool plug.
6. Add 1.0 mL of carbon disulfide to each vial and cap securely.
7. Let each vial stand for 30 minutes with occasional agitation.
8. Analyze each sample by GC.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working calibration standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of calibration stock solution to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg methyl acrylate).
10. Determine the desorption efficiency (DE) at least once for each lot of Anasorb CMS used for sampling in the calibration range (step 9).
    a. Prepare three tubes at each of five levels plus three media blanks.
    b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each Anasorb CMS tube.

c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5-8) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg methyl acrylate recovered.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2552-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with carbon disulfide solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method development was a result of requests to update and improve problematic gas chromatography methods. After determining that Anasorb CMS sorbent tubes resulted in improved DE recoveries when compared to the results previously obtained using coconut shell charcoal tubes [1], the desorption efficiency was determined for methyl acrylate at 5 levels ranging from 19.2 µg to 172.3 µg. The average DE for methyl acrylate was determined to be 92.3% using Anasorb CMS sorbent tubes [1] while the previously determined DE for methyl acrylate using charcoal tubes was 81% [4]. The LOD was determined to be 0.5 µg per sample. The precision, as determined from the pooled relative standard deviation (S_r), was determined to be 0.007. Methyl acrylate storage stability @ 0.5xREL was acceptable after 30 days (105.3%) [1].

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

METHYL AND ETHYL METHACRYLATE 2537

(1) $H_2C=C(CH_3)COOCH_3$	MW: 100.12	CAS: 80-62-6	RTECS: OZ5075000
(2) $H_2C=C(CH_3)COOC_2H_5$	114.15	97-63-2	OZ4550000

METHOD: 2537, Issue 3 **EVALUATION: (1) FULL (2) PARTIAL** **Issue 1: 15 August 1990 Issue 3: 15 March 2003**

OSHA: (1) 100 ppm; (2) None
NIOSH: (1) 100 ppm; (2) None
ACGIH: (1) 100 ppm; (2) None

(1) 1 ppm = 4.10 mg/m³
(2) 1 ppm = 4.68 mg/m³

PROPERTIES: (1) liquid; d = 0.944 g/mL @ 20°C; BP = 100°C; VP = 4.7 kPa (35 mm Hg) @ 20°C; explosive range 1.7 to 8.2% v/v in air.
(2) liquid; d = 0.917 g/mL @ 20°C; BP = 119°C; flash point = 21.1°C; index of refraction = 1.4116 (25°C).

SYNONYMS: (1) Methyl ester of methacrylic acid, methyl-2-methyl-2-propenoate
(2) Ethyl ester of methacrylic acid; ethyl-2-methyl-2-propenoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2, 400/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 8 L

SHIPMENT: In dry ice

SAMPLE STABILITY: 7 days @ 25°C; 31 days @ 5°C [1]

BLANKS: 2 - 10 samples per set

ACCURACY

RANGE STUDIED: (1) 193 to 725 mg/m³ (3-L samples) [3]
(2) Not studied

BIAS: (1) 2.55% [3]
(2) Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): (1) 0.063 [3]
(2) Not determined

ACCURACY: (1) +/- 12.6% [3]
(2) Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Methyl and ethyl methacrylate

DESORPTION: 2 mL CS_2 with sonication for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 50°C (3 min) to 150°C (8°C/min)

CARRIER GAS: Helium, 5.0 mL/min

COLUMN: Capillary, fused silica, 30-m x 0.53-mm ID, 3-µm film crossbonded® 35% diphenyl-65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of analytes in CS_2

RANGE: (1) 0.9 to 8240 µg [1,2]
(2) 1.5 to 275 µg [1]

ESTIMATED LOD: (1) 0.4 µg/sample (Instrumental)[1]
(2) 0.5 µg/sample (Instrumental)[1]

PRECISION ($\hat{S}_r$): (1) 0.009 (2) 0.025 [1]

APPLICABILITY: The working range for methyl methacrylate is 0.07 to 670 ppm (0.30 to 2747 mg/m³) and for ethyl methacrylate is 0.11 to 19.7 ppm (0.50 to 91.7 mg/m³) for a 3-L air sample.

INTERFERENCES: None identified. Chromatographic conditions may be modified to resolve any interferences.

OTHER METHODS: This method updates NMAM 2537, Issue 2 (4th ed.) [4] which previously revised NIOSH method S43 [5]. Improvements include the evaluation and addition of ethyl methacrylate to the method, higher desorption efficiency (DE) recoveries at lower study levels for both analytes, lowered LOD values, the incorporation of capillary column chromatography for analyte resolution, and the completion of a 30 day storage stability study.

REAGENTS:

1. Methyl methacrylate, ACS reagent grade.*
2. Ethyl methacrylate, ACS reagent grade.*
3. Carbon disulfide, low benzene grade.*
4. Helium, prepurified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing two sections (front = 400 mg, back = 200 mg) of XAD-2 resin (20/50 mesh), separated by silylated glass wool plugs (SKC # 226-30-06 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible tubing attached.
3. Gas chromatograph, flame ionization detector, suitable integrator system, and Rtx®-35 or equivalent fused silica capillary column.
4. Syringes, 10-µL, 25-µL, 250-µL, and 1-mL.
5. Flasks, 10-mL volumetric type.
6. Vials, 5-mL, glass with PTFE-lined screw caps, and 2-mL autosampler vials.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a dangerous fire and explosion hazard (flash point = -30°C) so work in a hood is mandatory. Methyl and ethyl methacrylate are strong irritants and lachrymators.

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 a known flow rate between 0.01 to 0.05 L/min for a sample size of 1 to 8 L.
4. Cap the samplers. Pack securely in dry ice for shipment.

SAMPLE PREPARATION:

5. Place the front (along with first glass wool plug) and back sorbent sections in separate 5-mL vials. Discard remaining plugs.
6. Add 2.0 mL of carbon disulfide to each vial and cap securely.
7. Place each vial in a sonication bath for 30 minutes.
8. After sonication, transfer aliquots from each sample to 2 mL autosampler vials and attach crimp caps.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary additional standards may be added to extend the calibration curve.
   a. Add known amounts of calibration standards to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11and 12).
   c. Prepare calibration graph (peak area vs. µg analyte).
10. Determine the desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the calibration range (step 9).
    a. Prepare three tubes at each of five levels plus three media blanks.
    b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each XAD-2 tube.

c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5-8) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg analyte recovered.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2537-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with the carbon disulfide solvent, reanalyze and apply the appropriate dilution factor corrections in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), for each 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 each analyte in the air volume sampled, V(L):

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

NOTE: µg/L=mg/m^3

EVALUATION OF METHOD:

Initial Method Development Effort (Issues 1 and 2)

Method S43 (methyl methacrylate) was issued on July 6, 1979, and validated over the range of 193 to 725 mg/m^3 [3]. Average DE recovery results achieved in two independent studies were 98.1% [3] and 96-100% [5] over the range of 560 to 2350 µg/sample. Overall precision (S_{rT}) was estimated to be 0.063. Breakthrough volume was 6.46 L at a generated air concentration of 786 mg/m^3 for methyl methacrylate under conditions of 90% relative humidity [3]. Subsequent storage stability results indicated that methyl methacrylate was stable for 32 days (97.3%) and ethyl methacrylate for 23 days (95-100%) @ 4°C [5].

Current Method Development Effort (Issue 3) [1]

The current method development effort was the result of requests to evaluate and improve problematic gas chromatography methods as part of the NMAM methods update project. Initial evaluations confirmed that XAD-2 (400/200 mg) sorbent tubes were still the most suitable media for the sampling and analysis of both methyl and ethyl methacrylate. The average DE recoveries, using substantially lower analyte concentration ranges than in previous studies (10x LOQ to 0.1x REL vs. 0.5x REL to 2.0x REL), were 100.4% for methyl methacrylate and 102.3% for ethyl methacrylate. The LOD values for both methyl and ethyl methacrylate were lowered by a factor of 20 to 0.4 and 0.5 µg/sample, respectively. A 31-day storage stability study was completed for both methyl methacrylate (96.2% @ 0.05x REL/PEL) and ethyl methacrylate (99.8% @ 0.05x REL/PEL) at 5°C.

REFERENCES:

[1] Pendergrass SM [1999]. Method Development Effort Backup Data Report for Methyl and Ethyl Methacrylate, NIOSH, DPSE, ARDB, ACS, (unpublished).
[2] Tanguay JF [1988]. Method Modification Effort for Methyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished).
[3] NIOSH [1979]. Backup Data Report for Methyl Methacrylate (S43), prepared under NIOSH Contract 210-76-0123.
[4] NIOSH [1994]. Methyl Methacrylate: Method 2537, Issue 2. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[5] NIOSH [1980]. Methyl Methacrylate, Method S43. In:Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control. DHHS (NIOSH) 80-125.

METHOD WRITTEN BY:

ISSUE 1 and 2:

Robert W. Kurimo, NIOSH/DPSE; S43 originally validated under NIOSH Contract No. 210-76-0123.

ISSUE 3:

Stephanie M. Pendergrass, NIOSH/DART

METHYLTIN CHLORIDES 5526

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

METHOD: 5526, Issue 1 **EVALUATION: FULL** **Issue 1: 15 March 2003**

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

PROPERTIES: See Table 1

SYNONYMS:
Methyltin Trichloride: Trichloromethylstannane, Monomethyltin trichloride
Dimethyltin Dichloride: Dichlorodimethylstannane, Dichlorodimethyltin
Trimethyltin Chloride: Chlorotrimethylstannane, Chlorotrimethyltin, Trimethylstannyl chloride

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (OVS Tube: 13-mm glass fiber filter; XAD-2, 270/140 mg)

FLOW RATE: 0.25 to 1 L/min

VOL -MIN: 15L
-MAX: 75L

SHIPMENT: Ship assembled sampler cold

SAMPLE STABILITY: 14 days @ 4 °C

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 2

BIAS: Table 2

OVERALL PRECISION ($\hat{S}_{rT}$): Table 2

ACCURACY: Table 2

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FPD (tin-specific filter)

ANALYTE: Sodium tetraethylborate derivatives of the analytes

DESORPTION: 2 mL 1% acetic acid in acetonitrile

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: Cool-on-column
-DETECTOR: 250 °C
-COLUMN: 50 °C (3min), 12°C/min to 200°C (1min)

CARRIER GAS: He, 6 mL/min

COLUMN: Capillary, fused silica, 30m x 0.53mm ID, 1.5-µm film, 5% phenyl, 95% methyl silicone, DB-5 or equivalent.

CALIBRATION: Analytes in hexane

RANGE: 0.01 to 15 µg/sample (as tin) [1]

ESTIMATED LOD: 0.01 µg [1]

PRECISION ($\hat{S}_r$): 0.065 [1]

APPLICABILITY: This method was developed for air monitoring of methyltin chlorides.[1]

INTERFERENCES: None were identified.

OTHER METHODS: NMAM 5504 is another method for the measurement of organotin compounds using a filter with a sorbent tube for collection and HPLC/AA for analysis [3].

REAGENTS:

1. Acetic Acid, 99+%.*
2. Acetonitrile, HPLC grade.*
3. Diethyl Ether, 99+%.*
4. Hexane, HPLC grade*.
5. Methyltin Trichloride, 97%.
6. Dimethyltin Dichloride, 97%.
7. Trimethyltin Chloride.
8. 1% acetic acid in acetonitrile solution, (v/v).
9. Sodium tetraethyl borate.*
   NOTE: Purity of sodium tetraethyl borate is critical. It should appear as a fine white powder. Clumping or yellowing indicates that the compound must be replaced.
10. Sodium Acetate - Acetic Acid Buffer, pH 4.0 ± 0.2. Commercially available from Fisher Scientific.
11. Derivatizing Solution: Prepare a solution containing 1% (w/v) of sodium tetraethylborate in diethyl ether. Prepare the solution fresh daily, preferably immediately before use.
12. Calibration Stock Solution: Prepare a stock calibration solution by accurately weighing (to ± 0.1 mg) about 0.1 g each of methyltin trichloride, dimethyltin dichloride and trimethyltin chloride into a 50 ml volumetric flask. Dilute to volume with 1% acetic acid in acetonitrile. The stock solution contains about 1000 µg/ml (as tin) of each component. Stored in a freezer, this solution remains stable for several weeks.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: OSHA Versatile Sampler (OVS tube), 13-mm OD inlet, 6-mm OD outlet. Front section contains 270 mg 20/60 mesh XAD-2 sorbent held in place by an 11-mm diameter glass fiber filter and Teflon® ring, separated from the back section of 140 mg XAD-2 sorbent by a short plug of polyurethane foam. The back section is held in place with a plug of polyurethane foam. The tube is available commercially from SKC, Inc. (cat. #226-30-16) and Supelco, Inc. (cat. #ORBO-49P).
2. Personal sampling pump: 0.1 to 1 L/min with flexible and inert connecting tubing.
3. Gas chromatograph equipped with a cool on-column injection port, automated injector, DB-5 capillary column, flame-photometric detector (FPD) with a tin-specific filter (610 nm), and data collection system or equivalent (page 5526-1).
4. Balance capable of weighing to ±0.1 mg.
5. Mechanical shaker.
6. Vials, 10-mL, with PTFE-lined screwcaps.
7. Transfer pipettes or eyedroppers.
8. GC autosampler vials with PTFE-lined caps.
9. 5-mL,10-mL and 50-mL volumetric flasks.
10. Pipettes capable of accurately delivering 10 µL and 1.0 and 2.0 mL.
11. Refrigerant packs for shipping.

SPECIAL PRECAUTIONS: Concentrated acetic acid is corrosive and an irritant. Sodium Tetraethylborate is sensitive to air and moisture. This chemical should be stored and handled under a nitrogen atmosphere. Acetonitrile, diethyl ether, and hexane are all flammable. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap the sorbent tube immediately before sampling and connect to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.25 L/min for full shift sampling and 1 L/min for 15 minutes samples (STEL) for a maximum of 75 L.
4. Cap the samplers. Pack securely for shipment with cold refrigerant packs.
   NOTE: After receipt at the laboratory, samples should be stored at 4°C and analyze within 14 days of collection.

SAMPLE PREPARATION:

5. Remove the retaining ring from the sorbent tube and discard. Transfer the glass fiber filter and the main resin bed to a 10-mL sample vial.
6. Remove and discard the foam plug that separates the two resin sections in the sorbent tube. Transfer the backup resin bed to a second 10-mL sample vial.
7. Into each vial, add 2 ml of 1% acetic acid in acetonitrile to desorb the methyltin chlorides. Put the vials on a mechanical shaker for 30 minutes.
8. Into each vial, add 2 ml of pH 4 buffer and 1 ml of derivatizing solution. Place the vials on the mechanical shaker for 15 minutes.
9. Extract the solution with three 1 ml portions of hexane. Combine the hexane fractions in a 5 ml volumetric flask and dilute to volume with hexane.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of interest.
    a. Accurately pipette 10 µl of the calibration stock solution into a vial that contains 5 mL of 1 % acetic acid in acetonitrile. Derivatize like a sample following steps 7 through 9.
    b. Serially dilute this standard derivatized solution with hexane to produce solutions over the range of 0.2 to 0.02 µg/mL (as tin) of each methyltin chloride.
    c. Transfer to gc autosampler vials with PTFE-lined caps.
    d. Analyze together with samples and blanks (steps 12 through 14).
    e. Prepare calibration graph (peak areas vs. µg tin for each methyltin chloride).
11. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 10). Prepare three samplers at each of six levels plus three media blanks.
    a. Transfer the front sorbent section of the OVS sampler to a 4mL vial.
    b. Inject a known volume of calibration stock solution, or serial dilution, directly onto the front sorbent bed of each OVS tube.
    c. Cap vial and allow spiked sorbent bed to stand overnight.
    d. Desorb (steps 7 through 9) and analyze together with standards and blanks (steps 13 through 15).
    e. Prepare a graph of DE vs. µg for each methyltin chloride recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5526-1.
14. Inject a 1-µL sample aliquot manually using solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze, and apply the appropriate dilution factor in the calculations.
15. Measure the areas of the peaks of the methyltin chlorides. A sample chromatogram is shown in Figure 1.

CALCULATIONS:

16. Determine the mass, µg (corrected for DE), for each methyltin 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.
17. Calculate concentration, C, of each methyltin chloride in the air volume sampled, V (L):
    NOTE: µg/L = mg/m^3

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

EVALUATION OF METHOD:

This method, developed to collect air samples and analyze the methyltin chlorides, was adapted from existing methodology for measuring organotin compounds in air [3,4]. Reference 1 details the validation of this method for sampling and quantifying of trimethyltin chloride, dimethyltin dichloride and methyltin trichloride in air. The validated method was needed to provide air monitoring capabilities during methyltin chloride and stabilizer production. Table 2 lists the results of the validation experiments which followed the guidelines established by NIOSH [2]. However, fewer replicates and concentration levels were used than recommended. This method met the NIOSH criteria for accuracy, bias and sample stability. The recommended sampling conditions are 250 ml/min for 5.5 hours maximum for time-weighted average (TWA) sampling and 1000 ml/min for 20 minutes maximum for short-term exposure limit (STEL) sampling.

REFERENCES:

[1] Yoder RE [2000]. Validation of a Method for the Collection and Quantification of Methyltin Chlorides in the Air. Philadelphia, PA: Atofina Chemicals. Unpublished.
[2] NIOSH [1995]. Guidelines for Air Sampling and Analytical Method Development. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.
[3] NIOSH [1994]. Organotin Compounds (as Sn): Method 5504. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th Ed. Cincinnati, OH: U.S. Department of Health and Human Services,Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[4] Shangwei H [1997]. Development of a Method for the Sampling and Analysis of Dimethyltin Dichloride and Trimethyltin Chloride [Dissertation]. New Orleans, LA: Tulane University, Department of Environmental Sciences, School of Public Health and Tropical Medicine.

METHOD WRITTEN BY: R.E. Yoder, C. Boraiko, Atofina Chemicals; P.F. O'Connor, NIOSH/DART.

TABLE 1. GENERAL INFORMATION

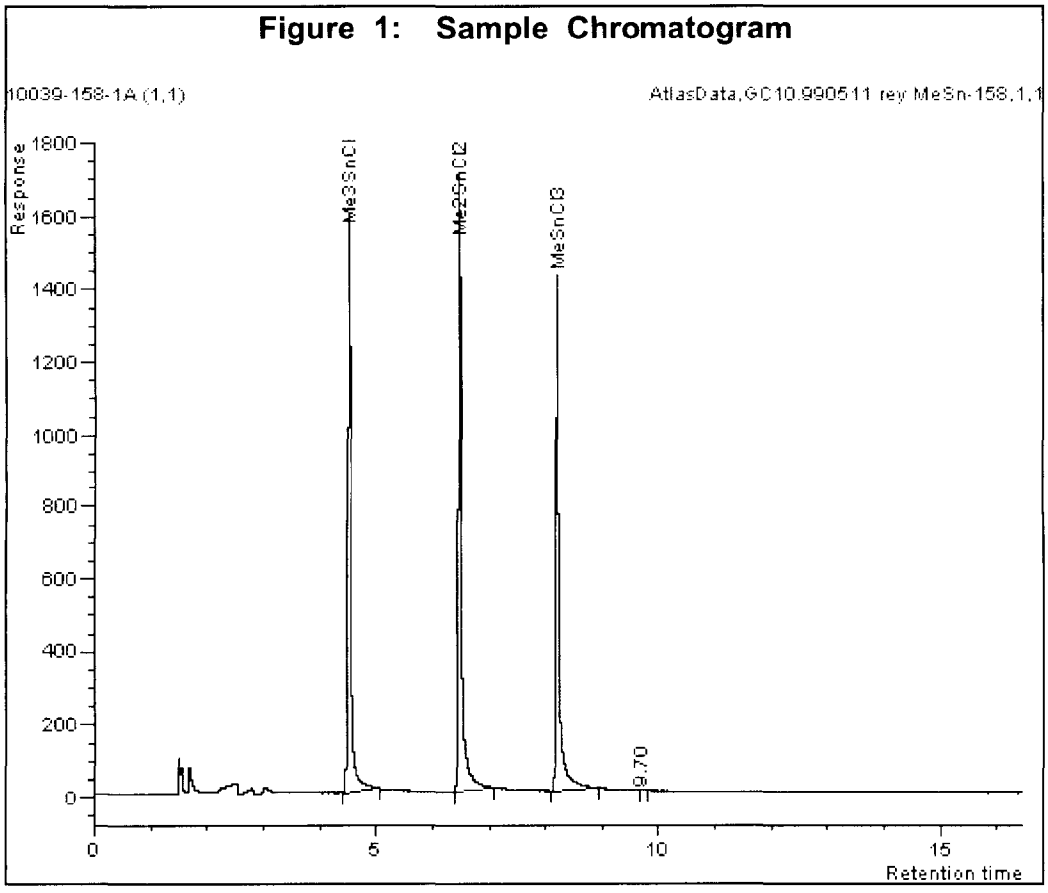
Analyte	Formula	Mol. Wt.	CAS#	RTECS#	Properties	OSHA PEL[a] (mg/m^3)	NIOSH REL[b] (mg/m^3)	ACGIH TLV[c] (mg/m^3)
Methyltin trichloride	CH_3Cl_3Sn	240.04	993-16-8	WH858550	Colorless Crystals MP 48-51°C BP 171°C	0.1	0.1	0.1 0.2 STEL (skin)
Dimethyltin dichloride	$C_2H_6Cl_2Sn$	219.67	753-73-1	WH7245000	Colorless Crystals MP 103-105°C BP 188-190°C	0.1	0.1	0.1 0.2 STEL (skin)
Trimethyltin chloride	C_3H_9ClSn	199.25	1066-45-1	WH685000	Colorless Crystals MP 37-39°C BP154 °C	0.1	0.1	0.1 0.2 STEL (skin)

[a]- OSHA PEL is measured as the amount of Tin (Sn) for organotin compounds in air.
[b]- NIOSH REL is measured as the amount of Tin (Sn) for organotin compounds in air.
[c]- ACGIH TLV is measured as the amount of Tin (Sn) for organotin compounds in air.

TABLE 2. METHOD EVALUATION [1]

	Range Studied	Bias (%)	Precision(S_{rT}) (%)	Accuracy (%)
Trimethyltin chloride	0.46 - 9.29 µg/sample (tin)	0.3	5.2	11
Dimethyltin dichloride	0.42 - 9.17 µg/sample (tin)	-2.5	5.8	12
Methyltin chloride	0.07 - 10.48 µg/sample (tin)	-5.2	7.6	16

Figure 1: Sample Chromatogram



1-NITROPYRENE IN DIESEL PARTICULATES 2560

$C_{16}H_9NO_2$ MW: 247.26 CAS: 5522-43-0 RTECS: UR2480000

METHOD: 2560, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solid; d 1.246 g/cc @ 20 °C; MP 154-157 °C; BP 231 °C

SYNONYMS: None

SAMPLING

SAMPLER: FILTER (Glass Fiber, 37-mm)

FLOW RATE: 1.0 to 2.0 L/min

VOL-MIN: 480 L
-MAX: 960 L

SHIPMENT: Ship in container at ambient temperature.

SAMPLE STABILITY: At least 28 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Generated atmospheres not studied

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NITROGEN CHEMILUMINESCENCE DETECTOR

ANALYTE: 1-Nitropyrene

DESORPTION: 1 mL toluene; place on a rotary shaker for minimum of 12 hours.

INJECTION VOLUME: 20 µL

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: Furnace: 850 °C
-COLUMN: Initial: 100 °C, ramp at 7.5 °C/min to 305 °C

CARRIER GAS: Helium @ 10.0 mL/min (splitless)

COLUMN: Capillary, fused silica, 30m x 0.53-mm ID; 1.5 µm film 5% diphenyl-95% dimethyl polysiloxane.

CALIBRATION: Liquid standard solutions of 1-nitropyrene in toluene.

RANGE: 0.020 to 50 µg per sample

ESTIMATED LOD: 0.010 µg per sample (see Evaluation of Method)

PRECISION ($\bar{S}_r$): 0.02 @ 1 to 50 µg per sample

APPLICABILITY: The working range is 0.021 to 104 µg/m³ for a 500 L sample. An appropriate range of calibration standards should be used to bracket the expected analyte concentration range. Because of sensitivity and accuracy considerations, a single calibration curve will not be appropriate for the entire working range. This method was developed to analyze 1-nitropyrene in a diesel particulate matrix (see Figure 2).

INTERFERENCES: None identified - however, compounds with a similar retention time may interfere. Positive identification may be confirmed by dual column chromatography using an appropriate alternative capillary column. Identification can also be confirmed by mass spectrometry.

OTHER METHODS: None identified.

REAGENTS:

1. Toluene, HPLC or GC grade.*
2. NIST, SRM 1650, Diesel Particulate Matter.
3. 1-Nitropyrene Standard Solution, 5000 µg/mL in toluene. (AccuStandard Inc., New Haven, CT, or equivalent).*
4. 1-Nitropyrene Standard Solution, 1000 µg/mL in toluene. (AccuStandard Inc., New Haven, CT, or equivalent).*

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Glass fiber filter (Type A/E) 1-µm pore size, 37-mm diameter (Gelman Sciences, Ann Arbor, MI, or equivalent), backed by a cellulose support pad 37-mm OD, in a two part, 37-mm cassette filter holder.
2. Spacer Ring, 37 mm (SKC, Eighty Four, PA or equivalent).
   NOTE: For calibration and QC samples, filter spacer rings are used instead of a support pad.
3. Personal sampling pump capable of operating for 8 hr at 2 L/min, with flexible connecting tube.
4. Labquake Rotary Shaker or equivalent.
5. Vials, Autosampler, glass with PTFE-lined crimp top cap, 1.8 mL.
6. Micro volume inserts for autosampler vials.
7. Forceps.
8. Syringes, glass: 5-µL, 10-µL, 1-mL, other sizes as needed.
9. Syringe filter with tube tip, 4-mm, 0.45-µm, PVDF.
10. Syringe, disposable: 1-mL volume.
11. Gas Chromatograph: HP-5890 with HP-7673 Autosampler (or equivalent), Antek Model 704E Nitrogen Chemiluminescence Detector (or equivalent). Restek Rtx-5-ms®, 30 m X 0.32 mm id., 1.0-µm film thickness (or equivalent).

SPECIAL PRECAUTIONS: 1-Nitropyrene is a cancer suspect agent and mutagen. Toluene is a flammable liquid, toxic.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate of 1.0 to 2.0 L/min for a volume of 480 to 960 L.
3. After the sample is collected, place the plastic plugs in the tubing connector stubs on the sampling cassette.

SAMPLE PREPARATION:

4. Extract Filters:
   a. Remove the filter from the cassette with a pair of forceps, discard the support pad, fold the filter and transfer to a GC autosampler vial.
   b. Add 1 mL of toluene and cap the vial with a septum crimp top.
   c. Place the vial on the rotary shaker. Rotate the samples for a minimum of 12 hours.
5. Prepare the filter extract for analysis.
   a. Carefully remove the septum cap from the vial containing the extracted filter.
   b. Using a transfer pipette, remove as much liquid extract from the extraction vial as possible and transfer to a 1 mL disposable syringe with a 4-mm syringe filter attached.
   c. Filter the extract into a micro volume insert in a GC autosampler vial. Cap the vial with a septum crimp cap.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six calibration standards to cover the concentration range of the samples. A typical gas chromatogram is shown in Figure 1.
   a. Prepare calibration standards by adding known amounts of the 1-nitropyrene standard solution or a secondary stock solution prepared from the standard solution to a GC autosampler vial containing 1 mL toluene.
   b. Analyze with samples and blanks (steps 9 & 10).
   c. Prepare a calibration graph (peak area vs. µg 1-nitropyrene).
7. Determine the recovery (R) of the analyte from the sampling media using the glass fiber filters with analyte spikes in the concentration range of the samples (see step 6). Prepare three filters at each of five levels plus three media blanks.
   a. Place a filter spacer ring in the bottom section of a two part 37 mm filter cassette. Place a 37 mm glass fiber filter on top of the spacer ring (do not use a support pad).
   b. Inoculate the filter with a known amount of calibration stock solution with a microliter syringe, place the top section of the cassette in place and seal the filter in place by squeezing the two sections together.
   c. Place the plugs in the inlet and outlet tubing stubs and set the cassettes aside for a minimum of twelve hours.
   d. Prepare the filter samples (steps 4 & 5) and analyze with the calibration standards.
   e. Prepare a graph of R vs. µg 1-nitropyrene.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2560-1. Inject sample with autosampler or by manual injection.
   NOTE: If peak area is above the linear range of the calibration standards, dilute the sample with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
10. Measure peak area of 1-nitropyrene peak and determine µg per sample from calibration graph.

CALCULATIONS:

11. Determine the mass, µg (corrected for R) for the sample (W), and average media blank (B).
12. Calculate concentration, C, of 1-nitropyrene in the air volume sampled, V(L):

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

NOTE: mg/L = mg/m^3

EVALUATION OF METHOD

This method was not evaluated with laboratory generated air samples. All of the recovery, storage studies, and LOD/LOQ determinations have been performed with laboratory spiked filters for the development of this method.

The method LOD and LOQ as determined using spiked media samples were 3.4 ng/sample and 11.5 ng/sample respectively. However, because the detector was operating at its maximum sensitivity settings, the normal baseline noise at the lowest analyte levels often made the peak difficult to be properly integrated. Therefore, more realistic and repeatable values for the LOD and LOQ are 10 and 20 ng/sample respectively.

Average recoveries of 1-nitropyrene from spiked glass fiber filters ranged from 88.4% to 101.2% for analyte quantities of 1.0 to 50.0 µg/filter using liquid standards as the spiking solution. Recovery of 1-nitropyrene from NIST SRM-1650 Diesel Particulates weighed on glass fiber filters and carried through the extraction and sample preparation process yielded recoveries of 73% to 114% (see NOTE) for sample quantities of 1.63 mg to 26.6 mg.

A thirty day storage stability study of 1-nitropyrene spiked on glass fiber filters indicates that the recovery of the analyte at a level of 10 µg/filter is 102%. The samples were stored in a closed cardboard container at room temperature for the duration of the study.

NOTE: The rated concentration of the NIST SRM-1650 for 1-Nitropyrene is 19±2 ug/g diesel particulate. The uncertainty in the amount is ±10.5%. This accounts for the wide range of recoveries of the NIST standard, particularly at the low amounts used in the recovery studies which were used to mimic the real world samples.

REFERENCES:

[1] IARC [1984]. 1-Nitropyrene. IARC Monograph on Evaluation of Cancer Risk of Chemicals to Humans, *33*:209-22, Apr.
[2] IARC [1997]. 1-Nitropyrene. IARC Monograph on Evaluation of Cancer Risk of Chemicals to Humans, *46*:321-358, Apr.
[3] NIST [1991]. "Certificate of Analysis." Standard Reference Material 1650, Diesel Particulate Matter. Gaithersburg, MD: National Institute of Standards and Technology, December 12.
[4] Jaycox LB [2002]. Backup Data Report, 1-Nitropyrene. Cincinnati, OH: National Institute for Occupational Safety and Health, DART. (unpublished report).

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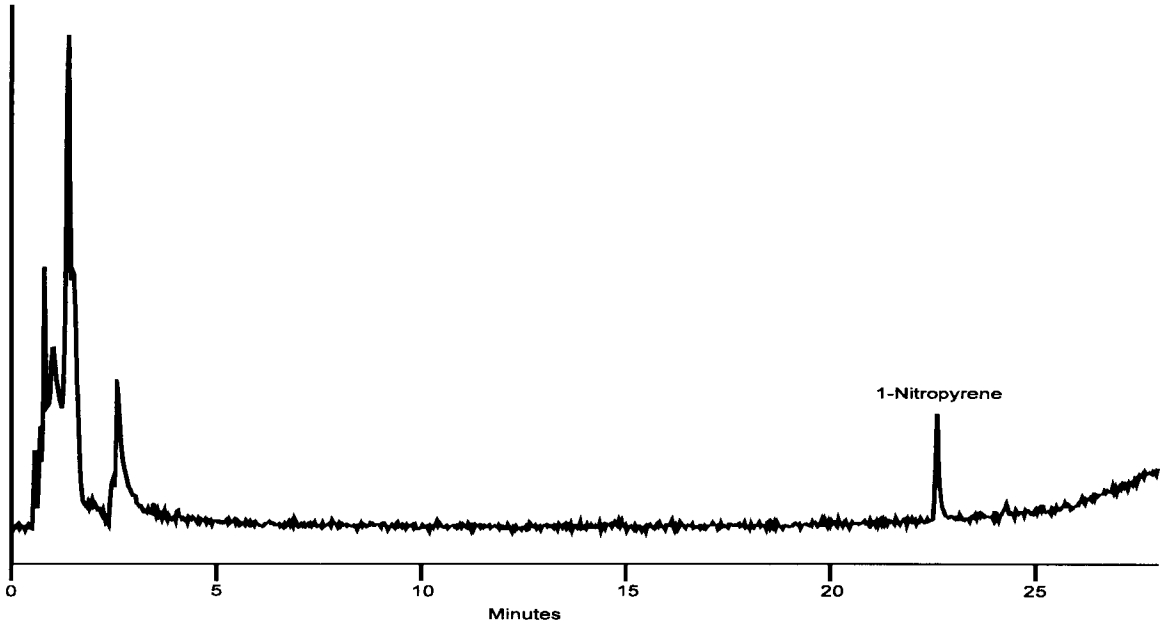

FIGURE 1: This is a chromatogram of a 1-nitropyrene 60 ng standard. The major peak at approximately 22.5 minutes is 1-nitropyrene. This chromatogram shows some hydrocarbon response and a baseline with a higher than normal noise level due to the effort to obtain as much sensitivity as possible for samples in the low nanogram region.

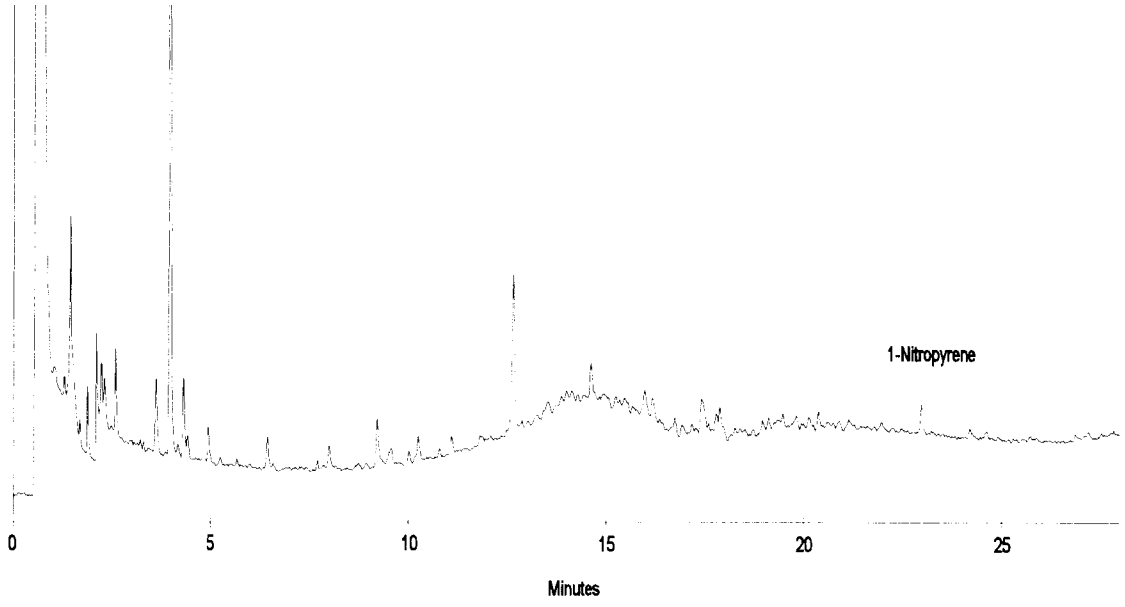

FIGURE 2: The chromatogram shown here is from the analysis of the NIST SRM-1650 Diesel Particulates. The diesel particulate, 2.10 mg, was weighed on a glass fiber filter and carried through the complete sample extraction and preparation procedure. The quantity of 1-nitropyrene in this sample was 39.9 µg.

ORGANIC AND INORGANIC GASES BY EXTRACTIVE FTIR SPECTROMETRY

3800

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

METHOD: 3800, Issue 1 **EVALUATION: FULL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

SYNONYMS: See example compounds in Table 1

SAMPLING		MEASUREMENT	
SAMPLER:	Portable direct-reading instrument (filter, if required)	**TECHNIQUE:**	EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY
FLOW RATE:	~0.1 to ~20 L/min (system-dependent)	**ANALYTE:**	See Table 1 (Additional compounds may be identified/quantified according to data quality objectives and QA/QC requirements)
VOL-MIN:	Instrument dependent		
-MAX:	None		
PRESSURE:	Extracted gases between 725 and 795 mm Hg absolute	**ANALYTICAL FREQUENCIES:**	See Table 2 for example compounds
TEMPERATURE:	Extracted gases between 10 and 30 °C	**CALIBRATION:**	Calibration gas standards
BLANKS:	Nitrogen gas, or zero air	**IDENTIFICATION:**	Infrared spectra interpretation and computerized reference library searches
ACCURACY		**RANGE:**	See Table 2 (dependent on compound and absorption pathlength)
RANGE STUDIED:	See Table 1	**ESTIMATED LOD:**	See Table 2 for example values at 10-meter absorption pathlength
BIAS:	See Appendix E	**PRECISION ($\bar{S}_r$):**	See Appendix E, 2B and 2C
OVERALL PRECISION ($\hat{S}_{r,T}$):	See Appendix E		
ACCURACY:	See Appendix E		

APPLICABILITY: The usefulness of FTIR techniques has been demonstrated in ambient air and combustion gas mixtures [7,8]. With the participation of an experienced analyst (see Appendix A), the method can be used for the characterization of workspace air containing mixtures of volatile organic and inorganic compounds. See Table 1 for examples.

INTERFERENCES: Overlap of infrared absorption features may affect the quantification of each compound. By appropriate use of multivariable least squares analyses, the analyst may be able to obtain accurate compound concentrations for overlapping compounds.

OTHER METHODS: This method is based on portions of EPA Method 320 [1] and its addendum [2] which describe the determination of gaseous compound concentrations by extractive FTIR spectrometry. Several compatible ASTM standards describing infrared techniques and terminology are also available [3-6].

REAGENTS:

1. Nitrogen gas (N_2) or zero air, HP or better.
2. Calibration Transfer Standard (CTS) Gas, 2% accuracy or better. The proper concentration depends on both the compound used and the system absorption pathlength. For ethylene in nitrogen, a standard concentration leading to a concentration - absorption pathlength product of 100 to 400 ppm-m is recommended. (For example, a standard of 10 ppm to 40 ppm ethylene in nitrogen is recommended for a 10 meter absorption cell).
3. Liquid nitrogen* (LN_2) for cooling the infrared detector, if required.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. FTIR spectrometer system (source, interferometer, sample absorption cell, and detector) configured with absorption. A minimum instrumental linewidth (MIL) 2 cm^{-1} or lower is recommended.
   NOTE:A lower or higher MIL may be required or suitable for specific gas matrices. Choose internal absorption cell materials to minimize surface/analyte interactions.
2. Computer system with hardware, software, and required reference spectra for acquisition, storage, and analysis of sample spectra. (A data backup system is recommended.)
3. Sampling pump, 0.1 to 10 L/min, with appropriate particulate filters.
4. Non-reactive gas regulators and sample tubing.
5. Rotameters or other devices, 20% accuracy, for measuring flow rates of sample and calibration gases.
6. Temperature measurement and/or control equipment for all sampling system elements and IR absorption cell.
   NOTE:Temperature control equipment required if ambient temp. <10 °C or >30 °C.
7. Pressure gauge for measuring absolute gas pressure in absorption cell, 5% accuracy at one atmosphere (760 mm Hg) absolute pressure.
8. For system tests (but not for normal operation): Vacuum pump and gauge capable of 100 mm Hg abs. pressure; mid-infrared attenuating filters (50% and 25%); impinger.

SPECIAL PRECAUTIONS: This method requires the use of compressed gases and/or cryogenic liquids and/or toxic chemicals. These materials are dangerous and should be handled only by experienced personnel and according to relevant safety standards. This method does not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations.

NOTE: Please refer to the Appendices for explanations of the terminology used in this document (Appendix A) and several FTIR system tests which must be completed before any testing is performed (Appendix B). Appendices C, D, and E provide (respectively) a general description of FTIR spectrometry, considerations for preparing reference libraries, and examples of calculations required for performance of this method.

PRE-TEST PROCEDURES:

The following procedures (Steps 1 and 2) may be performed only by an experienced "analyst" (see Appendix A).

1. Verify that the FTIR system has been tested for wavenumber reproducibility, minimum instrumental linewidth (MIL), absorption pathlength, system response time, residual squared area (RSA), and detector linearity as described in Appendix B. If the system is new and/or has been recently assembled and/or has been recently serviced, perform and document results of the tests described in Appendix B before proceeding.
2. Prepare a test plan. The plan must include the following:
   a. The proposed system configuration, including the absorption pathlength and integration time for sample spectra.
   b. The data quality objectives, analytical regions, and expected Limit of Detection (LOD) values for each analyte. See Table 2 and Appendix E for example values and calculations.
   c. The names of all "operators" and "analysts" to be involved in the test. Analysts must be experienced in all aspects of the test procedures listed below, and may perform any or all of the test procedures. Operators must be experienced in the performance of Steps 3 through 13 listed below, and may perform *only* those portions of the test procedures.
   d. Verification that the system configuration, existing RSA values, and related LOD values are consistent with the test's data quality objectives. (See Appendix E, Section 3.)

The following procedures (Steps 3 through 13) may be performed by an experienced operator or analyst.

3. Activate the FTIR system according to the manufacturer's instructions. Allow sufficient time for the infrared source, the infrared detector, and (if required) the temperature control systems to stabilize.
4. Verify that the computer system is programmed to store interferograms; if the available data storage capacity is insufficient for storage of all interferograms, store single beam spectra instead. Verify adequacy and performance of the (recommended) data backup system.
5. Bypassing the sampling system, flow N_2 or zero air directly into the infrared absorption cell until a stable infrared response and moisture levels are reached. Record a background spectrum using an integration time equal to or greater than that planned for subsequent sample spectra.
6. Use the entire FTIR system (including all sampling components) to record an absorbance spectrum of a sample stream of N_2 or zero air. Use the integration time planned for subsequent sample spectra. Verify that the sample flow rate meets or exceeds that specified in the system response time documentation. Examine the resulting "system zero" (SZ) spectrum and verify the absence of contaminants in the sampling system and infrared absorption cell. If contaminants are detected, clean or replace the appropriate sampling system components and/or infrared absorption cell and record a new SZ spectrum. If contaminants cannot be eliminated, the test results and LOD values may require revision during the quality control procedures (see Steps 14 through 17).

CALIBRATION:

7. Using the entire sampling system, acquire two or more pre-test CTS spectra and use them to calculate the system absorption pathlength L_S (see Appendix B, Section 1). Use the integration time planned for subsequent sample spectra. Verify that L_S is within 5% of the value quoted in the test plan. Verify that the sample temperature and pressure are within 10 to 30 °C and 725 to 795 mm Hg, respectively.
8. When possible, perform the following system checks before sampling. If necessary, they may be delayed until performance of the (post-testing) quality control procedures (see Steps 14 through 17). If performed after sampling, the results of these procedures may require revision of the test results and LODs.
   a. LOD Check. Using one of the SZ spectra, calculate the RSA values (see Appendix B, Section 2) and LOD values (see Appendix E, Section 2) in the analytical regions pertaining to the test analytes. Verify that the system pathlength, current RSA values, and current LODs are consistent with the test's data quality objectives (see Appendix E, Section 3).

b. Wavenumber Reproducibility Check. Record a preliminary workspace air sample spectrum and perform the calculations described in Appendix B, Section 3.

SAMPLING:

9. Using the integration time specified in the test plan, obtain samples and record infrared spectra of the desired ambient gases using the entire sampling system. The sampling location may be changed as desired. For tests of duration greater than 2 hours, or if the FTIR system is moved during sampling, monitor the system's single-beam response level. If changes greater than 5% in non-absorbing regions of the single beam spectrum occur, suspend sampling and record a new background spectrum (see Step 5). Sample spectra must be acquired at each sampling location for a time period no less than the system response time (see the system test documentation).
10. Repeat Step 6; acquire at least one post-test SZ spectrum of N_2 or zero air; confirm the absence of sampling system contaminates.
11. Record at least one post-test CTS spectrum (see Step 7); confirm that the system configuration and the system absorption pathlength (to within 5%) match those of the test plan.
12. (Optional) Acquire a post-test background spectrum (see Step 5).

SAMPLE ANALYSIS:

13. Using the analytical regions specified in the test plan, employ an appropriate mathematical analysis (see Appendix E) to determine preliminary analyte concentrations and their 3σ uncertainties from the sample spectra, reference spectra, absorption pathlength, and gas pressure.
    NOTE: Reference spectra for all analytes must meet or exceed the QA/QC requirements of Appendix D. The reference library must include at least one wavenumber standard spectrum and at least one calibration transfer standard (CTS) spectrum. The sample absorption due to any analyte may not exceed the maximum concentration-pathlength product represented in the reference library for that compound.

QUALITY CONTROL:

The following procedures (Steps 14 through 18) may be performed only by an experienced analyst.

14. Using one of the SZ spectra, calculate the RSA and LOD values (see Appendix E) in the analytical regions pertaining to the test analytes. Verify that the system pathlength, current RSA values, and current LODs are consistent with the test's data quality objectives. Using a suitable workspace air spectrum, perform the Wavenumber Reproducibility and Resolution tests described in Appendix B, Sections 3 and 4. If either the Wavenumber Reproducibility or Resolution results fail to meet the specifications, corrective actions are necessary (see Step 17).
15. Perform qualitative and/or quantitative analyses of the pre- and post-test SZ spectra and confirm the absence of sampling system contaminants. If contaminants are found which possess significant absorbance in any analytical region, corrective actions may be necessary (see Step 17). Perform qualitative and/or quantitative analyses of the pre- and post-test CTS spectra and confirm that the system absorption pathlength is within 5% of the value quoted in the test plan.
16. Verify that the reference spectra and results meet the data quality objectives of the test plan (see Appendix D). If they do not, corrective actions may be necessary (see Step 17). Examine the results of the quantitative sample analysis (Step 13) and verify some subset of them (including those with relatively high and relatively low concentrations) manually to ensure proper operation of analytical program. (Techniques for generating spectra representing the analytes at the concentration indicated by the analysis - "scaled spectra," as defined in Appendix A are described in Appendix E. The analyst should generate such spectra and compare them, either visually or mathematically, to the indicated sample spectra.)
17. Corrective actions: If the results of Steps 14 through 16 indicate that the data quality objectives of the test plan have not been achieved, the analyst may perform one or more of the following actions:
    - Averaging of sequential sample spectra to reduce the residual noise area (RSA).
    - Inclusion of contaminant reference spectra in the mathematical analysis.

- Development of more accurate analyte or interferant reference spectra.
- Inclusion of reference spectra for additional compounds in the mathematical analysis.
- Exclusion from the mathematical analysis of analyte and/or interferant compounds which are clearly absent in the samples.
- De-resolution or wavenumber adjustment of the reference spectral library to match that of the sample spectra (or vice versa).
- Revision of the original data quality objectives (those included in the test plan) to levels supported by the test data.

NOTE: After performing any such corrective actions, the analyst must repeat Steps 13 through 16 and re-evaluate the LOD value for each analyte compound.

REPORTING:

18. Reporting requirements include the analyte and interferant concentrations, the concentration uncertainties, the FTIR spectrometer configuration, the sampling locations and conditions, the source(s) of the reference spectra, the CTS spectral analysis results, the results of QA/QC procedures, and certificates of analysis for all standard gases. Any variations of the test procedures and original data quality objectives from those included in the test plan should also be documented and reported. (Several of the terms used here are defined in Appendix A and described in the following Appendices. In particular, see Table D1 for a description of the FTIR spectrometer configuration parameters.)

EVALUATION OF METHOD:

Field evaluations of extractive FTIR methods have been performed for many compounds (see, for example, References 7 and 8) according to EPA Method 301 (Reference 9).

REFERENCES:

[1] U.S. EPA (proposed); Method 320 - Measurement of vapor phase organic and inorganic emissions by extractive FTIR spectroscopy; Federal Register V63 No.56, pp.14219-14228 (March 24 1998); also available (on May 19 1999) at http://www.epa.gov/ttn/oarpg/t3/fr_notices/, file frprop.pdf.

[2] U.S. EPA (proposed); Addendum to Method 320 - Protocol for the use of FTIR spectrometry for the analysis of gaseous emissions from stationary sources; Federal Register V63 No.56, pp.14229-14237 (March 24 1998); also available (on May 19 1999) at http://www.epa.gov/ttn/oarpg/t3/fr_notices/, file frprop.pdf.

[3] ASTM Designation D 6348. Standard test method for determination of gaseous compounds by extractive direct interface fourier transform infrared (FTIR) spectroscopy.

[4] ASTM Designation D 1356. Standard terminology related to sampling and analysis of atmospheres.

[5] ASTM Designation E 168. Practice for general techniques of infrared quantitative analysis.

[6] ASTM Designation E 1252. Practice for general techniques for obtaining infrared spectra for qualitative analysis.

[7] EPA Fourier Transform Infrared (FTIR) method validation at a coal-fired boiler, available (on May 19 1999) at http://www.epa.gov/ttnemc01/ftir/reports, file r03.html.

[8] W.K. Reagen et al., Environmental Science and Technology 33, pp. 1752-1759 (1999).

[9] EPA Validation Protocol, Method 301, available (on May 19, 1999) through links provided in the document http://www.epa.gov/ttn/emc/promgate.html.

[10] EPA FTIR Library of Hazardous Air Pollutants, available (on May 19 1999) at http://www.epa.gov/ttnemc01/ftir/data/entropy/. This library contains multiple quantitative spectra for approximately 100 compounds with 0.25 cm-1 resolution (boxcar apodization). The user must calculate spectra for the desired MIL and apodization from the interferometric data provided at the site http://www.epa.gov/ttnemc01/ftir/data/igram/ (see Reference 2, Appendix K). Some of these spectra were recorded at elevated gas temperatures and may not be suitable for quantitative workspace air analyses.

11] NIST Standard Reference Database #79. This library may be purchased through links provided at the website http://www.gases.nist.gov/spectral.htm; it contains quantitative spectra of 24 different compounds for several MILs and several apodization functions.
[12] NIOSH Pocket Guide to Chemical Hazards, US Department of Health and Human Services Centers and Prevention for Disease Control, June 1997.
[13] 1998 TLV's and BEI's Threshold Limit Values for Chemical Substances and Physical Agents, American Conference of Governmental Industrial Hygienists.
[14] CRC Handbook of Chemistry and Physics 75th Edition, CRC Press, 1994.
[15] Griffiths PR and de Haseth JA, Fourier transform infrared spectroscopy, John Wiley and Sons (New York), 1986.
[16] Hamilton WC, Statistics in physical science, Ronald Press Company, New York, 1964, Chapter 4.
[17] "Traceability protocol for establishing true concentrations of gases used for calibration and audits of continuous emissions monitors (Protocol Number 1)," June 1978, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods, EPA-600/4-77-027b, August 1977.
[18] Plummer GM and Reagen WK, "An examination of a least squares fit FTIR spectral analysis method," Annual Meeting of the Air and Waste Management Association, Nashville, Tennessee, June 1996; Paper No. 96.WA65.03.

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TABLE 1. REPRESENTATIVE VOLATILE COMPOUNDS AND CHEMICAL DATA

Compound /Synonyms	CAS# RTECS	Empirical or Molecular Formula	MW[a]	BP[b] (°C)	VP[c] @ 25°C (mmHg)	Exposure Limits (ppm) [d,e,f] (ACGIH[g] / NIOSH[h] / OSHA)
Aromatic Hydrocarbons						
Benzene /benzol	71-43-2 CY1400000	C_6H_6	78.11	80.1	95.2	0.5-C / Ca[e]/10, 25-C
o-xylene	95-47-6 ZE2450000	$C_6H_4(CH_3)_2$	106.7	144.4	6.7	100 / 100/ 100
m-xylene	108-38-3 ZE2275000	$C_6H_4(CH_3)_2$	106.7	139.1	8.4	100 / 100/ 100
p-xylene	106-42-3 ZE2625000	$C_6H_4(CH_3)_2$	106.7	138.4	8.8	100 / 100/ 100
Styrene	100-42-5 WL3675000	$C_6H_5CH=CH_2$	104.2	145	5	20 / 50 /100, 200-C
Toluene /toluol	108-88-3 XS5250000	$C_6H_5CH_3$	92.1	110.6	28.4	50 / 100/ 200, 300-C
Aliphatic Hydrocarbons						
n-Hexane /hexyl-hydride	110-54-3 MN9275000	C_6H_{14}	86.18	68.7	151.3	50 / 50
Ketones						
Acetone /2-propanone	67-64-1 AL3150000	C_3H_6O	58.08	58	232	500 / 250
2-Butanone /methyl ethyl ketone	78-93-3 EL6475000	C_4H_8O	72.11	79.6	95	200 / 200
Alcohols						
Methanol /methyl alcohol	67-56-1 PC1400000	CH_3OH	32.04	64.5	95	200 / 200
Halogenated Hydrocarbons						
Methylene chloride /dichloromethane	75-09-2 PA8050000	CH_2Cl_2	84.94	40	349	50 / Ca[e]
Vinylidene Fluoride /1,1 difluoroethene	75-38-7 KW0560000	$F_2C=CH_2$	64	-85	498.9	NA[i] / 1
Trichloroethylene /TCE	79-01-6 KX4550000	$ClCH=CCl_2$	131.4	87	73.5	50 / Ca[e]

Compound /Synonyms	CAS# RTECS	Empirical or Molecular Formula	MW[a]	BP[b] (°C)	VP[c] @ 25°C (mmHg)	Exposure Limits (ppm) [d,e,f] (ACGIH[g] / NIOSH[h] / OSHA)
Tetrafluoroethylene /TFE	116-14-3	$F_2C=CF_2$	100	-76	>2000	5 [i]
Aldehydes						
Formaldehyde	50-00-0 LP8925000	H_2CO	30	-21	gas	0.3 - Ceiling / Ca[e]
Epoxides						
Ethylene Oxide	75-21-8 KX2450000	C_2H_4O	44	10.5	gas	1 / 5 - Ceiling
Ethers						
Tetrahydrofuran	109-99-9 LU5950000	C_4H_8O	72.1	66	165	200 / 200/200
Inorganic Compounds						
Nitrous Oxide	10024-97-2 QX1350000	N_2O	44	-53	>2000	50 / 25
Carbon Disulfide	75-15-0 FF6650000	CS_2	76.1	116	297	10/1/20
Sulfur Dioxide	7446-09-5	SO_2	64.1	-10	gas	2/2/2
Ammonia	7664-41-7 BO0875000	NH_3	17.0	-28	gas	25/25/50
Inorganic Acids						
Hydrogen Fluoride	7664-39-3 MW7875000	HF	20.0	20	783	3/3/3

[a] Molecular Weight (Obtained from References 12 - 14)
[b] Boiling Point (Obtained from References 12 - 14)
[c] Vapor Pressure (Obtained from References 12 - 14)
[d] Exposure limit as an 8-hour TWA (Time Weighted Average) in ppm (parts per million), by volume. Ceiling values denoted as "Ceiling" following limit.
[e] Ca NIOSH listed carcinogen (See Appendix A of Reference 12)
[f] NA TLV for this chemical not published (See Reference 13)
[g] Published 1998 ACGIH TLV (See Reference 13)
[h] Published NIOSH REL (See Reference 13)
[i] Manufacturer's Recommended Exposure Limit

TABLE 2. REPRESENTATIVE INFRARED DATA FOR THE COMPOUNDS OF TABLE 1

NOTE: The Limit of Detection (LOD) may vary from laboratory to laboratory, analyst to analyst, instrument to instrument, and day to day. Therefore, any determination of this value should be performed under the same conditions used for sample analysis and reported only with those analyses. It is stressed that the values below are only conservative estimates of the expected performance of this method.

Compound	Analytical Region (cm^{-1})	Reference Spectrum Filename[a]	LOD at 10m[b] (ppm)	Max. conc. at 10m[c] (ppm)	Max. RSA[d] (abs-cm^{-1})	Reference Spectrum Source
Aromatic Hydrocarbons						
Benzene	3000 - 3150	015mav01.spc	0.32	149	.0360	EPA[e]
o-xylene	709 - 781	171mav01.spc	0.65	150	.0444	EPA[e]
m-xylene	782 - 805	172mav01.spc	1.36	146	.0377	EPA[e]
p-xylene	749 - 840	173mav01.spc	1.17	151	.0561	EPA[e]
Styrene	738 - 944	147mav01.spc	1.84	150	.0363	EPA[e]
Toluene	701 - 768	tolmav01.spc	1.16	463	.0499	EPA[e]
Aliphatic Hydrocarbons						
n-Hexane	2778 - 3051	095mav01.spc	0.10	150	.0639	EPA[e]
Ketones						
Acetone	1163 - 1265	192mav01.spc	0.95	148	.0211	EPA[e]
2-Butanone	1127 - 1235	mekmav01.spc	0.27	463	.0233	3M[f]
Alcohols						
Methanol	941 - 1100	104mav01.spc	0.28	151	.0447	EPA[e]
Halogenated Hydrocarbons						
Methylene Chloride	701 789	117mav01.spc	0.31	150	.0620	EPA[e]
Vinylidene Fluoride	1080 1215	dfemav05.spc	0.21	25.7	.0930	3M[f]
Trichloroethylene	762 966	tcemav01.spc	0.43	464	.1071	3M[f]
Tetrafluoroethylene	1080 1215	tfemav05.spc	0.17	25.7	.0930	3M[f]

Aldehydes						
Formaldehyde[g]	2727 2844	087bb.spt	0.40	1125	.0267	EPA[e,g]
Epoxides						
Ethylene Oxide	3059 3070	084mav01.spc	0.11	138	.0025	EPA[e]
Ethers						
Tetrahydrofuran	2750 - 3085	thf405.spc	0.18	41	.0782	3M[f]
Inorganic Compounds						
Nitrous Oxide	1226- 1333	n2omav01.spc	0.36	904	.0301	3M[f]
Carbon Disulfide	2109 - 2200	028mav01.spc	0.13	151	.0123	EPA[e]
Sulfur Dioxide[h]	1290 - 1410	so2.spc	0.35	~200[g]	.1394	NIST[h]
Ammonia	998 - 1131	nh3mav01.spc	0.77	470	.0363	3M[f]
Inorganic Acids						
Hydrogen Fluoride	4034 - 4206	21hfrav	0.93	15.8	0.15	3M[f]

[a] Used in LOD calculations; averaged spectra from the quoted libraries; data available from the authors.

[b] Approximate Limit of Detection (LOD) for a 10 meter absorption pathlength. Typical values of the RSA, the quoted Analytical Regions, and the quoted reference spectral data were used to calculate the LOD as described in Appendix E, Equation E1.

[c] The maximum ppm-m value available for the compound in the quoted reference spectrum source.

[d] Maximum Squared Residual Area (RSA) in the specified Analytical Regions consistent with the quoted LOD values. See Appendix E, Section 1.

[e] See Reference 10. Average absorbance and accepted standard concentration values for the low-concentration pairs of spectra were used. Interferograms were truncated to 0.5 cm^{-1} resolution and triangular apodization was employed.

[f] Data available from the authors.

[g] From EPA reference spectra recorded at 100° C (Reference 10).

[h] NIST Standard Reference Database #79 (Reference 9). The quoted maximum concentration for SO_2 is based on linearity studies of 0.5 cm^{-1} resolution spectra with triangular apodization. Non-linear absorbance leads to errors of less than 10% at 1000 ppm-m.

APPENDIX A. Terminology.

absorption cell - a structure which contains a fluid sample, but allows light to pass through a sample at known temperature, pressure, and absorption pathlength.

absorption band - a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

absorption pathlength - the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

absorbance (units: abs) - in terms of the incident and transmitted intensities I_0 and I, the absorbance A is given by $A = -\log(I/I_0)$. From a pair of FTIR single beam spectra A (the background spectrum) and B (the sample spectrum), the sample absorbance for each wavenumber value (with index i) in the spectra is approximated by $A_i = -\log(B_i/A_i)$.

absorbance linearity - a characteristic of (ideal) absorbance spectrum; for such a spectrum, the measured absorbance is described by Beer's Law (Equation C1).

absorptivity - a measure of the fraction of the incident infrared radiation that is absorbed by a particular compound per molecule and per absorption pathlength; see equation C1.

analytical region - a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analytes. Note: The quantitative result for a single analyte may be based on data from more than one analytical region.

analyst - a person familiar with and experienced in performance of all aspects of this FTIR-based method. Analysts may perform any portion(s) of the method, and must perform certain portions of the method (see also "operator").

analyte - a compound whose concentrations in a sample is of interest and must be accurately quantified (see also "interferant").

aperture - an optical device which physically restricts the diameter of the optical beam.

apodization - modification of the interferogram through its multiplication by a weighing function whose magnitude varies with the position of the interferometer's moving element.

background spectrum - the single beam spectrum obtained with all system components and without sample present (or in the presence of a non-absorbing gas replacing the sample).

baseline - any line (or smooth function of wavenumber) drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beer's Law - the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration. See Equation C1, which also describes the more general case of gas mixtures.

calibration transfer standard (CTS) gas - a gas standard of a compound used to measure the sample absorption pathlength; see Step 7, Step 11, Appendix B (Section 1), and Appendix D, (Section 5).

cm^{-1} - see wavenumber

compound - a substance possessing a distinct, unique molecular structure.

concentration - the quantity of a compound contained in a unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended, and is equivalent to the volume basis for ideal gases.

concentration-pathlength product (CCP) - the mathematical product of concentration of the species and the absorption pathlength. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's Law. The units "ppm-meters" (ppm-m) are recommended.

data quality objectives - parameters pertaining to a certain application of this method, including the estimated LOD values for each compound.

de-resolve - to form spectra of lower resolution (higher FWHM) from spectra of higher resolution (lower FWHM); see Reference 2 (Appendix K) and Reference 11 for de-resolution procedures and programs.

detector linearity - a characteristic of an (ideal) IR detector; for such a detector, the measured detector output voltage, when plotted against the total IR in a broad-band IR signal incident on the detector, would form a straight line.

double beam spectrum - a transmittance or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

> Note: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

extractive - the type of spectroscopy which includes extracting and transporting a sample stream from gases at a certain location to an absorption cell, and isolating the sample in the absorption cell for analysis. Other types of spectroscopy in which the sample is not isolated in an absorption cell include "remote", "open path", and "local open path" techniques.

filter - (1) A device made of inert materials which physically removes solid and liquid phase particles from a gas stream. (2) An optical device which transmits some fraction of the radiation incident on it; "neutral density" and "mesh" filters transmit an approximately constant fraction of the incident radiation at all wavelengths over a specified wavelength range.

FFT (Fast Fourier transform) - a discrete (digital) approximation to an FT (Fourier transform; see below) involving the factoring of the original data into sparse matrices containing mostly zeros.

FT (Fourier transform) - the mathematical process for converting an analytical (non-discrete) amplitude-time function to an amplitude-frequency function, or vice versa.

FTIR (Fourier transform infrared) spectrometer - an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the infrared power vs. infrared frequency. See Figures C1 and C2.

FTIR spectrometry - use of an FTIR system to perform quantitative measurements.

FTIR system - the combination of an FTIR spectrometer and a sample interface.

FTIR system configuration - the set of parameters required to reproduce, as closely as possible, results from a particular FTIR system at a later time. This set includes (at least) the nominal MIL, the absorption pathlength, the apodization function, the gas temperature, the gas pressure, the zero filling factor, the measured wavenumbers of specific water absorption bands, the sources of the reference library spectra, the integration time, the detector type and serial number, the detector gain (including hardware and software settings).

FTIR system response time - the minimum time required for the output of an FTIR system to accurately reflect a sudden change in the sample gas composition; see Appendix B, Section 5.

frequency, ν - the number of cycles per unit time; for light, $\nu = s/\lambda$, where s is the speed of light and λ

is the light's wavelength. Unlike the speed and wavelength, which are medium-dependent, the frequency of light is independent of the medium through which the light travels. The term "frequency" is often used to denote the wavenumber (**w**, cm^{-1}) in FTIR spectroscopy because (in a given medium) the wavenumber is proportional to the frequency ν . (See Appendix C, Section 4, and "wavenumber" in this Appendix.)

full-width-half-maximum (FWHM) - for a single, symmetric absorption band, the full width of the band (in cm-1) between its 50% relative maximum absorption levels.

impinger - a device constructed of inert materials which passes a gas stream through a liquid phase.

infrared source - a device which emits a pattern, stable in intensity and wavelength profile, of infrared radiation over a wide range of infrared wavelengths. High temperature filaments or ceramic elements, in conjunction with appropriate focusing optics, are often employed.

infrared detector - a device which (ideally) produces a voltage proportional to the total infrared power incident on it. Examples are 1) the mercury-cadmium-telluride (MCT) detector, which requires cooling (and is often cooled to liquid nitrogen temperature), and 2) the deuterated triglycine sulfate (DTGS) detector, often operated at ambient temperature.

interferogram - record of the IR detector's response to the modulated component of the interference signal measured as a function of retardation.

interferometer - device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

integration time - the total time over which the interferometric results of single scans are averaged to produce an interferogram (and its subsequent single- and double-beam spectra). Most software packages allow selection of the number of scans rather than the integration time. The integration time is approximately equal to (but is always less than) the time interval over which the selected number of scans is actually executed.

interferant - a compound whose presence in a sample spectrum must be taken into account to accurately determine one or more analyte concentrations, but whose concentration need not be accurately determined.

least squares fitting (LSF) algorithm - a calculation whereby one or more compound concentrations are estimated from a sample spectrum by minimizing the squared error in Beer's Law within a defined analytical region (see Equations C1 through C6).

limit of detection (LOD, ppm) - for a defined FTIR system configuration and sample matrix, an estimate of the lowest detectable concentration of a specific analyte based on the FTIR system's RSA and the analyte's integrated absorbance for a selected analytical region.

line - see absorption band

linewidth - see full-width-half-maximum (FWHM) and minimum instrumental linewidth (MIL).

metering valve - a gas valve allowing reproducible adjustments of a gas stream flow rate on the order of 2% of the valves full flow rate.

mid-infrared (MIR) - the region of the electromagnetic spectrum from approximately 400 to 5000 cm-1.

minimum instrumental linewidth (MIL) - for a given FTIR spectrometer and FTIR system configuration, the minimum measured FWHM for any absorption band. In wavenumbers, the MIL is often estimated as the reciprocal of the retardation expressed in centimeters. The MIL depends on the choice of apodization function, and is often larger than the MIL estimated from the retardation.

multi-pass cell - an absorption cell which uses mirrors to pass the infrared radiation through the gas

sample more than once; this leads to an absorption pathlength larger than the physical length of the cell (see also "White cell").

mm Hg - a measure of pressure difference which results in the vertical displacement of a column of liquid mercury by one millimeter. A pressure difference of one atmosphere (atm) is equal to 760 mm Hg, to 1.01×10^5 Pascals (Pa), and to 14.7 pounds per square inch (psi).

operator - a person familiar with and experienced in performance of only some aspects of this FTIR-based method. Operators may perform many portions of this method, but specific portions of the method (see above) must be performed by an "analyst".

peak - see absorption band

qualitative analysis - examination of sample spectra to determine the presence or absence of particular compounds in a sample.

quantitative analysis - estimation of the actual concentrations of a specific set of compounds using a specific set of analytical regions.

reference spectra - absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

relative wavenumber accuracy (RWA, %) - the percent difference in wavenumber values measured by an FTIR spectrometer relative to a reference library standard. The RWA is estimated through spectral comparisons of the wavenumbers of two isolated water vapor absorption. See Appendix B, Section 3.

residual squared area (RSA) - a measure of the noise (random and systematic) and/or spectral artifacts for an absorbance spectrum in some analytical region; see Appendix B, Section 2 for a mathematical definition. The RSA can be used to estimate the LOD for a given compound measured with a given FTIR system configuration.

retardation - optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation." In the case of a standard Michelson interferometer, the retardation is simply twice the distance moved by a mirror in the interferometer during a scan.

rotameter - a device indicating the volumetric flow rate of a gas by the vertical displacement of an object suspended by the gas stream.

sampling location - the point in space at which sample gases enter the sample interface.

sample interface - that part of the FTIR system which comes in contact with the sample and/or calibration gases. It includes the sample probe, sample filter, sample line, sample pump, gas valves, internal surfaces of the absorption cell, pressure gauge, sample rotameter, the vent lines, and the calibration components (gas cylinders, regulators, and rotameters).

scaling - application of a multiplicative factor to the absorbance values in a spectrum.

scan - digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

single beam spectrum - Fourier-transformed interferogram, representing the relative detector response vs. wavenumber.

> Note: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmittance and absorbance spectra of a sample.

system zero (SZ) spectrum - the absorbance spectrum of a non-absorbing gas (nitrogen or zero air) acquired using those portions of the sampling interface used to acquire actual sample gases.

transmittance, T - the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra; often presented in %T (100 x T) in spectral representations.

uncertainty - a mathematical quantity determined in a least-squares fitting procedure, used to estimate the likely error in the determination of the sample concentration in a procedure; see Equations C1-C6.

wavelength λ, - the physical distance between successive maxima in the electromagnetic waves which comprise light. The wavelength and speed of light depend on the medium through which the light travels.

wavenumber, **w** - the reciprocal of the wavelength, also the number of wavelengths of light per unit length, usually expressed in the units cm^{-1}. As is true of both the speed and wavelength of light, the wavenumber is dependent on the medium through which the light travels. (See Appendix C, Section 4, and "frequency" in this Appendix.)

wavenumber adjustment - reassignment of the cm^{-1} values associated with single- and/or double beam spectra. Adjustments may be made locally by shifting or stretching the wavenumber scale, or globally stretched by changing the laser wavenumber during the FFT.

White cell — alternate name for a "multi-pass" absorption cell (see above) indicating its inventor.

zero filling - the addition of zero-valued points to the end of a measured interferogram. In most computer programs, specification of a zero filling "factor" of N results in an interferogram with N times as many points as the original interferogram.

APPENDIX B. System Tests.

These procedures must be conducted at least once on new or significantly altered (by replacement of components, dis- and reassembly, etc.) systems. The tests described in Sections B2 and B4 must also be repeated during either the pre-test preparations or quality assurance procedures. In all cases, activate the FTIR system and allow sufficient time for the infrared source, the infrared detector, and (if required) the temperature control systems to stabilize before proceeding.

B1 Absorption pathlength

Obtain one or more absorbance spectra of a calibration transfer standard (CTS) gas (ethylene at 200 to 300 ppm-meters is recommended) at the gas temperature and pressure of a reference CTS spectrum of the same compound. For each spectrum, calculate the indicated absorption pathlength according as

$$L_S = \frac{L_R P_R A_S}{P_S A_R} \qquad \text{Equation B1}$$

where

L_S = pathlength indicated by the sample CTS spectrum (meters).
L_R = pathlength of the reference CTS spectrum (meters).
A_S = area of the reference CTS spectrum (abs cm^{-1}).
A_R = area of the reference CTS spectrum (abs cm^{-1}).
P_S = pressure of the sample CTS spectrum (mm Hg).
P_R = pressure of the reference CTS spectrum (mm Hg).

When multiple CTS spectra are available, assign to L_S the mean of the single-spectrum L_S results. The reference CTS spectrum pathlength and concentration used must be based on multiple, high-quality gas standards and physical length measurements (see Appendix D, Section 5). The analyst must document criteria for the selection of the analytical region and any baseline correction procedures employed.

B2 Residual Squared Area

Note: If the following calculations are performed during testing or as part of the QC procedures (steps 14 through 17), perform them using a workspace air spectrum instead of the "water vapor (absorbance) spectrum" described in the two paragraphs below.

Use the integration time selected for field testing in recording the spectra described below. Record a background spectrum of dry N_2 gas or zero air. Using a suitable impinger, humidify the N_2 or zero air stream and record a single-beam spectrum at an absolute pressure between 725 and 795 mm Hg. Form the absorbance spectrum of this water vapor sample from the single beam spectra. Assign the spectrum a unique filename and save it for the calculations described below.

From this water vapor spectrum, subtract a scaled spectrum (see Appendix A) formed from the water vapor reference spectrum to be used in subsequent quantitative analyses. The scaling factor may be varied to minimize the absorbance in the resulting difference spectrum in the various analytical regions to be used in the analyses. Subtract a constant offset, a linear function, or a quadratic function from the difference spectrum in each analytical region to form a residual spectrum R for each region. For each residual spectrum R with discrete absorbance value R_i for i = p to q, in the wavenumber range w_p to w_q, the residual squared area (RSA) is defined as:

$$RSA = \frac{[w_p - w_q]}{q - p + 1}\sqrt{\sum_{i=p}^{i=q}\frac{(R_i)^2}{q-p}}$$ Equation B2

The RSA has the dimensions (abs cm^{-1}), and serves as a measure of the integrated absorbance of spectral noise and water subtraction artifacts over the analytical region. The RSA is compared to the total absorbance of a compound in the same region to estimate the LOD for the compound in that region (see Appendix D, Section 9 and Appendix E, Section 1).

The calculation described above assumes that water is the only significant infrared absorber in the samples besides the analytes, and that only one analyte absorbs in any analytical region. If other analytes or interferants are present, a more conservative RSA may be estimated by adding the absorbance of the additional compounds to the difference spectrum using a set of suitable reference spectra, then subtracting their absorbance using a *different* set of reference spectra.

B3 Minimum Instrumental Linewidth (MIL)

Evacuate the absorption cell to a pressure below 100 mm Hg and record a background spectrum. Obtain a workspace air sample at an absolute pressure of approximately 300 mm Hg. Record the absorbance spectrum of this low-pressure sample. Measure at the FWHM (full width at half maximum) linewidth, in absorbance, of at least two isolated water vapor lines (for example, the lines near 1918 cm^{-1} and 2779 cm^{-1}). The MIL is the mean of these FWHM measurements.

B4 Wavenumber Reproducibility

Note: If this calculation is performed during testing or as part of the QC procedures (see Steps 6 and 10), perform these determinations using a workspace air spectrum instead of the water vapor absorbance spectrum described in Section B2.

Using a water vapor spectrum recorded as described in Section B2, determine the center wavenumber values w_{S1} and w_{S2} of two isolated water vapor absorption features; the peaks near 1918 cm^{-1} and 2779 cm^{-1} are suggested, though any other pair of isolated lines separated by 500 cm^{-1} or more is suitable. Compare these results to those center wavenumber values w_{R1} and w_{R2} and for the same absorbance features in the water vapor wavenumber standard associated with the reference library to be used in quantitative analyses as follows: Calculate the relative wavenumber accuracy (RWA) in percent for each of the two absorption bands according to

$$RWA = ABS(w_{Ri} - w_{Si})$$ for i = 1, 2. Equation B3

Compare the maximum of these two values to the MIL for the FTIR system (see Section B3). If the ratio ***RWA/MIL*** exceeds 2%, adjustment of the wavenumber scale for the sample spectra may be required.

Mathematical wavenumber adjustments may be made locally by shifting or stretching the wavenumber scale, or globally stretched by changing the laser wavenumber during the FFT. However, large shifts (on the order of 5% or more of the MIL) indicate that the system requires physical adjustments, such as re-alignment of the laser system responsible for control of the interferometer's moving element. In addition, mathematical wavenumber adjustments require some sort of interpolation procedure in conjunction with the quantitative spectral analysis, and those procedures may result in spectral mismatches whose effects on the accuracy of the analysis are not easily quantified.

The necessity of such wavenumber adjustments depends, in part, on the widths of the absorption peaks of the compounds involved in the spectral analysis. Because many of the absorption bands of water a nearly ubiquitous interferant in workspace air IR analysis are very narrow, an accurate analysis usually requires the relatively stringent limits placed above on the RWA to MIL ratio. However, it is possible to obtain accurate results when this ratio exceeds the recommended limit, especially when only broad absorbance features are actually employed. The analyst may choose

to approve analytical results obtained when this ratio exceeds the recommended limit.

B5 System Response Time

Direct N_2 or zero air through the entire sample interface and record spectra at approximately 30 second intervals. Abruptly replace the N_2 or zero air gas flow with CTS gas and continue to record spectra. The system response time is the subsequent time required for the FTIR system to generate an absorbance spectrum in which the CTS compound's calculated concentration reaches 95% of the final (stable) concentration value indicated in later spectra.

B6 Detector Linearity

For the chosen optical configuration, attenuate the power incident on the detector by either 1) modifying the aperture setting or 2) placing filters (neutral density or mesh) in the infrared beam path (see Figure A1). At approximately 100%, 50% and 25% of the system full IR power level, collect pairs of background and CTS spectra. Compare the areas of the CTS bands for the three spectra and verify that they are equal to within 5% of their mean value. If they are not, apply software linearization corrections to the interferometric data according to the manufacturer's instructions. If this option is unavailable, it is necessary to either 1) characterize the system non-linearity and/or apply appropriate concentration corrections or 2) operate the system with attenuation sufficient to ensure linear detector response.

APPENDIX C. General Description of FTIR Spectrometry.

C1. FTIR Spectrometer Components

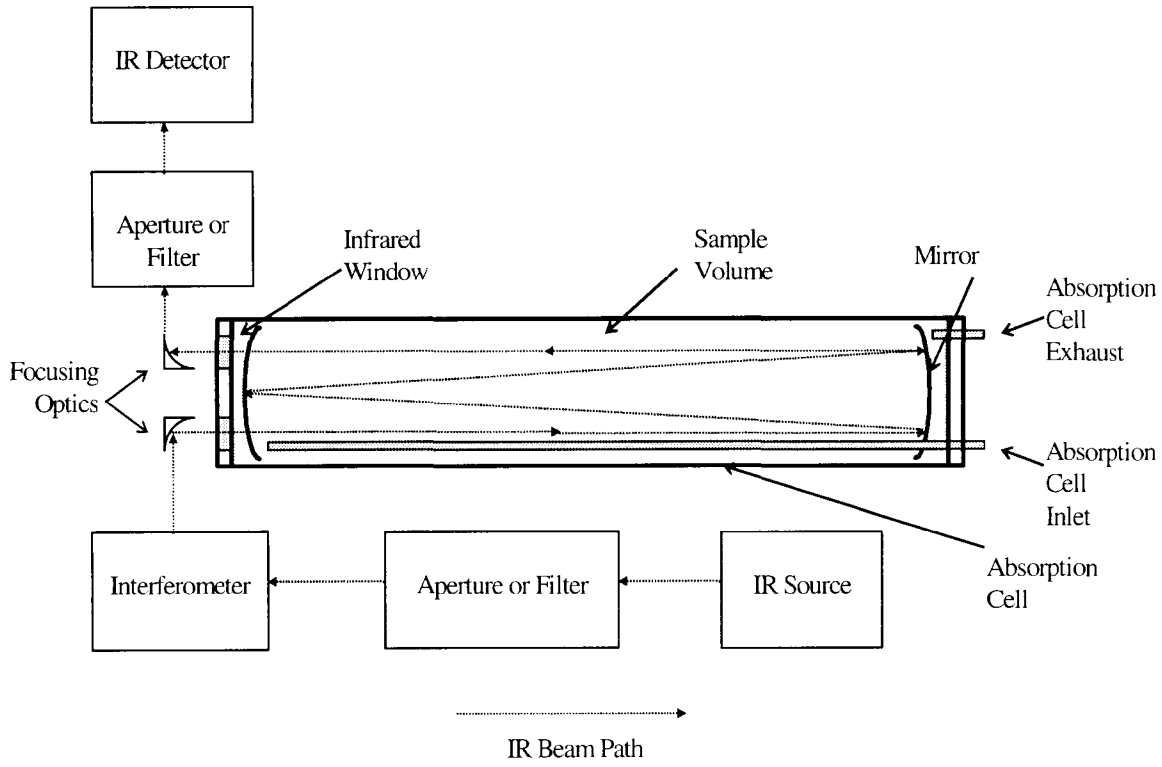

Figure C1. FTIR Spectrometer Components and Beam Path

Figure C1 illustrates the basic FTIR spectrometer configuration required for gas phase analyses. The infrared radiation emitted by the infrared (IR) source contains energy at all wavelengths between 2.0 and 20 microns; this is the portion of the electromagnetic spectrum usually referred to as the "mid-infrared" (MIR). In the units typically employed in FTIR spectroscopy (wavenumbers, or cm^{-1}), this is the wavenumber range 5000 to 500 cm^{-1}. The IR radiation passes through an interferometer, where the motion of an optical element - usually a mirror - optically modulates the infrared beam. The modulated IR beam then enters an absorption cell through a window (typically made of KBr or ZnSe) and interacts with the gases of interest. The physical length over which this interaction takes place is the "absorption pathlength." In "multi-pass" (or "White") absorption cells, mirrors within the cell direct the IR beam through the sample gas many times; in such cells, the absorption pathlength can be from 4 to 50 (or more) times the cell's physical length. (A larger absorption pathlength generally leads to greater sensitivity.) The IR beam then exits the sample cell via a second window and is re-focused onto an IR detector. Because this extractive technique requires the transport of gas samples through the FTIR absorption cell, the design and integrity of the sampling system is of great importance. It is also important that the sampling system allow the operator to perform all the necessary calibration and sampling procedures without compromising the speed and flexibility of the analytical system. Figure C2 illustrates a sampling system configuration that meets these requirements, though other configurations are possible. A computer controls the actions of the interferometer and records the voltage output of the IR detector throughout the motion of the interferometer's optical element. Ideally, the detector voltage is proportional to the total power in the IR beam. The computer must accurately record the detector voltage as a function of the position of the moving element in the interferometer, so a secondary, laser-based optical system is usually used to measure the moving element's position very precisely. In most circumstances, the motion of the mirror or other optical element is repeated many times, and the resulting individual "scans" are

"co-added" (averaged) to reduce the system's residual noise area (RSA). A plot of the resulting IR power-vs.-position signal, referred to as an interferogram, is shown in Figure C3. This interferogram is the co-added result of 64 scans with only nitrogen gas (and some low level of water vapor) present in the absorption cell. Nitrogen is one of the few compounds which does not interact with infrared radiation, so this interferogram very closely represents the fundamental FTIR system response in the absence of a sample. Note that the signal is relatively large near the beginning of the interferogram, where the "zero phase difference (ZPD) burst" is located. The ZPD is often used to rapidly obtain an estimate of the IR signal strength during alignment of the optical system.

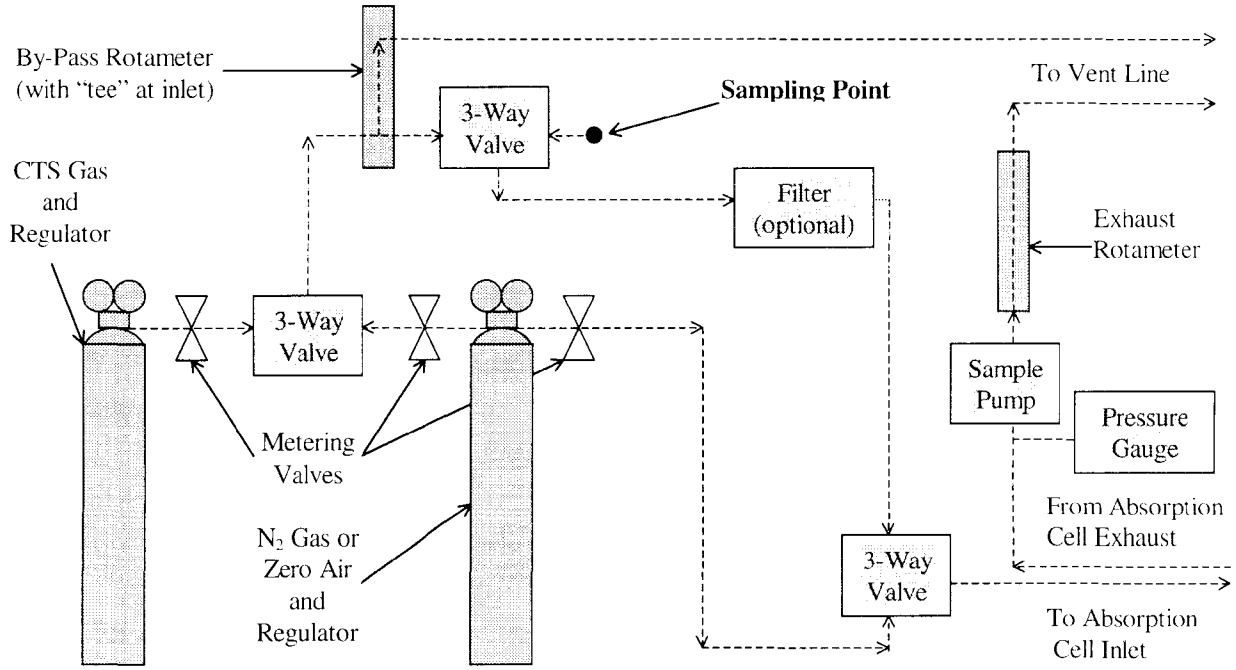

Figure C2. Sampling Components and Sample Paths

Figure C3. Mid-Infrared Interferogram

C2. The Fast Fourier Transform (FFT)

Every data point in the interferogram contains intensity information about every infrared wavelength transmitted from the source to the detector. It is possible to recover the intensity information as a function of wavelength through application of a Fast Fourier Transform (FFT), from which the FTIR technique's name is derived. This digital transformation of the interferogram can be thought of as the mathematical inverse of the optical modulation applied to the infrared beam as it passes through the interferometer. Its function is similar to that of the human brain and ear, which provide intensity information (loudness) versus wavelength (pitch) for complex signals (sound waves) incident on the eardrum. (Note that, as for an interferogram, each point in a complex sound wave contains intensity information about every pitch contained in the wave. Yet the ear and brain allow a symphony audience to immediately perceive, for instance, that the piccolo is playing very loudly while the tuba is playing very quietly.) Reference 15 (Chapter 3) provides a complete mathematical description of the FFT.

C3. Instrument Resolution, Apodization Function, and Minimum Instrumental Linewidth (MIL)

Most software packages supplied with FTIR systems provide several options associated with the collection of data and application of the FFT. These typically include - at least - the nominal "instrument resolution" (specified in cm^{-1}) and the "apodization function" (e.g., "Boxcar" and "Triangular"). These parameters are very important in quantitative spectroscopy, and are addressed in turn below.

The instrument resolution is the most fundamental and important instrument parameter. It specifies the nominal minimum full-width-at-half-maximum (FWHM, in cm^{-1}) of any spectral "peak" (or "line") in the final instrument output. Every FTIR instrument has a minimum FWHM determined by the maximum distance traversed by the interferometer's moving element during a single scan. (For the basic Michelson interferometer, the FWHM in cm^{-1} is equal to $(2d)^{-1}$, where d is the distance in cm traversed by a moving mirror during a scan.) Clearly, instruments with low FWHM provide more spectral information than instruments with higher FWHM capability. However, this additional information comes at high costs associated with the design, construction, size, mechanical stability, portability, speed, and residual noise area (RSA) of the instruments.

It is important to recognize the two uses of the word "resolution" in the nomenclature used to describe FTIR spectrometers: Instruments of high resolving power, or "*high* resolution," provide spectral features of *low* FWHM; when the nominal resolution is specified in units of cm^{-1}, a *lower* cm^{-1} specification corresponds to *higher* resolving power, or "higher resolution". Most commercially available FTIR spectrometers suitable for field use provide FWHM values greater than or equal to 0.5 cm^{-1} - that is, they are systems whose nominal spectral resolution is specified as a number higher than 0.5 cm^{-1}. Most of the instruments capable of higher resolution (lower FWHM) are suitable for use only in very stable laboratory environments.

Standard FTIR operating software always provides options for recording spectra with FWHM values higher than the instrument's actual lower FWHM limit. These options simply move the mirror (or other optical element) through only some fraction of its maximum possible travel. Operating the instrument in this manner results in larger FWHM values ("lower" resolution, and shorter interferograms) than the instrument is mechanically capable of providing. Spectra of lower resolution (higher FWHM) provide less information, but can be generated more quickly and, in most cases, with lower RSA than spectra of higher resolution.

The instrument operator can also choose the apodization function to be used in the generation of FTIR spectra. Apodization is a mathematical alteration of the interferogram that can be performed before application of the FFT. Several standard alteration functions have been devised, and each affects the final absorption spectrum of the sample gas in a different way. As with the selection of instrument resolution, each choice has its advantages and drawbacks. The simplest choice, known as the "boxcar apodization" function, results in the lowest FWHM but also in relatively low S/N ratio. (Spectra generated with the boxcar function are often referred to as "unapodized" spectra.) Other choices (triangular, Norton-Beer, and several other apodization functions) provide higher S/N ratio at the cost of higher FWHM values and other tradeoffs in quantitative spectroscopy. Reference 15 provides a more thorough description of the characteristics of various apodization functions.

For a given instrument configuration which includes the nominal spectral resolution and the choice of apodization function every FTIR system is capable of generating absorption bands with a minimum instrumental linewidth (MIL). Unlike the actual spectral resolution (which has several accepted physical

definitions — see Reference 15, Chapter 1, Section IV) and nominal spectral resolution parameters, the MIL is a parameter which is readily measured to the accuracy required for practical applications of FTIR spectrometry. It can be measured using the water absorption bands present in low-pressure workspace air samples (see Appendix B, Section 3).

C4. Single Beam Spectra

The mathematical result of the FFT (applied to an apodized IR interferogram) is a called a single beam spectrum. Single beam spectra represent the infrared power transmitted through the FTIR spectrometer as a function of the infrared "wavenumber" **w**, which is usually expressed in the units of reciprocal centimeters (cm^{-1}). The wavenumber is actually a measure of the frequency, rather than the wavelength, of the infrared radiation. In a vacuum, the wavelength and frequency are related through the equation $\nu = s/\lambda$, where λ is the wavelength (cm), ν is the frequency (sec^{-1}, or Hz), and s(cm/sec) is the speed of light, equal to $2.99792954 \times 10^{10}$ in a vacuum. In these units, the wavenumber in cm^{-1} is given by the equation $w = 1 / \lambda = \nu / s$. Figure C4 presents the single beam spectra for two samples consisting mainly of nitrogen gas (≥99%) but with different concentrations (≤ 1%) of water vapor. The vertical scales of the two spectra are nearly identical, but they have been offset for clarity. The detected infrared power in certain wavenumber regions is clearly lower in the high moisture sample, indicating both the qualitative nature and strength of water's absorption of infrared radiation.

C5. Double-Beam Spectra - Transmittance and Absorbance

Combinations of pairs of single beam, such as the pair of spectra S and B shown in Figure C4, are referred to as double beam spectra; they provide the quantitative basis for FTIR spectroscopy. One type of double

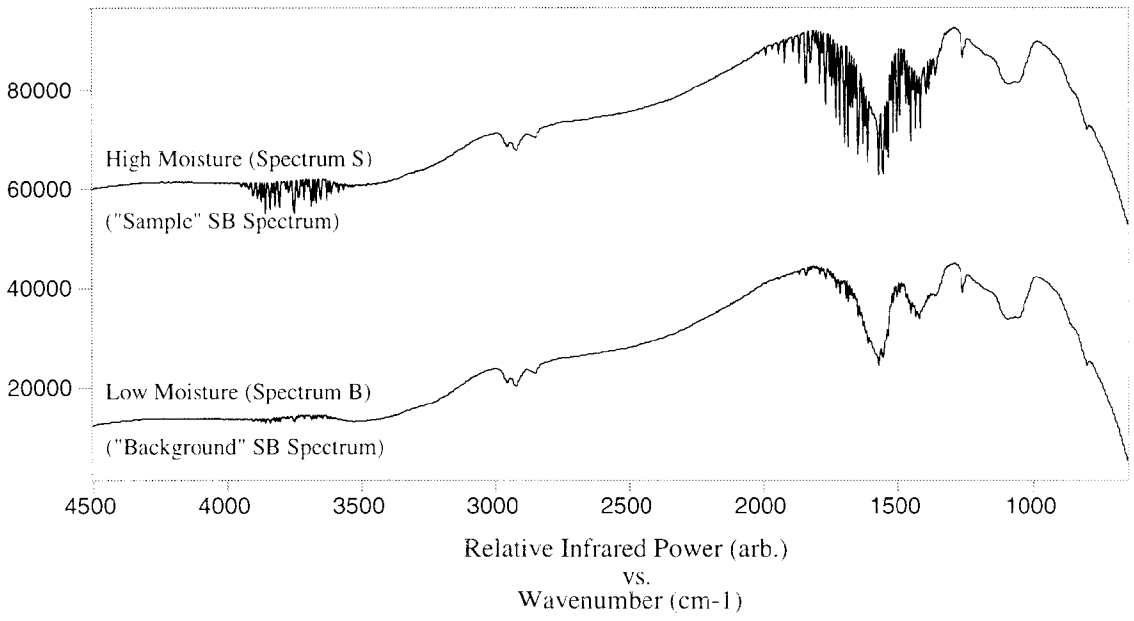

Figure C4. Single Beam Spectra of N2 at Different Moisture Levels

beam spectrum is the transmittance. The percent transmittance of a sample gas possessing the single-beam spectrum S — with respect to the background single-beam spectrum B — is defined as T(%) = 100 * S/B ; a transmittance value is defined for each wavenumber value of the two spectra. If the background spectrum B closely represents the response of the FTIR system to a transparent sample, then the percent transmittance T closely approximates the percentage of the infrared radiation transmitted by the sample (represented by the spectrum S). Because water is the only absorbing compound present in the single-beam spectrum B, the spectrum T (shown in Figure C5) closely approximates the percent transmittance spectrum of water.

The same pair of spectra define the (double beam) absorbance A of the sample through the equation $A = -\log_{10}(S/B)$. The absorbance spectrum of water, as approximated by the two single-beam spectra S and B, is shown in Figure C6. The absorbance is the desired quantity because it appears in the general linear absorption model known as Beer's Law (see below).

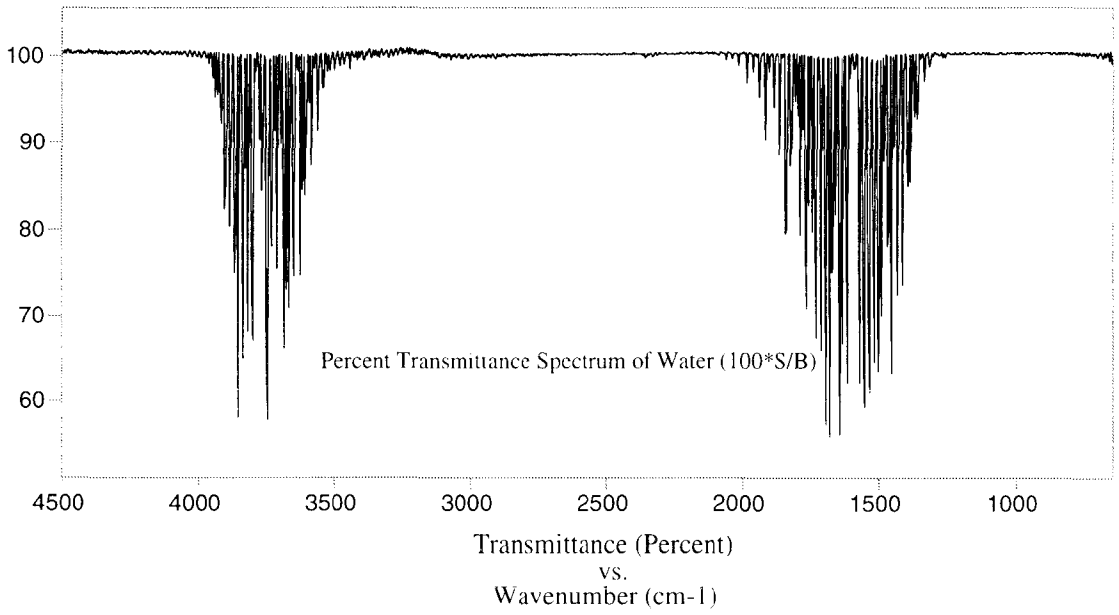

Figure C5. Double Beam Transmittance Spectrum of Water

C6. Beer's Law

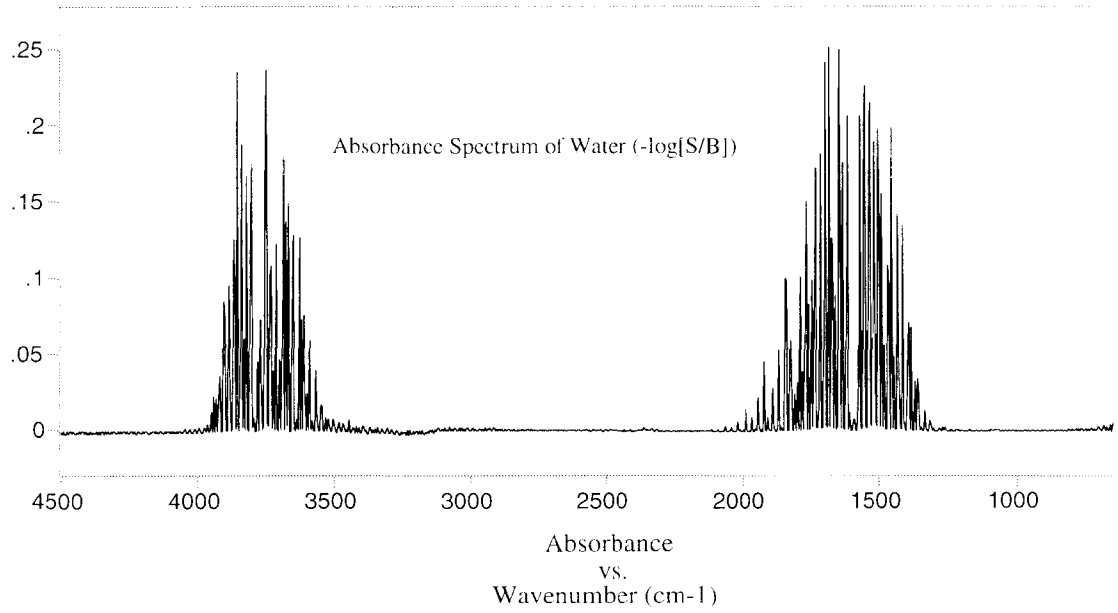

Figure C6. Double Beam Absorbance Spectrum of Water

The absorbance spectrum of a sample gas is determined from single beam spectra of an infrared-transparent gas (the background spectrum) and the sample gas (see Section 5). The fundamental relationship connecting the absorbance spectrum of a sample gas to the concentrations of the compounds comprising the sample is referred to as Beer's Law. This relationship can be written as

$$A_i = \sum_{j=1}^{M} L_S a_{ij} C_j \qquad \text{(Equation C1)}$$

where

i = an index labeling the frequencies of the observed absorbance values in the sample's absorbance spectrum.
A_i = the observed absorbance of a sample at the i^{th} wavenumber (abs).
L_S = the sample absorption pathlength (meters).
j = an index labeling the absorbing compounds comprising the sample.
a_{ij} = the absorptivity of the j^{th} compound at the i^{th} wavenumber (abs/ppm/meter).
C_j = the volumetric concentration of the j^{th} compound (ppm).
M = the number of absorbing compounds in the sample.

The procedures described in this method are all related to the parameters which comprise Beer's Law. The following list describes these procedures and relationships in a general context:
1) Record a reference absorbance spectrum for each interesting compound of a nitrogen-diluted sample of the pure compound, at a known concentration and pathlength, then divide the absorbance at each point in that spectrum by the product of the concentration and pathlength. This process yields the absorptivity spectrum (a_{ij}), or reference spectrum, for each compound.

2) Measure the absorbance A_i for the mixture of compounds (see Steps 5 and 9 above).
3) Determine the pathlength L_S for the current measurement of A_i (see Steps 5 and 7 above).
4) Select the analytical region that is a set of frequencies, corresponding to the possible values of the index i which are to be used to determine the concentration of each compound, and then mathematically invert Equation C1 to determine the desired concentrations C_j. (Appendix E addresses the topic of spectral analysis in detail.)

NOTE: The true absorptivity for a single gaseous compound is a characteristic only of the compound's structure. However, details of the FTIR system performance and operation affect the observed absorptivity and its accuracy. Similarly, FTIR measurements provide only an approximation of the true absorbance spectrum of a mixture of gaseous compounds, though it is, under many circumstances, a sufficiently accurate approximation. It is the responsibility of the analyst to verify and ensure that the reference and sample spectra provide a sufficiently accurate quantitative analysis according to Beer's Law. The following sections of this Appendix describe the mathematics of such an analysis. Appendix D addresses the topics of developing and using reference spectral libraries. Appendix E provides an illustrative example of the design and evaluation of the quantitative analytical process.

C7. Determining Concentrations with Least Squares Fitting Algorithms.

When a sample gas contains only one absorbing compound, Equation C1 simplifies to

$$A_i = L_S a_{ij} C_j \qquad \text{(Equation C2)}$$

This means that in any analytical region where only one gas absorbs, any one (of the usually many) absorbance spectrum values A_i can be used to yield the concentration C_j.
The absorbance area A_s for single-component spectrum in an analytical region (from i = p to i = q) can be written as

$$A_S = \sum_{i=p}^{i=q} A_i = \sum_{i=p}^{i=q} L_S a_{ij} C_j = L_S C_j \sum_{i=p}^{i=q} a_{ij} = L_S C_f A_R \qquad \text{(Equation C3)}$$

where A_R is the area in the reference spectrum for that compound in the same analytical region. (This is the basis of the absorption pathlength L_S calculation described in Step 7 and Appendix B, Section 1.) Because calculation of the absorbance area involves many points in the sample spectrum, Equation C3 leads to much more accurate results than the single-point calculation represented by Equation C2.

However, when many absorbing compounds are present in a sample, the absorption patterns of the various compounds often overlap. In this case, there is usually not an isolated analytical region for each compound in which only that compound absorbs infrared radiation; no single absorbance point and no simple absorbance area is suitable for determining any of the component concentrations. In this case, the simplest method for determining concentrations is to use a least squares fitting (LSF) algorithm.

LSF algorithms use the fact that there is some set of estimated concentrations D_j which minimizes the "squared error" in Beer's Law for any given analytical region, for any set of compounds. The only requirement on the chosen analytical region is that it must contain a sufficient number of data points; since each FTIR spectrum contains many thousands of absorbance values, this requirement is nearly always fulfilled.

If we use the estimated concentrations D_j (rather that the true concentrations C_j) in Beer's law, they will lead to some estimated error e_i at each value of i (that is , at each point in the analytical region we choose). Equation C1 becomes:

$$A_i = e_i + \sum_{j=1}^{M} L_S a_{ij} D_j \qquad \text{(Equation C4)}$$

The estimated squared error (or "variance") in Beer's Law using the estimated concentrations is:

$$E^2 = \sum_{i=1}^{N} (e_i)^2 = \sum_{i=1}^{N} [\sum_{j=1}^{M} (L_S a_{ij} D_j) - A_i]^2 \qquad \text{(Equation C5)}$$

where N represents the number of absorbance values in the analytical region. Reference 16 demonstrates that 1) for N >M there is a unique set of estimated concentrations D_j which minimizes the estimated squared error; 2) this set of values is calculable from the known quantities in Equations C1 through C5; and 3) estimates σ_j of the uncertainties in the quantities D_j are also calculable from the same quantities. The value $3\sigma_j$ is generally accepted as a conservative estimate of the statistical uncertainty in the related estimated LSF concentration (see Reference 3).

The estimated LSF error at each point in the analytical region,

$$e_i = A_i - \sum_{j=1}^{M} L_S a_{ij} D_j \qquad \text{(Equation C6)}$$

is usually stored following the analysis as a "residual spectrum," which can provide an estimate of the LODs for other compounds. In addition, the residual spectrum and the concentration uncertainties can allow the analyst to detect and identify compounds which are actually present in the sample gas but which were not included in the mathematical analysis. Appendix E provides an example illustrative of these procedures.

The above description illustrates a simple and easily-interpreted LSF analysis. More sophisticated LSF analytical techniques, possibly more accurate for particular types of samples, are described in the literature (see, for example, Reference 18 and references therein).

C8 Calibration Transfer and Reference Libraries

Equations C1 through C6 demonstrate the importance of quantities L_S (the absorption pathlength) and a_{ij} (the absorptivity) in FTIR spectrometry. Accurate determinations of these quantities allow the use of reference libraries for quantitiative analyses without the necessity of compound-specific field calibrations. The system tests described in the procedures and in Appendix B are intended to ensure suitability of the system configuration for such calibration transfers, as are the requirements of obtaining CTS spectra in field. Appendix D describes procedures for recording and processing reference library spectra.

C9 Corrections to Deviations from Beer's Law Exhibited by FTIR Spectra

Beer's Law is based on fundamental, well-established physical principles. It holds absolutely for gas samples which are at thermal equilibrium and dominated by induced (rather than spontaneous) emission and absorption processes. (See Note A1 below). However, *this is* ***not*** *to say that the absorbance, as measured by an FTIR spectrometer, follows Beer's Law under all conditions.* Deviations from Beer's Law in FTIR spectra are often observed; however, they indicate inaccuracies in the FTIR spectra, not "violations" of Beer's Law. For example, deviation from Beer's Law is commonly exhibited by sets of single-component reference spectra recorded over a range of absorbance levels. At large enough values of the absorbance, the points A_i of stronger absorption bands of such spectra no longer increase linearly with the concentration-pathlength product $L_R C_j$; this is why Table 2 specifies a maximum ppm-m value for the listed reference spectra. If the assumption of detector linearity does not hold (see Appendix B), similar effects are often present in reference and sample spectra; this is the basis for the system test described in Appendix B, Section 6.

Mathematical correction of the concentration estimates D_j derived from Beer's Law can often reduce the error in sample analyses when either type of non-linear effect occurs. Figure C7 provides an example of such a correction. The actual and calculated ppm-m values for a set of reference spectra are plotted against each other; a "piece-wise linear" approximation to the pattern is shown by the solid line, and the dashed line indicates the ideal linear behavior based on the spectrum of lowest absorbance. At any ppm-m value indicated in a Beer's Law sample analysis (that is, for any y-axis value up to approximately 900 ppm-m in the example), reasonably accurate values are available from the corresponding x-axis position of the solid line. If the analyst

employs such corrections, he or she should also calculate the residual (Equation C6) using the reference spectrum which minimizes the squared error (Equation C5). FTIR analysts and manufacturers have devised other correction procedures to improve the sample analysis accuracy in such circumstances, and these are included in some commercially available software packages.

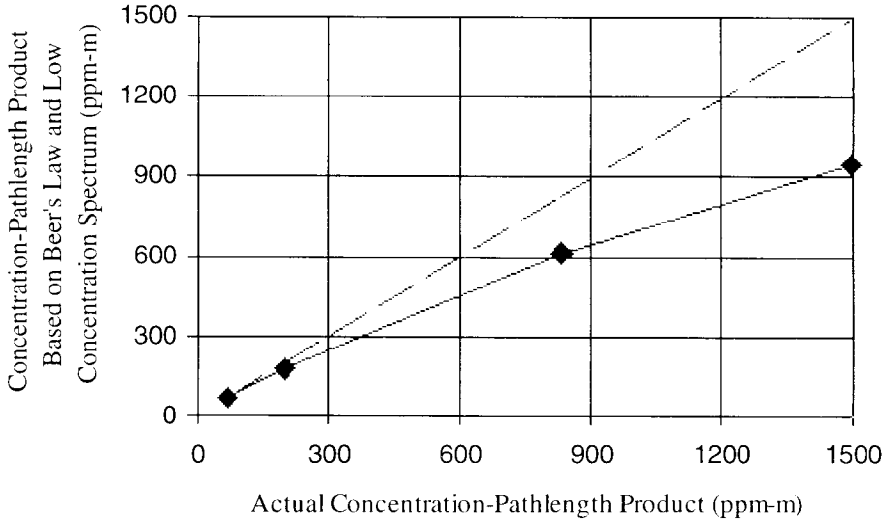

Figure C7. Example Absorbance Non-Linearity for a Set of Single-Component Reference Spectra

Note: Intense infrared radiation, such as that produced by some lasers, can induce non-equilibrium populations of a molecule's rotation-vibration energy states. However, the thermal infrared sources used in commercially available FTIR spectrometers are much weaker than such lasers. In gases at atmospheric pressure, the commercially available thermal sources induce transition rates between quantum energy states which are small compared to those of the competing collisional relaxation processes, and cannot induce non-equilibrium energy state populations. In addition, the induced transition rates related to absorption and emission at mid-infrared frequencies are much larger than the corresponding spontaneous (natural) emission rate. As a result, all *accurate* FTIR measurements at mid-infrared frequencies obey Beer's Law to within the uncertainty related *only* to the S/N ratio of the measured spectra.

APPENDIX D. Purposes, Preparation, and Use of Reference Spectral Libraries.

D1. Purposes of Reference Spectral Libraries

FTIR analyses rely on the availability of libraries of spectral information on the compounds of interest. For gases, the measured absorbance of a single component is often completely independent of the concentrations of other gases comprising the sample, and single-component reference spectra are usually employed. (For condensed phases, there are often strong interactions between components, and reference spectral libraries of mixtures are usually required.) Reference libraries may be used for quantitative measurements of analyte concentrations, for the mathematical removal of spectral features of interferants in a mixture, or simply for the identification of compounds in a mixture. Clearly, the required level of quantitative accuracy of the library is different for these three tasks; the highest quality is required for analyte concentration determinations, while no quantitative information is required for interferant removal and compound identification.

A useful characteristic of extractive FTIR spectrometry is that it provides accurate field measurements for many compounds, but requires field calibration procedures involving only two compounds. The water vapor available in every ambient air sample serves to calibrate the wavenumber (x) axes of FTIR absorbance spectra; a single calibration transfer standard (CTS) gas serves to calibrate their concentration-related (y) axes. When these two field calibrations are combined with an appropriate reference spectral library describing additional compounds, the measurement capability of the technique is practically limited only by the quality and scope of the reference library. If the reference library is carefully prepared and properly employed, this characteristic can lead to greatly lowered field test costs, since the calibration materials need be handled only once, and only in the laboratory.

D2. Reference and Field FTIR System Configurations

In the ideal case, the reference library can be prepared on the field instrument, but this is often impractical; the reference library is usually prepared on specific laboratory systems and employed in measurements made with many field systems. Reference libraries recorded on a specific instrument provide accurate quantitative analyses for spectra recorded on other instruments only when the configurations of the various systems are compatible. The following table lists compatibility considerations for the reference system configuration parameters.

Table D1. Reference and Field System Configuration Parameters.

Parameter	Requirements for Reference and Field Systems
minimum instrumental linewidth	Reference MIL must be less than or equal to field MIL. See Appendix B, Section 3 for MIL measurement technique.
gas temperature	Reference temperature within 20°C of field temperature. Density corrections based on ideal gas law are accurate over only this narrow temperature range, and their exact accuracy is compound-dependent.
gas pressure	Reference pressure within 20% of absolute field pressure. Pressure corrections based on ideal gas law are accurate over at least this range, but their accuracy is compound-dependent. Atmospheric pressure is recommended for all measurements.
apodization function	Reference and field apodization functions must be the same. A single set of reference interferograms (background and sample) can be used to generate a multiple sets of absorbance spectra using different apodization functions.
zero filling factor	Reference and field zero filling factors must be the same. A single set of reference interferograms (background and sample) recorded with no zero filling can be used to generate a multiple set of absorbance spectra using different zero filling factors .
wavenumber accuracy	Characterized by the position of water absorption bands in a wavenumber standard spectrum (see below); if additions to an existing library are being made, care must be taken to match the x-axes of all spectra as closely as possible.

integration time	Reference integration times (for both background and sample interferograms) should be greater than or equal to expected field integration times. For reference libraries, the longest practical integration time is recommended.
detector type and serial number	If an MCT or other potentially non-linear detector is employed in the reference system, IR attenuation may be required to ensure linearity; see Appendix B, Section 6; because each detector may exhibit linearity to a specific degree, the serial number of the detector should be included in any specification of the system configuration.

D3. Wavenumber Standard Spectra

Except in extremely dry conditions, the IR absorption by water vapor in workspace air is detectable at even very short absorption pathlengths. The wavenumber positions of water vapor indicated by the reference system allow the analyst to confirm the wavenumber accuracy of sample spectra recorded on a different FTIR system in the field. Reference spectra used for this purpose are referred to here as the wavenumber standard spectra.

Every spectrum in a reference library should be associated with a wavenumber standard spectrum collected under the identical system configuration; even when the reference FTIR system is in a stable environment, it is recommended that a wavenumber standard spectrum be recorded daily with the system.

Before recording reference spectra, the analyst should check the most recent wavenumber standard spectrum against previous wavenumber standard spectra in the library; see Appendix B, Section 4 for recommended calculations. If the wavenumber reproducibility of the system is poor, the resulting reference spectra may not be suitable for quantitative use on other field systems.

D4. Obtaining and Preparing Standard Reference Gases

The accuracy of any FTIR quantitative analysis is limited by the accuracy of the concentrations of the gas standards used in preparing the reference library. It is therefore important to use gas standards of the highest available quality. NIST-traceable gravimetric standards are available from many commercial sources, and are quoted to 2% accuracy in many circumstances; EPA has also published guidance on the preparation of "Protocol 1" gases (see Reference 17), though these are available for only a limited number of compounds. Users should obtain documentation from the gas vendors regarding the analytical techniques applied and the stability limits (concentration and time) of the compounds in the cylinders. When possible, an alternative analytical method should be used to verify the quoted cylinder concentrations, especially for compounds which are reactive, corrosive, or have relatively high boiling points.

If cylinder standards are not available for a compound, the analyst may prepare reference gases based on gravimetric, barometric, or dynamic methods. In any case, the related mass, pressure, and flow measurements should be made with NIST-traceable equipment whenever possible. In general, methods which provide a stream of standard gas (dynamic methods) provide more reliable results than static methods, since the concentrations of static gases are more prone to change when reactions between the standards and the sampling system or absorption cell surface can occur.

D5. Determining the Reference Absorption Pathlength

The accuracy of any FTIR quantitative analysis is limited by the accuracy to which the pathlength of the absorption cell used in preparing the reference library is known. For single-pass absorption cells through which a collimated IR beam is passed, the pathlength can be physically measured to high accuracy. For multi-pass cells, the nominal pathlength can be estimated from the base pathlength and the number of passes. However, because focused beams and curved mirrors are required in multi-pass cells, the pathlength estimated in this fashion can differ significantly from the actual pathlength. Because of this, combinations of physical and spectroscopic measurements with multiple CTS gas standards (see below) and single-pass absorption cells should be employed to determine the actual pathlength of multi-pass absorption cells.

D6. Recording CTS Spectra

The CTS (calibration transfer standard) gas is used to characterize the absorption pathlengths of the reference and field FTIR systems. Ethylene in nitrogen, at concentrations leading to between 100 and 300 ppm-meter concentration-pathlength values for the systems, is recommended; for ethylene, spectra with ppm-m values greater than 300 begin to exhibit non-linear absorbance, and must be carefully analyzed (see Sections D8 and D9 below). Standards of this gas with 2% accuracy are readily available, and both the EPA and NIST libraries contain ethylene spectra which can be used to link those libraries to measurements performed with field instruments. However, almost any other stable compound with appropriate IR absorption characteristics can be used in developing an independent reference library and for accurate field measurements.

In the field, CTS spectra must be recorded both before and after sample spectra are acquired using the same system configuration employed in recording the sample spectra (see Steps 7 and 11 above).

When developing reference spectra, the analyst must record CTS spectra at least daily; each reference spectrum should be associated with at least one CTS spectrum. The analyst must use the same system configuration employed in recording the reference spectra, with one exception: The integration time used for the CTS spectra may be less than that used for the reference spectra, if the quality of the resulting CTS spectra is still sufficient for an accurate determination of the absorption pathlength. It is highly recommended that the analyst store all the interferograms from which the CTS absorbance spectra are generated, including all background interferograms. The interferometric data provide the most direct method of verifying the FFT calculations and/or adding reference absorbance spectra for other apodization function choices.

D7. Recording Reference Spectra

Before recording reference spectra, verify that the requirements specified for system checks, system configuration parameters, gas standards, absorbance pathlength determinations, and CTS spectra described in the pertinent sections of this Appendix and Appendix B have been met. Additional checks of the sample gas pressure and temperature should also be made periodically as the spectra are recorded.

It is highly recommended that the analyst store all the interferograms from which the reference absorbance spectra are generated, including all background interferograms. The interferometric data provide the most direct method of verifying the FFT calculations and/or adding reference absorbance spectra for other apodization function choices.

Beer's Law (Equation C1) describes the fundamental linearity of the infrared absorbance versus concentration. However, the resolution (and other) limitations of instruments typically used to generate field FTIR spectra often lead to non-linear behavior for many compounds, even at low absorbance levels. The expected accuracy of FTIR-based measurements results for a particular compound can be achieved only when 1) the reference absorbance is characterized at a sufficient number of concentration-pathlength values, up to some maximum value, and 2) the sample absorbance associated with any compound represents a value lower than that of the maximum concentration-pathlength value represented in the reference library for that compound.

For each analyte, the analyst should record two reference spectra at each of two concentration values (that is, at least four spectra) at a single absorption pathlength; the two concentrations should be separated by no more than a factor of ten, and a maximum factor of five is recommended. After recording these spectra, the analyst must 1) permanently record the system parameters and the maximum measured concentration-pathlength product and 2) characterize the linearity of the absorbance across the measured concentration-pathlength range (see Section D8). It may be necessary to record additional reference spectra for the analyte if either the absorbance linearity or maximum concentration-pathlength value proves unsuitable for later field measurements.

D8. Linearity Checks

The performance of linearity checks on a set of reference spectra is an important aspect of FTIR spectrometry, and is best illustrated by a practical example. The following example is based on a series of reference measurements performed in the 3M Environmental Laboratory on the compound tetrafluoroethylene, hereafter referred to as TFE.

Five absorbance spectra for TFE are shown in Figure D1. These spectra were recorded over the entire mid-IR wavenumber range, but only that portion of the spectra showing the most intense TFE absorption bands is included in the Figure. Each of the spectra was calculated by mathematically averaging a number of TFE absorbance spectra recorded with the system configuration parameters given in Table D2, and a linear baseline correction was applied to each of these spectra over the range illustrated in Figure D1.

The reference gas samples were generated by diluting with N_2 the output of a single standard gas cylinder of TFE. The TFE concentration of the standard cylinder was determined (by the gas vendor) according to NIST-traceable gravimetric measurements, and the flow rates of the cylinder gas were measured with a NIST-traceable volumetric device.

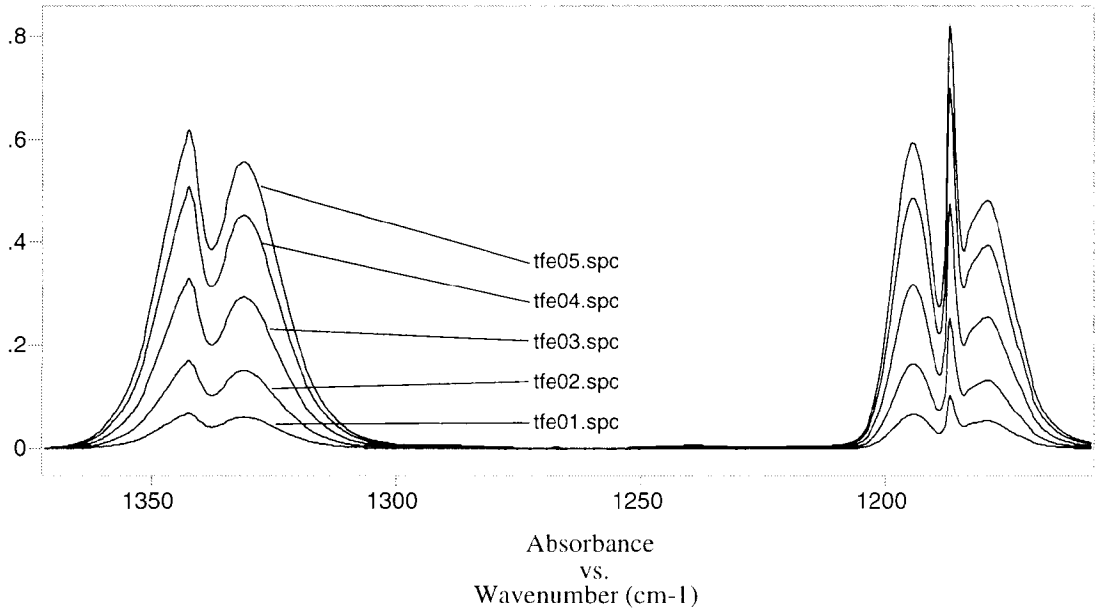

Figure D1. Reference Absorbance Spectra of TFE (x-axis truncated)

One technique to check for the linearity of this set is to form a normalized average of these five spectra and then use it in a linear analysis of the five original spectra. The normalization consists of dividing each spectrum by its concentration-pathlength product; these values, based on the CTS-derived pathlength of 10.23 meters, are given with the actual gas concentrations and new spectral filenames in Table D3. Figure D2 illustrates the normalized spectra, all of which represent spectra of concentration-product values 1.00 ppm-meters. These spectra are nearly equal to one another, as predicted by Beer's Law. Only the spectrum tfe01n.spc, based on the original 25.53 ppm spectrum, is easily discernable from the other spectra in the Figure.

Table D2. System Configuration Parameters for TFE Reference Spectra
(see Figure D1).

System Configuration Parameters	Values/Notes
MIL (cm^{-1})	0.5
integration time (sec)	1080 (120 sec/spectrum × 9 spectra)
absorption pathlength (m)	10.23
gas temperature (C)	15
gas pressure (mm Hg)	760 (±10)
apodization function	Triangular
zero filling factor	zero
detector type	MCT
detector gain (hardware)	jumpers BCD
detector gain (software)	1
reference CTS spectra	j2kety.spc
wavenumber standard spectrum	j2kety.spc

Table D3. Normalization Factors TFE Spectra

Original Spectrum	Concentration (ppm)	Concentration-Pathlength Product (ppm-meter)	Normalized Spectrum
tfe01.spc	2.50	25.5	tfe01n.spc
tfe02.spc	6.63	67.8	tfe02n.spc
tfe03.spc	13.3	133	tfe03n.spc
tfe04.spc	20.4	208	tfe04n.spc
tfe05.spc	25.1	257	tfe05n.spc

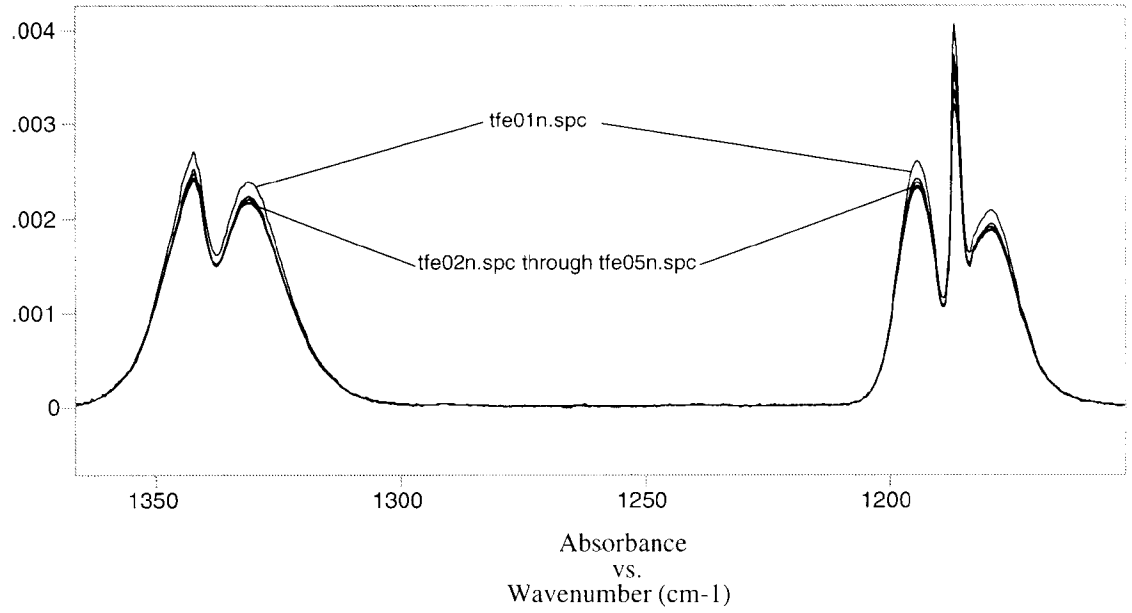

Figure D2. Normalized Reference Absorbance Spectra of TFE

Table D4 shows the results of a linear least-squares analysis using the *average* normalized spectrum as a single reference spectrum (with concentration-pathlength product 1.00 ppm-meters) over the analytical range 1050 to 1400 cm^{-1}. The bias in the linear method is clearly evident in the fourth column of the Table, which indicates that the analysis yields concentrations which are slightly too high at the lowest concentration and slightly too low at the highest concentration. The average of the last column in the table, which represents the absolute percent difference between the actual and calculated concentrations, the "fractional calibration uncertainty" (FCU; see Reference 2), is 3.2%. This value represents the average error over the concentration range for these reference spectra to be expected from the linear analysis up to the maximum concentration-pathlength value used in the analysis (257 ppm-meter). If additional accuracy is required, non-linear analyses or corrections such as those discussed above (Appendix B, Section 9) can be employed.

Table D4. Results of Linear Least Squares Analysis for TFE Reference Spectra.

TFE Reference Spectrum	Calculated Concentration (ppm)	Actual Concentration (ppm)	Actual - Calculated Concentration (ppm)	Absolute Percent Difference
tfe01.spc	2.69	2.50	0.19	7.7
tfe02.spc	6.64	6.63	0.01	0.2
tfe03.spc	12.8	13.0	- 0.2	1.4
tfe04.spc	19.8	20.4	- 0.6	2.9
tfe05.spc	24.2	25.1	- 0.9	3.7

D9. Calculating the Limit of Detection (LOD)

The estimated LODs are the concentrations for the given system configuration, reference spectra, and analytical region - at which each compound's absorbance area is equal to the RSA. For a specified system configuration and analytical region, an estimate of the LOD for a compound can be made from the absorbance area of a reference spectrum in that region (A_R, absorbance-cm^{-1}), the reference spectrum concentration-pathlength product (CPP, ppm-m), the sample absorption pathlength (L, meters), and the RSA values (absorbance-cm^{-1}) as

$$LOD = \frac{(CCP)(RSA)}{LA_R}$$ Equation D1

A simple trapezoidal approximation of A_R over the analytical region of interest, including baseline corrections when necessary, is suitable for the LOD estimate. The RSA is formed from the product of the FTIR system's typical root-mean-square noise level in absorbance and the width of the analytical region in cm^{-1} (see Appendix B, Section 2); the RSA estimate should reflect the error incurred in subtracting known spectral interferences. Appendix E, Section 1 presents detailed examples of RSA and LOD calculations.

D10. Using Existing Reference Libraries

The analyst may use any of the publicly available reference libraries for quantitative analyses, but it is strongly recommended that quantitative results for analytes be based only on spectra from libraries which meet the requirements discussed in this Appendix. If the reference library consists of spectra recorded at a spectral resolution different from that of the field system, the analyst must 1) de-resolve the spectra mathematically to that of the field data and 2) ensure that the library data are suitably linear over the desired measurement range *at the spectral resolution of the field system*.

APPENDIX E. Example Calculations.

This Appendix uses an analysis of tetrafluoroethylene (TFE) and 1,1-difluroethylene (DFE) in workplace air to illustrate the calculations of residual squared area (RSA) and limits of detection (LODs). The topics of designing, applying and verifying, and correcting a spectral analysis are also addressed below.

The FTIR system configuration assumed for this set of calculations is given below. These parameters are consistent with the LOD values presented in Table 2.

MIL:	0.5 cm^{-1}
absorption pathlength:	10 meters
apodization function:	triangular
gas temperature:	293 K
gas pressure:	760 Torr
zero filling factor:	none
wavenumbers of water bands:	1918 cm^{-1} and 2779 cm^{-1}
reference library sources:	3M Environmental Laboratory
integration time:	70 seconds (64 scans)
detector type:	MCT
detector gain - hardware:	Gain jumpers A, D, and H
detector gain - software:	1.0

E1. Residual Squared Area (RSA), Analysis Design, and Limits of Detection (LODs)

The analysis is to be carried out in workspace air, so the only potential spectral interferences are due to water and carbon dioxide. Figure E1 illustrates example reference spectra of TFE, DFE, and water. (The water spectrum shown is typical of workspace air samples; carbon dioxide does not absorb in any of the spectrum. As a result, the limited spectral region shown in Figure E2 is actually of the greatest interest for an analysis of DFE and TFE in workspace air.

Shown in greater detail in Figure E2 are the three reference spectra and two possible analytical regions. Analytical region 1, from 1370 to 1295 cm^{-1}, includes water bands which interfere with the TFE absorbance in the sample spectra. Analytical Region 2 (1215 to 1100 cm^{-1}) may be the best choice for analyzing samples for both TFE and DFE (though the weaker features near 3000 cm^{-1} remain an option for DFE); it avoids the TFE interference with water, but necessarily includes some spectral overlap between the two analytes. Until the relative TFE, DFE, and water concentrations in the samples are known, it is unclear which of the two regions will provide better concentration estimates for TFE, so calculations for both regions are described below.

Estimation of the LODs for TFE and DFE requires a calculation of the residual square area (RSA) in the actual sample spectra over the selected analytical regions. The RSA represents an estimate, based on the assumed sample matrix and available reference spectra, of the residual absorbance (see Equation A6) which will be used to calculate the concentration uncertainties from the actual sample spectra.

The reader should note that the RSA and derived LOD are only estimates. If the actual sample matrix differs substantially from that of the sample matrix assumed in the performance of these estimates, the actual concentration uncertainties and LODs may differ substantially from the RSA and LOD values obtained in the calculations described below. For workplace air samples, water is the only interfering compound which is certain to appear in any of the analytical regions considered below. A realistic

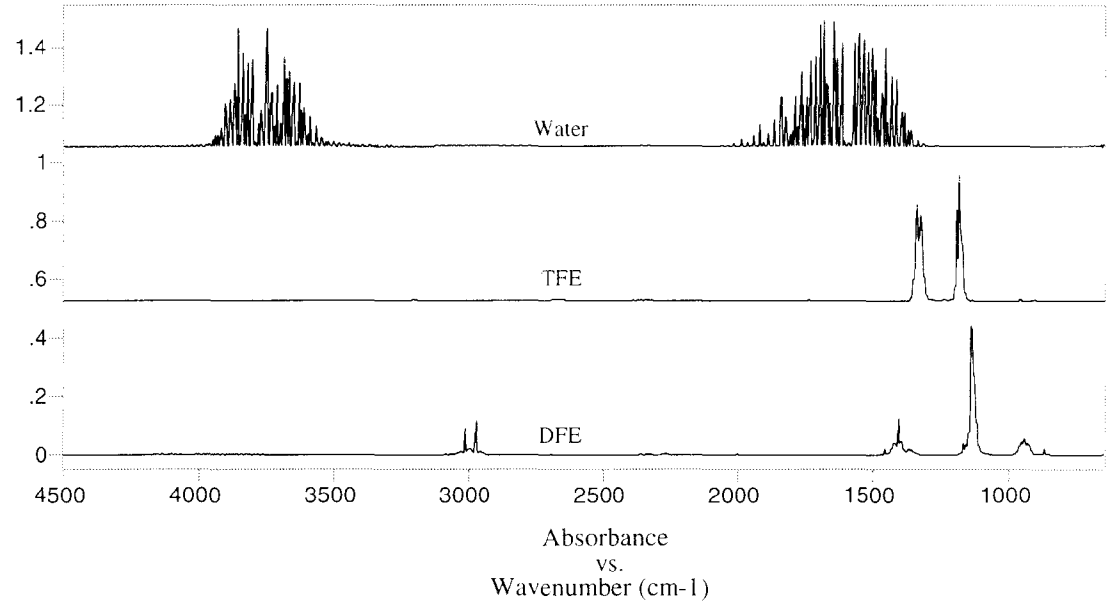

Figure E1. Absorbance Reference Spectra of TFE, DFE, and Water

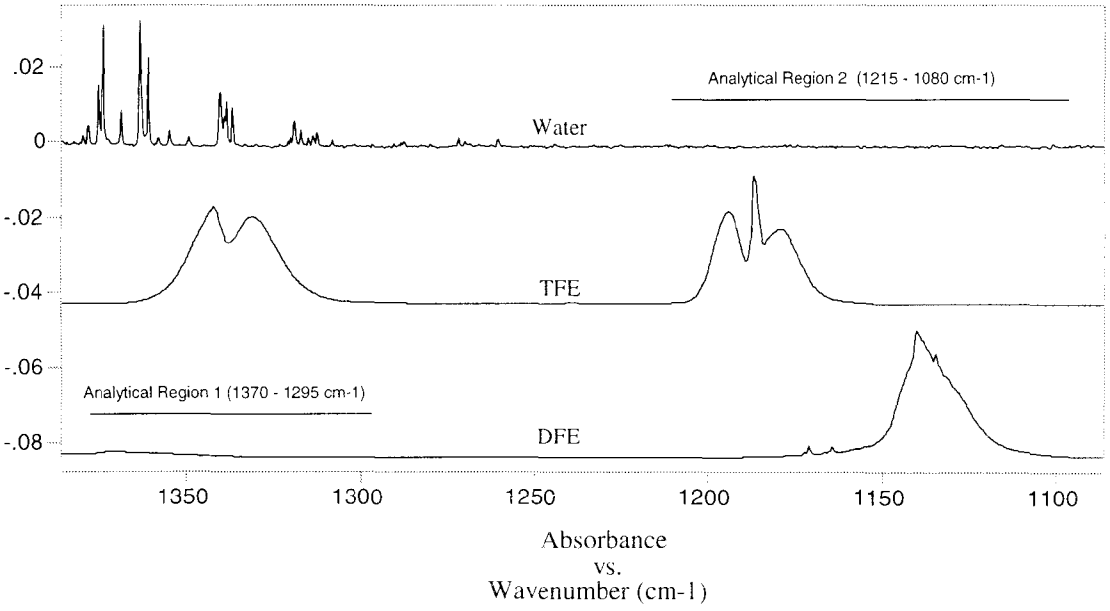

Figure E2. Possible Analytical Regions

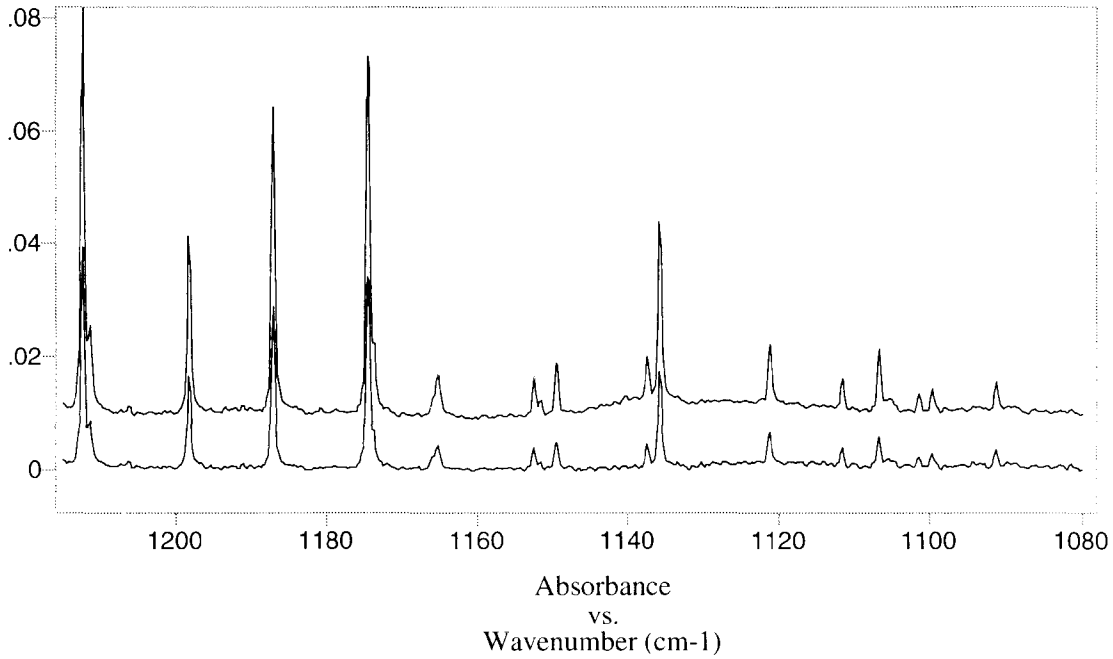

Figure E3. Water Spectra 1295 to 1080 cm-1

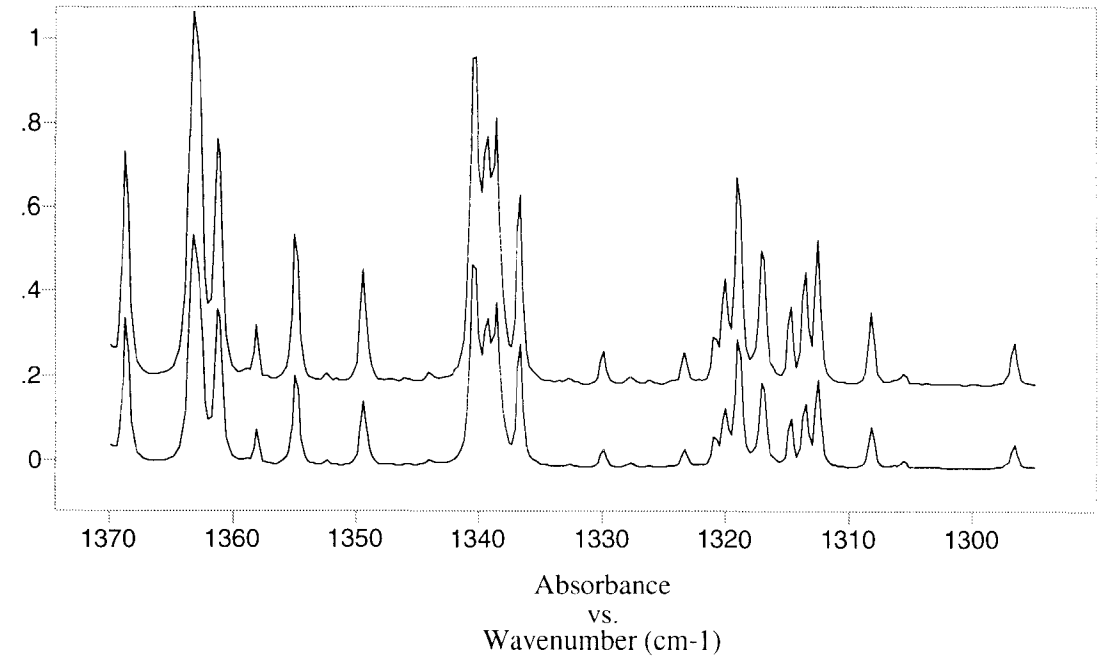

Figure E4. Water Spectra 1370 to 1295 cm-1

estimate of the RSA is therefore available by forming the mathematical difference of two water spectra — of substantially different water concentrations — recorded using the same FTIR system configuration. For each analyte, this estimate assumes that only water and that analyte will absorb substantially in the actual sample spectra. Later analyses based on the actual sample matrix could lead to either lower or higher concentration uncertainty and LOD estimates; examples of such analyses are detailed below.

Figures E3 and E4 illustrate two absorbance spectra recorded using the system configuration described above. They represent spectra of workspace air at approximately 20% and 40% relative humidity. The upper trace in each Figure is slightly offset for clarity.

Figure E5 shows two residual spectra formed by subtracting scaled versions of the lower-absorbance spectrum from the higher-absorbance spectrum. The scaling factors were determined in independent LSF analyses over the two analytical regions. Linear baseline corrections (offset and slope) were also determined during the analyses, so the mean value of each residual spectrum is zero. (These calculations were performed by using the ANOVA data analysis tool in Microsoft Excel 97). The residual squared area (RSA) values for the residual spectra are defined in Equation C2, and the related calculations are presented in Table E1. (The calculations also were performed in the program Excel by applying the function STDEV to the regression residuals.)

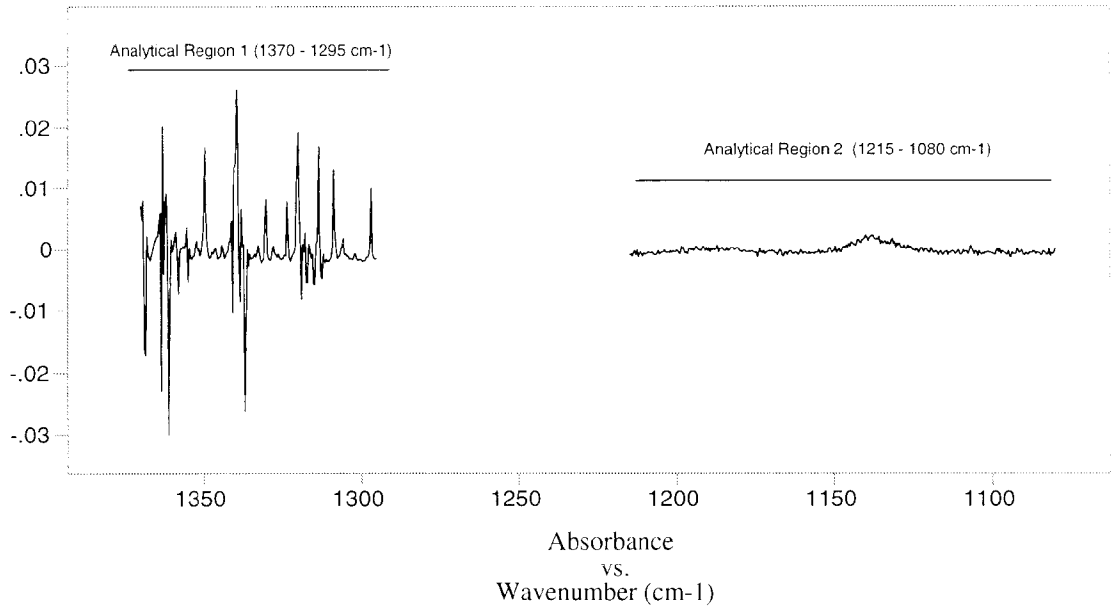

Figure E5. Water Residual Spectra

Table E1. Results of RSA Analysis from Water Reference Spectra.

Analytical Region (cm^{-1})	Calculated Scaling Factor	Scaling Factor Uncertainty (1 σ)	Residual RMS Standard Deviation (absorbance)	RSA (absorbance -cm^{-1}; Eq. B2)
1370-1295	1.636	0.003	0.00575	0.431
1215-1080	1.870	0.008	0.00069	0.093

An estimate of the LODs (ppm) for the two compounds for the specified system configuration can be made from the absorbance areas of the reference spectra over these analytical ranges (A_R,absorbance-cm^{-1}), the reference spectra concentration-pathlength products (CPP, ppm-m), the sample absorption pathlength L (meters), and the RSA values (absorbance-cm^{-1}) derived above.

The absorbance areas were determined using a standard trapezoidal approximation without baseline correction. (For these spectra, baseline corrections lead to values which differ from those quoted by less than 3%, and have been neglected below.) Figure E6 shows the spectral features of TFE and DFE used to calculate the A_r for the reference spectra tfeav05.spc (CCP = 256.7 ppm-m) and dfeav05.spc (CCP = 197.8 ppm-m).

The estimated LODs are the concentrations for the given system configuration, reference spectra, and analytical region - at which each compound's absorbance area is equal to the RSA. Mathematically, the LOD estimates are given by

$$LOD = \frac{(CCP)(RSA)}{LA_R} \qquad \text{Equation E1}$$

Table E2 lists the pertinent quantities and resulting LODs for DFE and TFE in the two analytical regions considered. The results indicate that the analytical region from 1215 to 1080 cm^{-1} is likely to provide the most reliable TFE concentrations.

Table E2. LODs for TFE and DFE from RSA Analysis of Water Reference Spectra.

Analytical Region (cm^{-1})	Compound	Reference Spectra			System Configuration		
		File Name	CCP (ppm-m)	Absorbance Area (abs-cm^{-1})	RSA (abs-cm^{-1})	L (m)	Estimated LOD (ppm)
1370-1295	TFE	tfe05.spc	256.7	16.03	0.431	10.0	0.69
1215-1080	TFE	tfe05.spc	256.7	13.97	0.093	10.0	0.17
1215-1080	DFE	dfe05.spc	197.8	8.72	0.093	10.0	0.21

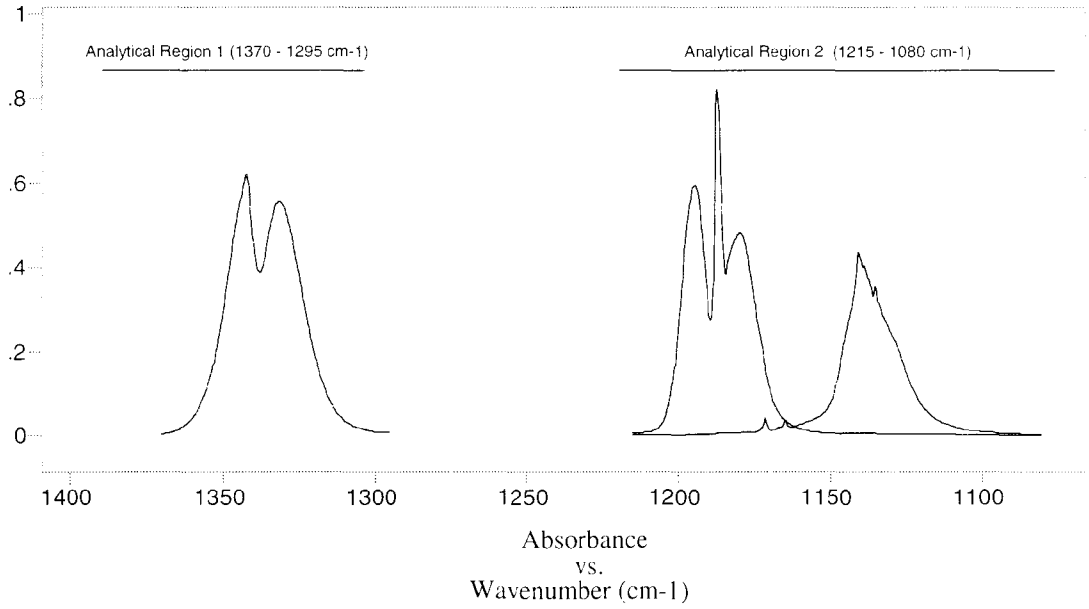

Figure E6. TFE and DFE Spectra for Asorbance Area Calculations

E2. LSF Determinations of TFE and DFE Concentrations

Presented in this section is a description of a least squares fit (LSF) analysis for the two compounds TFE and DFE in ambient air samples. As is always the case before actual measurements are taken, no actual sample data for mixtures of the compounds in the assumed matrix (ambient air) were available as these analyses were performed. Accordingly, the following description is based on synthetic spectra generated from available reference spectra for TFE, DFE, and water.

In order to *not* overestimate the effectiveness of the FTIR technique, the noise levels in the synthetic sample spectra were artificially raised, and the reference spectra used are not those most likely to provide an optimal analysis. This is the most prudent course available to an analyst attempting to predict the performance of the FTIR method under essentially unknown conditions, and it is the course recommended by the authors to analysts who find themselves in this common situation.

Estimates of the LOD for this sample matrix (see Appendix E, Section 1) indicate that the analytical region from 1215 to 1080 cm^{-1} will likely provide the most reliable TFE and DFE concentrations. The system configuration parameters used in those estimates are assumed to hold in the following description.

E2A. Generation and Analysis of Synthetic Sample Spectra of TFE and DFE

Table E3 describes the mathematical generation of synthetic samples for the following LSF analysis description. Each sample spectrum consists of the sum of scaled reference spectra for TFE (tfe4.spc, CCP = 208.3 ppm-m), DFE (dfeav05.spc, CCP = 197.8 ppm-m) and water (wat02bl.spc). The scaling factors indicated in Table E3 were used to generate synthetic sample spectra at the listed concentrations and the assumed absorption pathlength of 10.0 meters.

Table E3. Parameters Used to Generate Synthetic Sample Spectra Containing TFE, DFE, and Water.

TFE Scaling Factor	TFE Synthetic Conc. (ppm)	DFE Scaling Factor	DFE Synthetic Conc. (ppm)	H2O Scaling Factor	Synthetic Sample Spectrum File Name
0	0	0	0	0.6	S001.spc
0	0	0	0	1.2	S002.spc
1.200	25.0	1.264	25.0	0.6	S551.spc
1.200	25.0	0.253	5.00	0.6	S511.spc
0.240	5.00	1.264	25.0	0.6	S151.spc
1.200	25.0	1.264	25.0	1.2	S552.spc
1.200	25.0	0.253	5.00	1.2	S512.spc
0.240	5.00	1.264	25.0	1.2	S152.spc

A spectrum representing random absorbance noise was added to each synthetic spectrum. The noise spectrum was generated using the function RANDOM within the program GRAMS/32 V4.11 (Galactic, Inc.; see the Array Basic User's Guide, V4.1, page 316); similar functions are also available in Microsoft Excel. For the noise spectrum, the root mean square absorbance noise N_{RMS} (see also equation C2, which defines the RSA), calculated over the appropriate analytical region(s) according to

$$N_{RMS} = \sqrt{\sum_{i=p}^{i=q} \frac{(R_i)^2}{q-p}} \qquad \text{Equation E2}$$

was 0.00034 in the region 1438 to 1282 cm^{-1}; this is very close to the value obtained from actual absorbance spectra (provided by MIDAC Corporation) recorded with the quoted system configuration in the region 1005 to 932 cm^{-1}.

The synthetic spectra represent four different mixtures of TFE and DFE (including one "mixture" which contains neither compound), each at two different moisture levels.

Table E4 lists the results of a LSF analysis (program 4FTIMD V15, Rho Squared; see Reference 18) for TFE, DFE, and water in the analytical region 1215 to 1080 cm^{-1} using the reference spectral files TFE3.spc (CCP = 133.2 ppm-m) and dfeav04.spc (CCP = 133.3 ppm-m), and wat01bl.spc. Note that these are not the same reference spectra which were used in the generation of the synthetic sample spectra, and that the results for water are in arbitrary units. The analysis included the determination of two baseline correction parameters along with the compound concentrations.

Table E4. Original LSF Results for Original Synthetic Sample Spectra Containing TFE, DFE, and Water.

Synthetic Sample Spectrum File Name	TFE Synth. Conc. (ppm)	TFE LSF Result (ppm)	TFE LSF 3σ Uncert. (%)	DFE Synth. Conc. (ppm)	DFE LSF Result (ppm)	DFE LSF 3σ Uncert. (%)	H_2O LSF Result (arb)	H_2O LSF 3σ Uncert. (%)
S001.spc	0	0.02	52.5	0	0.07	13.7	1.12	1.23
S002.spc	0	0.03	32.2	0	0.14	8.95	2.24	0.80
S551.spc	25.0	**24.41**	**0.26**	25.0	**24.30**	**0.29**	0.87	**11.8**
S511.spc	25.0	**24.43**	**0.25**	5.00	**4.88**	**1.43**	0.87	**11.5**
S151.spc	5.00	**4.88**	**0.41**	25.0	**24.33**	**0.09**	1.07	**3.04**
S552.spc	25.0	**24.43**	**0.26**	25.0	**24.35**	**0.29**	1.99	**5.20**
S512.spc	25.0	**24.45**	**0.26**	5.00	**4.95**	**1.43**	1.99	**5.11**
S152.spc	5.00	**4.90**	**0.43**	25.0	**24.39**	**0.10**	2.19	**1.56**
Average Abs. % Concentration Difference*		**2.24**			**2.34**			
Average Abs. % Concentration Uncertainty*			**0.31**			**0.61**		**6.38**

*The averages exclude the spectra (S001 and S002) with zero synthetic TFE and DFE concentrations.

The LSF results for the non-zero TFE and DFE spectra are consistently good, being different from the synthetic concentrations less than 3% in every case. Listed in the Table for TFE and DFE are the average percent differences between the synthetic concentrations and those derived from the LSF analysis, which are 2.24% and 2.34%, respectively.

The concentration uncertainties listed in Table E4 are the statistically determined 3σ values from the LSF analyses. Included in the last row of the Table are the average percent concentration 3σ uncertainties for the non-zero TFE and DFE spectra. These percent uncertainty parameters and the visual appearance of the LSF residual spectra are important indicators of the quality of the least squares analysis, and are discussed further in the following section.

Though they are not included in the averages presented in the last two rows of Table 3, the TFE and DFE results for the two synthetic spectra which contain no absorption features of TFE and DFE (S001 and S002) are of interest and importance. The LSF concentration results are small. (Their maximum is 0.14 ppm). They are smaller in each case than the LOD estimates of Table E2, and their corresponding 3σ uncertainties from this LSF analysis are smaller still. Unfortunately, no consensus exists on the exact mathematical relationship between the LODs calculated as described in this document and the 3σ concentration uncertainties. This statement is supported by the contents of Section A2 in Reference 3 a consensus document which prescribes three different methods for calculating LODs (or, in the terminology of Reference 3, "minimum detectable concentrations"). These three prescriptions include one similar to the LOD method prescribed in this document, and one which is based on the concentration uncertainties derived from spectra similar to S001 and S002. In this limited example, two of the three prescriptions included in Reference 3 provide very different results, and they indicate that the LOD calculation described in this document provides the most conservative estimate that is, the highest estimate of the three LOD prescriptions of Reference 3.

E2B. Analyses of Synthetic Sample Spectra with an Interfering Compound

Every compound-specific quantitative analytical technique, including FTIR spectrometry, can fail to provide accurate results when interfering compounds appear in a sample. However, the results of a mathematical FTIR spectral analysis designed for a particular set of compounds provides clues to its failure in the presence of interferants. An experienced analyst can often adjust the analysis to accommodate the interferants and provide accurate results.

To illustrate this important aspect of FTIR spectrometry, a synthetic interference was introduced to the spectra described in Table E3. Scaled versions of a reference spectrum (hfpav06.spc, 256.6 ppm-m) of the compound hexafluoropropylene (HFP), representing the compound at two concentrations (5.00 and 10.0 ppm), were added to the original synthetic spectra. The resulting final synthetic sample spectra are described in Table E5 below. The least squares analysis described above for TFE and DFE only, when applied to these spectra containing spectral features of HFP, gives the results shown in Table E6 below.

Table E5. Parameters Used to Generate Synthetic Sample Spectra Containing TFE, DFE, Water, and HFP.

Original Synthetic Sample Spectrum File Name	HFP Scaling Factor	HFP Synthetic Conc. (ppm)	Final Synthetic Sample Spectrum File Name
S001.spc	0.195	5.00	S0011.spc
S002.spc	0.390	10.0	S0022.spc
S551.spc	0.195	5.00	S5511.spc
S151.spc	0.195	5.00	S1511.spc
S512.spc	0.195	5.00	S5121.spc
S511.spc	0.390	10.0	S5112.spc
S552.spc	0.390	10.0	S5522.spc
S152.spc	0.390	10.0	S1522.spc

Table E6. Original LSF Results for Final Synthetic Sample Spectra Containing TFE, DFE, Water, and HFP

Synthetic Sample Spectrum File Name	TFE Synth. Conc. (ppm)	TFE LSF Result (ppm)	TFE LSF 3σ Uncert. (%)	DFE Synth. Conc. (ppm)	DFE LSF Result (ppm)	DFE LSF 3σ Uncert. (%)	H_2O LSF Result (arb)	H_2O LSF 3σ Uncert. (%)
S0011.spc	0	1.00	39.6	0	-1.58	26.5	1.65	0.89
S0022.spc	0	2.01	39.5	0	-3.16	26.4	3.29	1.78
S5511.spc	25.0	**25.06**	**1.51**	25.0	**22.65**	**1.89**	1.43	**43.3**
S5112.spc	25.0	**25.73**	**2.90**	5.00	**1.57**	**53.8**	1.99	**61.4**
S1511.spc	5.00	**5.53**	**6.64**	25.0	**22.67**	**1.84**	1.63	**37.0**
S5522.spc	25.0	**25.73**	**2.90**	25.0	**21.05**	**4.01**	3.10	**39.2**
S5121.spc	25.0	**25.09**	**1.52**	5.00	**3.29**	**13.1**	2.55	**24.4**
S1522.spc	5.00	**6.20**	**11.87**	25.0	**21.09**	**3.96**	3.30	**36.4**
Average Abs. % Concentration Uncertainty*			**4.56**			**13.1**		**40.3**

*The average excludes the spectra (S0011 and S0022) with zero synthetic TFE and DFE concentrations.

The results shown in the last rows of Table E4 (those of the original LSF analysis *without* HFP interference) and Table E6 (those of the original LSF analysis *with* HFP interference) are clearly quite different. Averaged over the six synthetic spectra containing TFE and DFE in each case, the (absolute) percent concentration uncertainties for TFE, DFE, and H_2O are greater for the spectra with HFP interference. For TFE and DFE, the average percent uncertainties of Table E6 are over ten times greater than those of Table E4.

This exercise shows that:

- For sample spectra containing substantial TFE and DFE concentrations, the HFP interference causes large increases in the TFE and DFE relative absolute concentration uncertainties.

- For sample spectra containing low or zero concentrations TFE and DFE, the relative absolute uncertainties are NOT a reliable indicator of the HFP interference. However, for such spectra, the concentration results themselves are often clearly unreliable; note that the DFE concentration results are negative *and* large compared to the LOD estimate for this compound. (Note also that negative concentration results which are *small* compared to the LOD are statistically valid, and do not necessarily indicate a failure of the analysis.)

If the concentration results show anomalies such as those noted above, the residual spectra from the analyses will also exhibit anomalous behavior. This is illustrated in Figure E7, which shows the residual spectra for four analyses. Compared to the residual spectra resulting from analyses of spectra without the HFP interference, those with HFP interference show large absorbance features which cannot be modeled by the three reference spectra employed. The analyst needs to identify the interfering compound before proceeding. This can often be done by visually comparing the suspect residual spectra to reference spectra of a number of likely interferants, as illustrated in Figure E8.

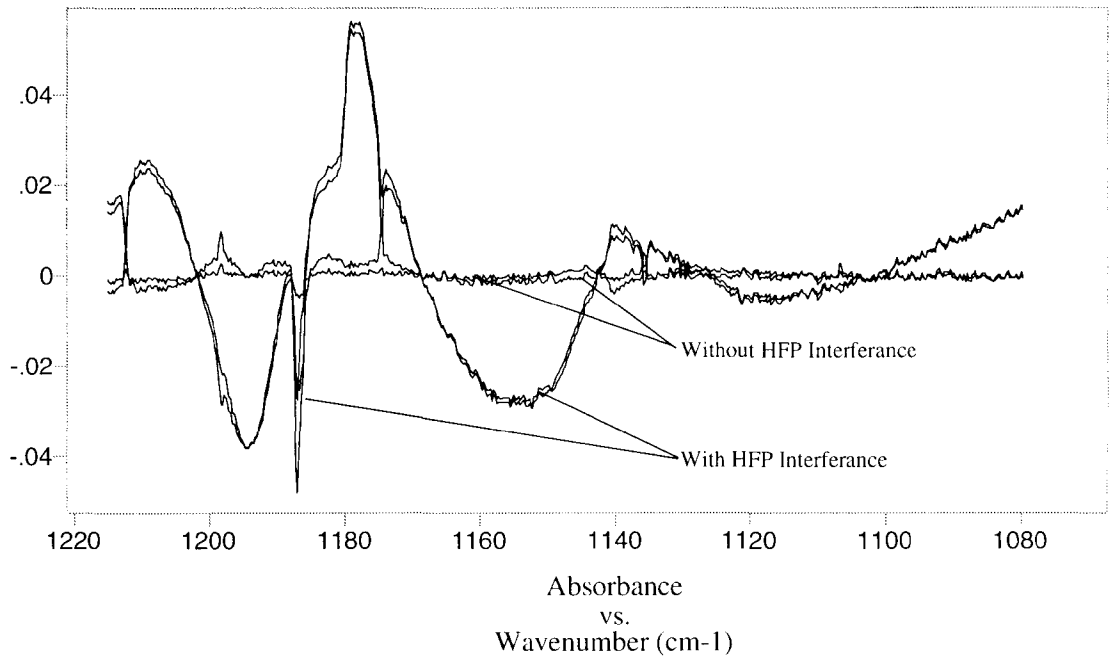

Figure E7. Residual Spectra With and Without HFP Interferance

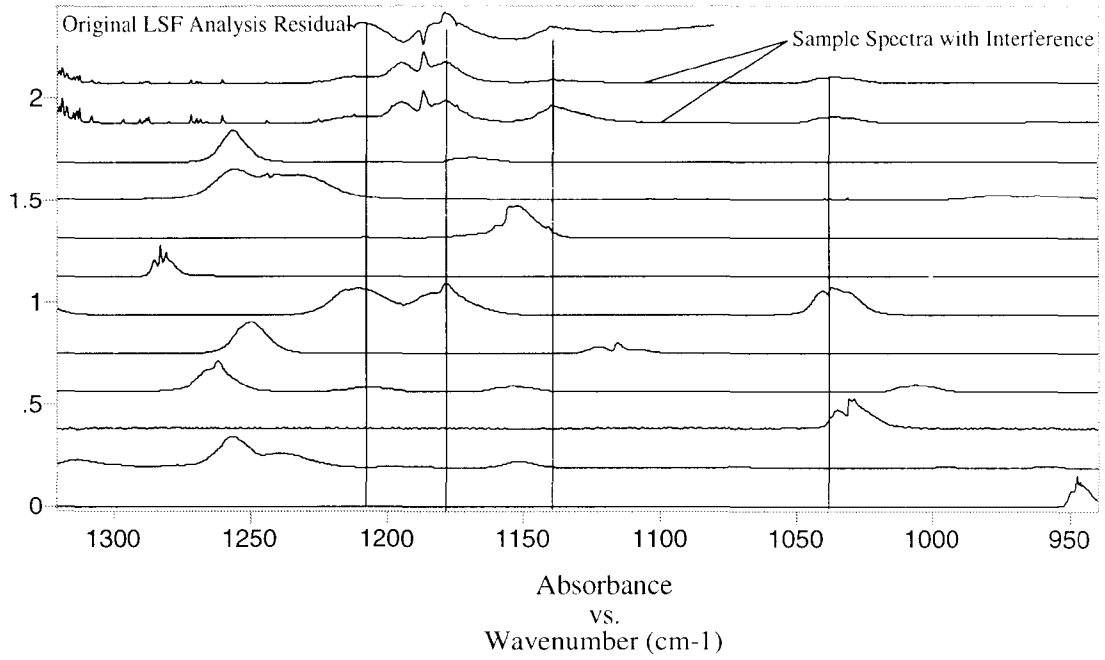

Figure E8. Comparisons of Residual, Sample, and Reference Spectra

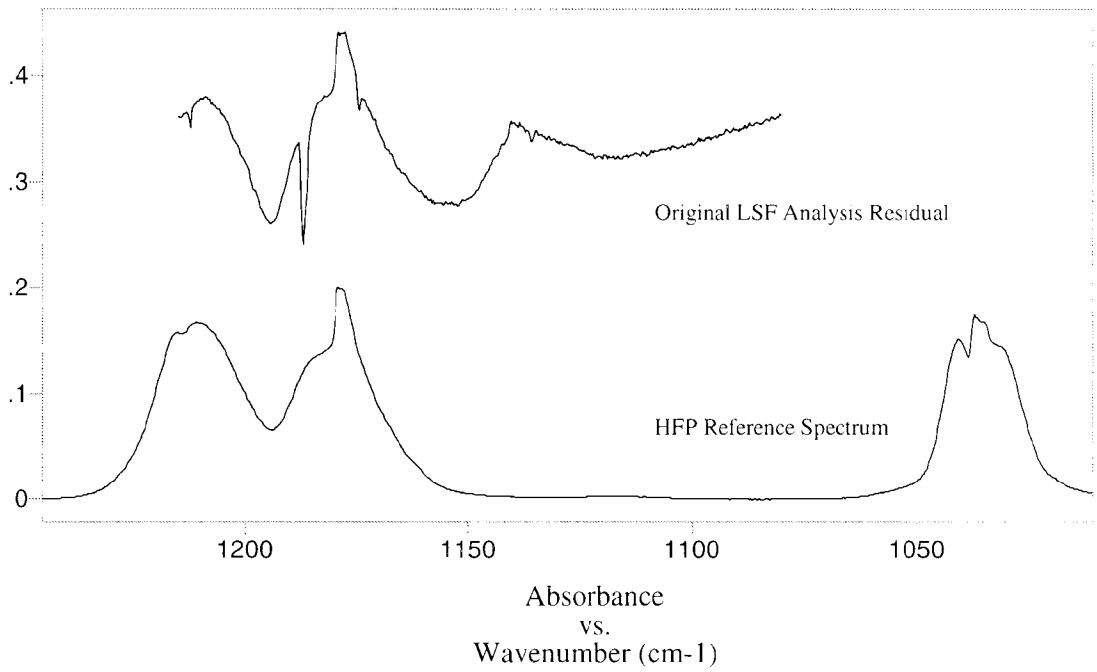

Figure E9. Original LSF Residual and HFP Reference Spectra

Figure E8 shows that the positions of three major relative maxima in the residual spectrum (top trace) correspond well to only one of the nine candidate reference spectra in the lower traces of the Figure. (The nine spectra shown are all of light, partially or fully fluorinated hydrocarbons.) An additional absorbance band from this single reference spectrum also corresponds to a large peak in both of the sample spectra (second and third traces from top of the Figure).

A closer examination of this reference spectrum — that of HFP, of course — is illustrated in Figure E10. It clearly shows a close relationship between the shape of the residual spectrum and the absorption features of HFP. The relationship is not exact because the sample spectrum has had incorrect amounts of the compounds TFE and DFE subtracted, and this distorts the residual spectrum.

Though this identification is tentative, it can be tested by including HFP in the LSF analysis. Table E7 shows the TFE, DFE and water concentrations resulting from an analysis identical to those described above except for the addition of HFP as a fourth compound. (As usual, an HFP reference spectrum different from the one used to add the synthetic interference was employed in the analysis.) To facilitate comparisons with the preceding tables, the HFP results have been excluded from Table E7; they were in all cases similar in quality to those obtained for the other compounds.

The results show that inclusion of HFP in the analysis yields results of the original (high) quality shown in Table E3 for TFE, DFE, and water. The percent relative uncertainties are slightly higher in the final analysis than in the original analysis; this is to be expected because the same amount of spectral information is being used to determine an additional parameter in the final analysis. The quality of the analysis could probably be further improved by extending the analytical region to include the entire HFP absorbance band shown in Figure E9.

Table E7. Final LSF Results for Final Synthetic Sample Spectra Containing TFE, DFE, Water, and HFP

Synthetic Sample Spectrum File Name	TFE Synth. Conc. (ppm)	TFE LSF Result (ppm)	TFE LSF 3σ Uncert. (%)	DFE Synth. Conc. (ppm)	DFE LSF Result (ppm)	DFE LSF 3σ Uncert. (%)	H_2O LSF Result (arb)	H_2O LSF 3σ Uncert. (%)
S0011.spc	0	1.00	39.6	0	-1.58	26.5	1.65	0.89
S0022.spc	0	2.01	39.5	0	-3.16	26.4	3.29	1.78
S5511.spc	25.0	**24.43**	**0.27**	25.0	**24.27**	**0.33**	0.87	**12.1**
S5112.spc	25.0	**24.45**	**0.27**	5.00	**4.81**	**1.72**	0.88	**12.34**
S1511.spc	5.00	**4.91**	**0.44**	25.0	**24.27**	**0.11**	1.08	**3.23**
S5522.spc	25.0	**24.46**	**0.28**	25.0	**24.27**	**0.35**	1.99	**5.51**
S5121.spc	25.0	**24.45**	**0.27**	5.00	**4.92**	**1.63**	1.99	**5.25**
S1522.spc	5.00	**4.94**	**0.57**	25.0	**24.29**	**0.14**	2.20	**2.05**
Average Abs. % Concentration Uncertainty*			**0.35**			**0.71**		**6.74**

*The average excludes the spectra (S0011 and S0022) with zero synthetic TFE and DFE concentrations.

QUARTZ in coal mine dust, by IR (redeposition) 7603

SiO_2 MW: 60.08 CAS: 14808-60-7 RTECS: VV7330000

METHOD: 7603, Issue 3 **EVALUATION: UNRATED** **Issue 1: 15 May 1989**
Issue 3: 15 March 2003

OSHA : quartz (respirable): 10 mg/m³/ (%SiO_2 + 2)
NIOSH: 0.05 mg/m³ (suspect carcinogen)
ACGIH: 0.1 mg/m³

PROPERTIES: solid; d 2.65 g/cm³; crystalline transformations: quartz to tridymite @ 867 °C: trydymite 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)
*see sampling section

FLOW RATE: HD cyclone: 2.2 L/min
nylon cyclone: 1.7 L/min

VOL-MIN: 300 L @ 0.1 mg/m³
-MAX: 1000 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: Rrequired for OSHA standard calculations; area respirable or settled dust

ACCURACY

RANGE STUDIED: 25 to 160 µg/sample [1]
(2 mg quartz/m³ 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 ABSORPTION 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: NIST SRM 1878a suspension 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 0.25 mg/m³ for a 1000-L sample. The method was specifically developed for respirable coal mine dust samples [1]. The precisions ($\hat{S}_r$ & $\hat{S}_{rT}$) stated above are based on ruggedization data [2]. IR is useful for a simple matrix like coal dust where the interference can be removed. See also discussion of crystalline silica in Chapter R of this volume [3].

INTERFERENCES: Calcite is used as a dusting agent in coal mines and interferes by reacting with quartz during muffle furnace treatment resulting in low quartz assay. Kaolinite is sometimes present in coal dust and interferes by absorbing radiation at the quartz analytical wavelength of 800 cm⁻¹. These 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 is similar to MSHA P-7 which was collaboratively tested [2,4]. Quartz can also be determined by Methods 7500 (XRD) and 7602 (IR). XRD can distinguish the three silica polymorphs and silica interferences can be eliminated by phosphoric acid treatment. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., Method 7601), but polymorphs cannot be distinguished. Visible absorption methods also have larger laboratory-to-laboratory variability than XRD and IR methods and therefore are recommended for research use only [5].

REAGENTS:

1. Quartz* (SRM 1878a, 2950, 2951, 2958), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards Technology, Gaithersburg, MD 20899; www.nist.gov.
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. Desiccant (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 back up 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).
   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 6 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; desiccator cabinet.
14. Magnetic stirrer with thermally insulated top,

EQUIPMENT: - cont.

and stirring bars.
15. Reagent bottles with ground glass stoppers, 500-mL, and volumetric flasks, 500-mL.**
16. Tweezers.
17. Petri dishes, plastic, for 47-mm diameter filters.
18. Polyethylene wash bottles; metal spatulas.
19. Serological pipets, various sizes as required.
20. Lighted viewing box (optional).

** Glassware should be detergent-washed, rinsed thoroughly with distilled or deionized water, and then with 2-propanol, and dried in a dust-free area.

SPECIAL PRECAUTIONS: Avoid inhaling quartz dust [6]. 2-Propanol is flammable. Hydrochloric acid is corrosive and should be handled in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Preweigh each filter to the nearest 0.01 mg.
3. Sample at 1.7 ± 5% L/min with nylon cyclone or 2.2 ± 5% L/min with HD cyclone for a total sample volume of 300 to 1000 L. Do not exceed 2 mg dust loading on the filter.

   NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything other than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

   NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [7]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [3].

SAMPLE PREPARATION:

4. Reweigh the filters under conditions identical to those before preweighing. The difference is the sample weight, W_s (µg).
5. Ash sample and blank filters by one of the following methods:
   a. **Low-temperature ashing.**
   Using forceps, transfer filter to a 50-mL beaker. Ash 2 h at 300 watts RF power and oxygen flow rate of 75 mL/min following techniques recommended in the instrument manual. After ashing, add 15 mL 2-propanol to each beaker.
   b. **Muffle furnace ashing.**
      (1) If the samples contain calcite in concentrations greater than 20% of the total dust loading, wash the filters with acid using the filtration apparatus with the 1.6-cm ID glass funnel. Place a 25-mm glass fiber filter over the frit area, then place a 0.5-µm, 37-mm PVC filter

over the glass fiber filter. Clamp down the filter funnel. Add 5 mL 2-propanol and check for leakage. Remove the sample filter from the cassette. Fold it in half with the collection surface inside, then in quarters. Place the folded filter into the funnel. If necessary, push the filter to the bottom half of the funnel with a glass rod. Add 10 mL HCl solution, then 5 mL 2-propanol. Apply suction and continue until all of the liquid has been removed. Press the folded sample filter onto the surface of the collecting filter if necessary to remove all the liquid. Remove both filters and place in a porcelain crucible. Allow filters to air-dry.

(2) If acid wash was not required, transfer filter samples and blanks to porcelain crucibles.

(3) Loosely cover the crucibles and place in a muffle furnace. Hold for 2 h at 600 °C. After ashing, add several mL 2-propanol to the ash, scrape the crucible to loosen all particles and transfer to a 50-mL beaker. Wash the crucible several times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to ca. 15 mL.

6. Redeposit the sample residue as follows using the filtration apparatus with the 1.0-cm funnel. With a slight vacuum applied, place a 25-mm glass fiber filter on the fritted base. Cut a 47-mm DM-450 filter in half. Superimpose one half over the other, glossy sides down, and place on the glass fiber filter. (The lower half of the DM-450 filter serves as a blank and is used in the reference beam of the infrared spectrometer). Position filter funnel, apply clamp and turn off vacuum. Add several mL 2-propanol to the funnel. Check that the funnel is securely and uniformly clamped. Place sample beakers into ultrasonic bath for at least 30 sec to ensure homogeneous dispersion. Remove a beaker, wipe excess water from the outside, transfer slurry to the filtration funnel and reapply vacuum. During filtration, rinse the beaker twice with 2-propanol to remove all dust and add rinsings to funnel. Control the filtration rate to keep the liquid near the funnel top during rinsing to avoid disturbing the deposit. When the depth of liquid in the funnel reaches ca. 4 cm above the filter, gently rinse the inside of funnel with 2-propanol and complete filtration. Remove the clamp and lift off the funnel, taking care not to disturb and deposit. Release the vacuum. Define the deposit area by marking around the circumference using a pencil or scriber. This is especially important for standards or light-colored samples. Place the DM-450 filter halves in petri dishes and allow to air-dry.

CALIBRATION AND QUALITY CONTROL:

7. Prepare and analyze NIST SRM 1878a standard quartz filters.

NOTE 1: Calibration standards are limited to NIST and USGS certified standards of known purity, particle size, and sample-to-sample homogeneity. At least 12 materials, including 5 µm Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none has been found to be an acceptable alternative to the certified standards cited within this method [3]. Standard reference materials should be corrected for phase purity.

NOTE 2: Establishing traceability of secondary calibration standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used in the industrial hygiene field can provide. In addition, particle size distribution measurements have considerable error. Therefore, the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.

NOTE 3: NIST SRM 2950 calibration set (α-quartz) may be useful for preparing working standards at known concentrations.

a. Place the flask containing the calibration stock solution in an ultrasonic bath for 30 to 45 min.

b. Move the flask to a magnetic stirrer and stir slowly while the flask cools to room temperature. Continue to stir slowly while preparing standards.

c. Mount a DM-450 filter in the filtration apparatus in the same manner used to redeposit the samples. Add 5 mL 2-propanol to the funnel. Withdraw an aliquot of the quartz suspension from the center of the flask. Draw liquid to the mark but do not attempt to adjust volume by draining pipet. Carefully wipe the outside of the pipet, then drain the suspension into the filter funnel. Rinse down the inside wall of the pipet with a few mL of 2-propanol, draining the washings into the filter funnel. Apply vacuum to complete the filtration. Prepare quartz standards to cover the range 10 to 250 µg per filter.

d. Carry an additional set of these standards and media blanks through steps 5 and 6 to monitor for contamination and losses.

NOTE: Accuracy depends on obtaining uniform deposition of samples and standards across the filter surface and obtaining reproducible aliquots from the quartz suspension. This requires some skill. The quartz calibration curve should be prepared before analyzing samples as a check on the analyst's ability to prepare uniform deposits. Repeatability should be <10% on replicate standards with more than 40 µg quartz.

8. Perform an IR scan for each standard filter using the other half of the filter in the reference beam (steps 10 through 12). Construct a calibration graph (absorbance at 800 cm^{-1} vs. µg quartz per filter). This graph should be linear and pass through the origin.
9. (Only for samples ashed in LTA). Prepare suspensions of at least 5 kaolinite standards in the range 100 to 600 µg per filter. Perform an IR scan of the kaolinite standards from 1000 to 650 cm^{-1}. Draw baselines as described in step 12 and measure the height of the absorbance bands at both 915 and 800 cm^{-1}. Prepare a graph with absorbance at 915 cm^{-1} as ordinate vs. absorbance at 800 cm^{-1} as abscissa. Plot a point for each standard. If possible, generate the correction curve data on the same day that coal mine dust samples are analyzed since curve parameters may vary somewhat from day to day. A curve through the points should be linear but will not pass through the origin since the peak at 915 cm^{-1} is more intense than the peak at 800 cm^{-1} and small amounts of kaolinite do not interfere with the quartz analysis.

   NOTE 1: Kaolinite correction calibration curve is required when samples are ashed in an LTA since kaolinite is not destroyed under these circumstances and has as interfering peak at 800 cm^{-1} for which a correction must be performed.

   NOTE 2: A more detailed discussion of IR peaks is given in the IR section of Chapter R of this volume [3].

   NOTE 3: Some training (university or short course) in geology or mineralogy can be useful for the analyst and/or laboratory management. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret crystal structure, matrix interferences and mineral transformation for the laboratory client.

MEASUREMENT:

10. Set appropriate instrument conditions for quantitative analysis.
11. Place the dry DM-450 filter-half containing the dust deposit on a holder. Center the deposit over the hole in the holder and secure the filter with a magnet. (A lighted viewing box facilitates this procedure). Insert the sample into the beam of the spectrophotometer. Place the other half of the DM-450 filter on another holder, secure with a magnet and insert it into the reference beam.

    NOTE: For the best precision, the reference filter should be half of the same DM-450 filter which contains the redeposit. However, for routine analysis, the same 2-propanol-treated blank can be used for all filters with the same lot number.
12. Run an infrared scan, in linear absorbance mode from 1000 to 650 cm^{-1}. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from ca. 820 to 670 cm^{-1}. Measure and record the absorbance at 800 cm^{-1}, baseline to maximum. If the sample was ashed in an LTA, the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw a baseline under this band from ca. 960 cm^{-1} to 860 cm^{-1}. Measure and record the absorbance at 915 cm^{-1}, baseline to maximum.
13. Analyze blanks. Check results for contamination.

CALCULATIONS:

14. Correct for kaolinite, if required. Using the sample absorbance at 915 cm^{-1}, refer to the kaolinite curve to find the absorbance at 800 cm^{-1} due to kaolinite. Subtract this amount from the sample absorbance at 800 cm^{-1}. Use this corrected value to calculate µg quartz in the sample.

15. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} determined in step 12. Determine the weight of quartz, W_q (µg), from the quartz standard curve. Since the deposition area for samples and standards is the same, it is not necessary to correct for area.
16. Calculate the percent quartz by dividing the weight of quartz, W_q (µg), by the total sample weight, W_s (µg).

$$\%quartz = \frac{W_q}{W_s} \cdot 100$$

EVALUATION OF METHOD:

This method is based MSHA P-7 which was collaboratively tested [2,4]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher, amount of calcite or kaolinite on the sample, ashing time, pH of solvent to remove calcite, shipment of samples and others. None of these factors was found to have an effect. Results obtained by this method are equivalent to those obtained by Method 7500. A collaborative study of the ruggedized method was performed with 15 laboratories participating [2]. The total errors and interlaboratory and intralaboratory errors were found to be dependent on the types of samples. For samples collected from laboratory-generated aerosols, using a set of matched-flow orifices, the lower and upper limits of the relative standard deviation over the range 60 to 150 µg quartz were:

	Lower	Upper
Total error (RSD)	0.13	0.22
Intralaboratory error	0.07	0.10
Interlaboratory error	0.08	0.14

The lower limit applies to samples containing up to 1 mg coal mine dust with less than 2% kaolinite; the upper limit was found for samples with 2 mg coal mine dust or a lower amount of coal mine dust with more than a few percent kaolinite. The total error increased to 0.36 to 0.40 (lower and upper range) when personal sampling pumps were used to collect the samples. The pump error increased the interlaboratory error. Precision for pure quartz samples is ca. 0.05 in the 100 to 500 µg range [4]. Precision for actual samples is not as good and depends on sample size and ashing technique.

This method is particle size dependent. The particle sizes of the standards and samples should be matched as closely as possible to prevent a bias in the results, which is not correctable with this method. A thorough study of the range of biases has not been done for IR methods.

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METHOD REVISED BY:

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SILICA, CRYSTALLINE, by XRD (filter redeposition) 7500

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
14464-46-1 (cristobalite) VV7325000 (cristobalite)
15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7500, Issue 4 **EVALUATION: FULL** **Issue 1: 15 August 1990**
Issue 4: 15 March 2003

OSHA : quartz (respirable) 10 mg/m³/(%SiO_2+2); cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m³; carcinogen
ACGIH: quartz (respirable) 0.1 mg/m³
cristobalite (respirable) 0.05 mg/m³
tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell (HD) cyclone, or aluminum cyclone + 5-µm PVC membrane) *see sampling section

FLOW RATE: Nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min; aluminum cyclone: 2.5 L/min

VOL-MIN: 400 L
-MAX: 1000 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 per set (see step 13.g.)

BULK SAMPLE: High-volume or settled dust; to identify interferences

ACCURACY

RANGE STUDIED: 25 to 2500 µg/m³ [1] (800-L sample)

BIAS: None known

OVERALL PRECISION ($\hat{S}_{rT}$): 0.09 (50 to 200 µg) [1]

ACCURACY: ± 18%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: Crystalline SiO_2

ASH: Muffle furnace or RF plasma asher or dissolve in tetrahydrofuran

REDEPOSIT: On 0.45-µm Ag membrane filter

XRD: Cu target X-ray tube, graphite monochromator
Optimize for intensity; 1° slit
Slow step scan, 0.02°/10 sec
Integrated intensity with background subtraction

CALIBRATION: NIST SRM 1878a quartz, NIST SRM 1879a cristobalite, USGS 210-75-0043 tridymite suspensions in 2-propanol.

RANGE: 0.02 to 2 mg SiO_2 per sample [2]

ESTIMATED LOD: 0.005 mg SiO_2 per sample [2]

PRECISION ($\hat{S}_r$): 0.08 @ 0.05 to 0.2 mg per sample [1]

APPLICABILITY: The working range is 0.025 to 2.5 mg/m³ for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is similar to the method in the Criteria Document [3] and P&CAM 259 [4] which has been collaboratively tested [1]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. XRD can distinguish the three silica polymorphs and silica interferences can be eliminated by phosphoric acid treatment. IR (methods 7602 and 7603) can also quantify quartz, cristobalite and tridymite if amorphorous silica and silicates are not present in large amounts. However sensitivity is reduced if multiple polymorphs are present and secondary peaks must be used. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., Method 7601), but polymorphs can not be distinguished. Visible absorption methods also have larger laboratory-to-laboratory variabilty than XRD and IR methods and therefore are recommended for research use only [10].

REAGENTS:

1. Silica Standards.
   a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899; www.nist.gov.
   b. Tridymite* (210-75-0043) available from U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.
2. 2-Propanol*, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. 1.5 % parlodion solution. (Dissolve 1.5 g of parlodion* in isopentyl acetate* and dilute to 100 mL with isopentyl acetate.)
7. Optional (if calcite present): 25% v/v concentrated hydrochloric acid* (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-µm pore size supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
      NOTE: Check each new lot of PVC filters by analyzing one or more by this method. For example, Gelman VM-1 filters (all lots) were found to be unacceptable because of high ash and background. If THF is used, check for complete dissolution by dissolving a blank PVC filter and following steps 5c through 8.
   b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), Aluminum (Al), or equivalent [11].
2. Area air sampler: PVC membrane filter, 37-mm diameter, 5-µm pore size; three-piece filter cassette.
3. Sampling pumps with flexible connecting tubing, capable of the following flow rates: nylon cyclone, 1.7 L/min; HD cyclone, 2.2 L/min; Al cyclone, 2.5 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size, available from Sterlitech Corp., 22027 70th Ave S, Kent, WA 98032-1911; www.sterlitech.com.
5. X-ray powder diffractometer (XRD) equipped with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone, or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher (LTA) or muffle furnace, or ultrasonic bath (≥150 W), for filter preparation.
8. Vacuum filtration assembly and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm, for wet sieving.
10. Analytical balance (0.001 mg); magnetic stirrer with thermally insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); 40-mL wide-mouth or 50-mL centrifuge tubes (THF method); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.
11. Explosion-resistant hot plate.
12. Teflon sheet, 0.3 to 1 mm thick.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3]. THF is extremely flammable and should be used in a fume hood. 2-Propanol, parlodion and isopentyl acetate are flammable. Hydrochloric acid is corrosive and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with nylon cyclone or 2.2 ± 5% L/min with HD cyclone for a total sample size of 400 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything other than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found to be optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [12]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [11].
3. Take an area air sample or collect a settled dust sample, if dust in the work environment has not been previously characterized.

SAMPLE PREPARATION:

4. Samples may be characterized by one of the following methods, as appropriate.
   a. **Interference check.** Prepare area dust sample or settled dust bulk sample for XRD analysis by mounting the collection sample directly on an XRD sample holder, or by depositing or redepositing the dust on another filter for mounting, or by packing an XRD powder holder. Proceed to step 11.
   b. **Qualitative Analysis.** Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust particle size. Wet sieve with a 10-µm sieve, 2-propanol, and an ultrasonic bath [13], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a desiccator. Deposit the end product on a filter (steps 7-8) or pack in a conventional XRD powder holder.
      NOTE 1: For quantitative determination of % SiO_2, weigh out, in triplicate, 2 mg sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.
      NOTE 2: In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be carefully treated in hot phosphoric acid [14] to dissolve the interfering compound(s) and avoid the loss of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD.
5. Use one of the following methods to prepare filter samples and blanks:
   a. **Low Temperature Ashing:** Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or
   b. **Muffle Furnace Ashing:**
      i. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of $CaSiO_3$. Remove the calcite by the following procedure: Place a 0.5-µm, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold, and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and

5 mL 2-propanol to the filter funnel and allow to stand for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.

ii. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or

c. **Filter Dissolution:** Using forceps and a spatula, remove the filter from the cassette, fold the filter three times, and place in the bottom of a 40- or 50-mL centrifuge tube. Add 10 mL THF and allow to stand for at least 5 min. Cap the centrifuge tube with aluminum foil to prevent contamination. Gently agitate the centrifuge tube by hand or with a vortex mixer making sure the THF does not go near the top of the tube. Place the tube in an ultrasonic bath (water level 2.5 cm from top) for at least 10 min. (The filter should be totally dissolved.) Just prior to filtering, agitate the sample for 10 to 20 sec on a vortex mixer. Continue with step 6, substituting THF for 2-propanol and centrifuge tube for beaker.

6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.

7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel. After the transfer, rinse the beaker several times and add rinsings to the funnel for a total volume of 20 mL. In order to minimize feathering of the sample outside the deposition area, allow the suspension to settle for a few minutes prior to applying vacuum. Do not rinse the chimney after the material has been deposited on the silver filter. Rinsing the chimney can disturb the thin layer deposition.

8. Leave the vacuum on after filtration to produce a dry filter. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the Teflon sheet which has been heated on the hot plate at a low temperature setting. When thoroughly dry, mount the silver filter in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze at least 6 levels of standard filters.

NOTE 1: Calibration standards are limited to NIST and USGS certified standards of known purity, particle size, and sample-to-sample homogeneity. At least 12 materials, including 5-µm Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none have been found to be acceptable alternatives to the certified standards cited within this method [10]. Standard reference materials should be corrected for phase purity.

NOTE 2: Crystalline silica methods require calibration standards of known purity, specific particle size and distribution, and sample-to-sample homogeneity. Establishing traceability of secondary calibration standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used in the industrial hygiene field can provide. In addition, particle size distribution measurements have considerable error. Therefore, the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.

NOTE 3: NIST SRM 2950 calibration set (α-quartz) and NIST SRM 2960 calibration set (cristobalite) may be useful for preparing working standards at known concentrations.

a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.

b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the bottle to a magnetic stirrer with thermally insulated top and add a stirring bar. Allow the solution to return to room temperature before withdrawing aliquots.

c. Mount a silver filter on the filtration apparatus. Place several mL of 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the stopper and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.

d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several times.

e. Allow the suspension to settle for a few minutes prior to applying vacuum. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the heated Teflon sheet. When thoroughly dry, mount the silver filter in the XRD sample holder. Prepare working standard filters, in triplicate, at e.g., 10, 20, 50, 100, 250, and 500 µg.

f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x^o and are then normalized (step 12.e) to obtain $\hat{I}_x^o$. Correct the intensities of working standards >200 µg for matrix absorption (steps 12.f and 13).

g. Prepare a calibration graph ($\hat{I}_x^o$, vs µg of each standard).

NOTE: Poor repeatability (>10% above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.

h. Determine the slope, m, of the calibration graph in counts/µg. The intercept, b, on the abscissa should be within ± 5 µg of zero.

NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.

10. NOTE: The following procedure for absorption correction is not necessary in situations that have been previously documented as requiring no corrections.

Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry, and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}$, for each media blank (step 12.g). Obtain an average value for the six media blanks, $\hat{I}_{Ag}^o$.

NOTE: The analyst is a critical part of this analytical procedure [12]. A high level of analyst expertise is required to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase [15]. The analyst should have some training (university or short course) in mineralogy or crystallography in order to have a background in crystal structure, diffraction patterns and mineral transformation. In addition, an intensive short course in the fundamentals of X-ray diffraction can be useful.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 °2θ) of the area air sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The diffraction peaks are:

Mineral	Peak (2-Theta Degrees)		
	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

NOTE: There is an alternative to scanning an area air sample, settled dust sample, or ground bulk sample to prove lack of contamination. A slow scan of the three main peaks of quartz (also cristobalite and tridymite if their absence has not been previously confirmed) on a personal air sample, with verification that their intensity ratios are within 15% of pure quartz, is sufficient evidence that other materials are not interfering in the silica determination.

12. Perform the following for each sample, working standard, and blank filter:
    a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (S_r <0.01) measured.
    b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

    f. Determine the normalized count, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Field blanks may be analyzed by scanning the 2-theta range used for the analyte and silver peaks to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blank. Each laboratory should determine the specifics of field blank use for its application. When contamination does occur, the reason should be investigated and appropriate action taken. In practice, contamination of field blanks is extremely rare and usually is not consistent across filters. The analysis of blanks may be abbreviated if experience indicates that contamination is not likely with current field and laboratory operations; however, occasional confirmation of non-contamination is prudent.

CALCULATIONS:

13. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(t) - b}{m \cdot V}, mg / m^3$$

$\hat{I}_x$ = normalized intensity for sample peak
b = intercept of calibration graph ($\hat{I}_x^o$ vs. µg)
m = slope of calibration graph, counts/µg
f(t) = $-R \ln T/(1 - T^R)$ = absorption correction factor (Table 1)

$R = \sin(\Theta_{Ag})/\sin(\Theta_x)$
$T = \hat{i}_{Ag}/(\text{average } \hat{I}^{o}_{Ag})$ = transmittance of sample
$\hat{i}_{Ag}$ = normalized silver peak intensity from sample
$\hat{I}^{o}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and ultrasonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [14] and when all standards and samples were Min-U-Sil 5. The relative standard deviations (S_r) for intralaboratory, total measurement and overall (including sampling) variability are:

	Analyte Level (µg)	Measurement Precision (S_r)	Overall Precision (S_{rT})
Intralaboratory	50-200	0.08 [1]	
	20	0.20 [5]	
	10	0.28 [9]	
Total (intra- and interlaboratory)	50-200	0.17 [1]	0.29 [1]

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METHOD REVISED BY:

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APPENDIX: INTERFERENCES

Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide.

The patterns for three forms of aluminum phosphate [JCPDS 10-423, 11-500, 20-44] are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite, if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-Williams [20] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations [16-21].

		f(T) (at indicated degrees 2-θ)							
Transmittance	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
1.00		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99		1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98		1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97		1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96		1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95		1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94		1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0635
0.93		1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92		1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91		1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90		1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89		1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88		1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87		1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86		1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85		1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84		1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83		1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82		1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81		1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80		1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79		1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78		1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77		1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76		1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75		1.2175	1.2535	1.2822	1.3297	1.2672	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3456	1.2806	1.3278	1.2849	1.3328
0.73		1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72		1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71		1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70		1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69		1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68		1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67		1.3103	1.3682	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66		1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65		1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64		1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63		1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62		1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61		1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60		1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995
0.59		1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58		1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57		1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56		1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55		1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54		1.4991	1.6858	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53		1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52		1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51		1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50		1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531

SILICA, AMORPHOUS 7501

SiO_2 MW: 60.08 CAS: Table 1 RTECS: Table 1

METHOD: 7501, Issue 3	EVALUATION: PARTIAL	Issue 1: 15 May 1985 Issue 3: 15 March 2003

OSHA:	Table 1	**PROPERTIES:**	solid; d 2.2 g/mL; MP >1600 °C
NIOSH:	Table 1		
ACGIH:	Table 1		

SYNONYMS: fumed amorphous silica (Aerosil, silica aerogel, silicic anhydride); fused amorphous silica (Cab-o-sil, colloidal silica, xerogel, diatomaceous earth); hydrated amorphous silica (Hi-sil).

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (Total) or CYCLONE + FILTER (Respirable) (10-mm cyclone, nylon or Higgins-Dewell + 5-µm PVC membrane)	**TECHNIQUE:**	X-RAY POWDER DIFFRACTION
		ANALYTE:	Cristobalite
FLOW RATE:	Total: 1 to 3 L/min Nylon cyclone: 1.7 L/min HD cyclone: 2.2 L/min	**ASH:**	Llow temperature plasma; acid wash; deposit on PVC filter
		XRD ANALYSIS:	XRD for quartz, cristobalite and tridymite before and after heating
VOL-MIN:	50 L		
-MAX:	400 L @ 5 mg/m³ (limit to ≤ 2 mg dust on filter).	**HEAT:**	1500 °C, 2 h (fumed amorphous silica) or 1100 °C, 6 h (other amorphous silica); redeposit on Ag filter
SHIPMENT:	Routine		
SAMPLE STABILITY:	Stable indefinitely	**CALIBRATION:**	Standard suspensions of amorphous silica in 2-propanol, converted to cristobalite as for samples
BLANKS:	2 to 10 field blanks per set	**RANGE:**	0.2 to 2 mg per sample
BULK SAMPLE:	High volume area air sample required	**ESTIMATED LOD:**	0.005 mg per sample
		PRECISION ($\hat{S}_r$):	0.10 @ 0.4 to 5 mg; 0.33 @ 0.2 mg [1]

ACCURACY

RANGE STUDIED:	Not studied
BIAS:	Not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	Not determined
ACCURACY:	Not determined

APPLICABILITY: This method is specific for amorphous silica in crystalline (e.g., quartz) matrices in the range 1 to 10 mg/m³ for a 200-L air sample. Amorphous silica usually contains some crystalline silica [2]. See also discussion of crystalline silica in Chapter R of this volume [3].

INTERFERENCES: Albite, ammonium phosphate and tridymite interfere with the largest peak of cristobalite. Quartz and cristobalite are quantitated prior to heat treatment and subtracted from the final quantity of cristobalite. Alkali and alkaline earth oxide prevent 100% conversion; these are removed by acid-wash prior to heat treatment. XRD signal intensity is proportional to particle size; similar particle size of samples and standards is desirable.

OTHER METHODS: This method makes improvements in sample handling and quality assurance to P&CAM 316, which it replaces [4,5]. The XRD analysis steps are similar to those in Method 7500 (Silica, crystalline).

REAGENTS:

1. Amorphous silica standard appropriate to the air sample, i.e., one of the following:
   a. fumed amorphous silica, grade CAB-O-SIL® M-5, available from Cabot Corp.; www.cabot-corp.com;
   b. gelled amorphous silica, grade Britesorb® D300 xerogel, available from The PQ Corp., PO Box 840, Valley Forge, PA 19482-0840; www.pqcorp.com;
   c. diatomaceous earth amorphous silica, grade Celite 521, available from Fisher Scientific; www.fishersci.com;
   d. precipitated amorphous silica, grade Zeothix® 265, available from J.M. Huber Corp.; www.hubermaterials.com.

   NOTE 1: Some gelled or precipitated amorphous silicas contain up to 7% moisture. Dry all amorphous samples overnight at 115 °C [5].

   NOTE 2: XRD signal intensity is proportional to particle size. Sieve the standards (10-µm sieve), if necessary, to match the particle size expected in the samples
2. 2-Propanol, reagent grade.
3. Water, deionized.
4. Sodium chloride, reagent grade.
5. Hydrochloric acid, 2% (v/v). Dilute 20 mL conc. HCl to 1L with deionized water.
6. Desiccant.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Total dust: 37-mm diameter, 5.0-µm pore size, polyvinyl chloride filter (MSA, Gelman GLA-5000, or equivalent) supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.

      NOTE: Gelman VM-1 and Millipore BS filters are unacceptable because of high ash or amorphous silica content.
   b. Respirable dust: PVC filter (1.a. above) plus cyclone, 10-mm nylon or Higgins-Dewell (HD), with sampling head holder. Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
   c. Area sample: PVC filter (1.a. above) at 3 L/min.
2. Personal sampling pumps 1 to 3 L/min (total or area); 1.7 L/min (nylon cyclone) or 2.2 L/min (HD cyclone).
3. Filters, PVC, 25-mm diameter, 0.45-µm pore size.
4. Filters, silver membrane, 25-mm diameter, 0.45-µm pore size, available from Sterlitech Corp., 22027 70th Ave S, Kent, WA 98032-1911; www.sterlitech.com.
5. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
6. Glue or tape for securing Ag filters to XRD holders.
7. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
8. Low temperature plasma asher (LTA) or muffle furnace.
9. Filtration apparatus with side-arm vacuum flask and 25- and 37-mm filter holders.
10. Sieve, 10-µm pore size, for wet sieving.
11. Furnace capable of maintaining 1100 °C for 6 h or 1500 °C for 2 h and of temperature programming to 500 °C at 50 °C/min.
12. Crucibles, platinum, with covers.
13. Analytical balance (0.01 mg).
14. Stirrer, magnetic, with thermally-insulated top.
15. Ultrasonic bath or probe.
16. Pipets, 2-to 25-mL.

EQUIPMENT - cont.:

17. Volumetric flasks, 1-L.
18. Desiccator.
19. Bottle, 1-L, with ground glass stopper.
20. Drying oven.
21. Wash bottle, polyethylene.
22. Mortar and pestle, agate.
23. Rubber policeman.
24. Beakers, 100-mL, with watchglass covers.

SPECIAL PRECAUTIONS: 2-Propanol is flammable. Hydrochloric acid is corrosive and should be handled in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1 to 3 L/min (total and area), 1.7 L/min (nylon cyclone) or 2.2 L/min (HD) for a total sample size of 50 to 400 L.
   NOTE 1: Do not allow the cyclone to be inverted at any time. Turning the cyclone to anything other than a horizontal orientation may deposit over-sized material from the cyclone body onto the filter.
   NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found to be optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [6]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [3].

SAMPLE PREPARATION:

3. Ash the sample filter in a 100-mL beaker in the LTA according to manufacturer's instructions. After ashing, carefully (so as to avoid loss of sample) add 50 mL 2% HCl to each beaker.
4. Cover the beaker with a watchglass. Agitate in an ultrasonic bath for at least 3 min (until the agglomerated particles are broken up). Wash the underside of the watchglass with distilled water, collecting the washings in the same beaker.
5. Place a 25-mm PVC filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL deionized water onto the filter. Pour the sample suspension from the beaker into the funnel, and apply vacuum. After the transfer, rinse the beaker several times with deionized water and add rinsings to funnel for a total volume of 20 mL. Allow the suspension to settle for a few minutes prior to filtration. Do not wash the chimney walls or add deionized water to the chimney after filtration has begun. Rinsing the chimney can disturb the thin layer deposition. When filtration is complete, keep vacuum on until filter is dry. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

6. Weigh ca. 100 mg dried amorphous silica to the nearest 0.01 mg. Quantitatively transfer to a 1-L bottle using 1.00 L 2-propanol. The resulting concentration is 100 µg/mL.
7. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the 1-L bottle to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
8. Prepare a series of standard filters, in triplicate, over the range 0.005 to 2 mg per sample.
   a. Mount a 37-mm PVC filter on the filtration apparatus. Place several mL 2-propanol on the filter. Turn off the stirrer and shake the bottle vigorously by hand. Immediately remove the stopper and withdraw an aliquot (e.g., 2 to 25 mL) by pipet from the center at half-height of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   b. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
   c. Allow the suspension to settle for a few minutes prior to applying vacuum. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposition is in place since this will rearrange the material on the filter. Leave vacuum on until the filter is dry. When thoroughly dry, mount the filter in the XRD sample holder.
9. Prepare and analyze standard filters exactly like samples.
   a. Ash in LTA; redeposit on 25-mm PVC filters (steps 3 through 5).
   b. Analyze by XRD (step 13).
   c. Heat to convert amorphous silica to cristobalite; redeposit on Ag filters (steps 14 through 16).
   d. Analyze by XRD (step 17).
10. Prepare calibration graph ($\hat{I}_x^\circ$ vs. µg of standard).
    NOTE: Poor repeatability (i.e., $S_r > 0.1$) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/S^2$ weighing) is preferable. Curvature can be eliminated with absorption corrections (step 20) [7].
11. Select six silver membrane filters to be analyzed as media blanks. Make the selection randomly from the same box of filters used for redepositing samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine net normalized intensity for the silver peak, $\hat{I}_{Ag}$, for each media blank. Obtain an average value fro the six media blanks, $\hat{I}_{Ag}^\circ$.
    NOTE: The analyst is a critical part of this analytical procedure [3]. A high level of analyst expertise is required in order to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase. XRD analysts should have some training (university or short course) in mineralogy or crystallography in order to have a background in crystal structure, diffraction patterns and mineral transformation. In addition, an intensive short course in the fundamentals of X-ray diffraction can be useful.

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 °2θ) of the bulk (high-volume respirable) sample to determine the presence of free silica polymorphs and interferences. The diffraction peaks are:

Mineral	Peak (2-Theta Degrees)		
	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

NOTE: For quantitative determination of amorphous silica in bulk samples, wet-sieve a portion of the bulk sample through a 10-µm sieve with 2-propanol in an ultrasonic bath. Evaporate the alcohol and dry in an oven 2 h. Weigh out, in triplicate, 2-mg portions of the sieved dust and transfer to beakers. Add 10 mL 2-propanol, deposit on a PVC filter (step 5) and continue with steps 13 through 17.

13. Perform the following for each sample, working standard and blank filter.
    a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (S_r <0.01) measured.
    b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

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 complete (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 normalized count, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.

CALCULATIONS:

18. Calculate the concentration of amorphous silica, C (mg/m^3), as the difference in cristobalite concentrations measured before and after heat treatment in the air volume sampled, V (L):

$$C = \frac{\frac{\hat{I}'_x - b}{m} f(t) - \frac{\hat{I}_x - b}{m}}{V}, mg/m^3$$

$\hat{I}'_x$ = normalized intensity for cristobalite sample peak on the Ag filter (step 17.a)
$\hat{I}_x$ = normalized intensity for cristobalite sample peak on the PVC filter before heating (step 13)
b = intercept of calibration graph ($\hat{I}^o_x$ vs. µg)
m = slope of calibration graph, counts/µg
f(t) = $-R \ln T/(1 - T^R)$ = absorption correction factor (Table 2)
R = $\sin(\Theta_{Ag})/\sin(\Theta_x)$
T = $\hat{I}_{Ag}/(\text{average } \hat{I}^o_{Ag})$ = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample (step 17.b)
$\hat{I}^o_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: Compute the applicable OSHA standard using the formulae in Table 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 [4,5] 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 [8], 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 ($S_r = \pm 6.6\%$).
4. Comparing the four slopes to a slope of a pure respirable cristobalite material, they were running approximately 30% lower in slope value. Therefore, field samples of amorphous silicas must be compared only to standards prepared from amorphous silicas.
5. Precision studies at 0.2-, 1-, and 2.5-mg levels (six samples per level) of gelled, precipitated, diatomaceous earth, and fumed silicas indicated a pooled precision, $\bar{S}_r$, of 8.8, 10.5, 5.6, and 21.5%, respectively, for the above silicas.
6. Recovery studies of the same silicas and concentration levels indicated average recoveries of 82, 115, 95, and 111%, respectively, with pooled $\bar{S}_r$ equal to 18.2, 13.1, 12.9, and 15.3%, respectively, for the gelled, precipitated, and fumed silicas, and diatomaceous earth.

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METHOD REVISED BY:

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TABLE 1. CAS Numbers, RTECS Numbers, and Exposure Limits for Amorphorous Silica Forms

Amorphous Forms	CAS#	RTECS	OSHA PEL (mg/m^3)	NIOSH PEL (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	69012-64-2 112945-52-5	VV310000	80/% SiO_2		2 (respir)
fused	60676-86-0	VV7328000			0.1 (respir)

Table 2. MATRIX ABSORPTION CORRECTION FACTORS FOR CRISTOBALITE (HEAT-CONVERTED AMORPHOUS SILICA) AND SILVER PEAKS.

	Degrees 2-Θ					
Cristobalite		21.93	21.93		21.93	21.93
Silver		38.12	44.28		38.12	44.28
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2806	1.3278
	0.99	1.0087	1.0100	0.73	1.2944	1.3440
	0.98	1.0174	1.0201	0.72	1.3084	1.3605
	0.97	1.0264	1.0305	0.71	1.3226	1.3774
	0.96	1.0355	1.0410	0.70	1.3372	1.3946
	0.95	1.0447	1.0517	0.69	1.3521	1.4122
	0.94	1.0541	1.0625	0.68	1.3673	1.4303
	0.93	1.0636	1.0736	0.67	1.3829	1.4487
	0.92	1.0733	1.0849	0.66	1.3987	1.4675
	0.91	1.0831	1.0963	0.65	1.4150	1.4868
	0.90	1.0932	1.1080	0.64	1.4316	1.5064
	0.89	1.1034	1.1199	0.63	1.4485	1.5266
	0.88	1.1137	1.1320	0.62	1.4659	1.5472
	0.87	1.1243	1.1443	0.61	1.4836	1.5684
	0.86	1.1350	1.1568	0.60	1.5018	1.5900
	0.85	1.1460	1.1696	0.59	1.5204	1.6122
	0.84	1.1571	1.1827	0.58	1.5394	1.6349
	0.83	1.1685	1.1959	0.57	1.5590	1.6582
	0.82	1.1800	1.2095	0.56	1.5790	1.6820
	0.81	1.1918	1.2232	0.55	1.5995	1.7065
	0.80	1.2038	1.2373	0.54	1.6205	1.7317
	0.79	1.2160	1.2516	0.53	1.6421	1.7575
	0.78	1.2284	1.2663	0.52	1.6642	1.7840
	0.77	1.2411	1.2812	0.51	1.6870	1.8112
	0.76	1.2540	1.2964	0.50	1.7103	1.8391
	0.75	1.2672	1.3199			

SILICA, CRYSTALLINE, by VIS 7601

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
14464-46-1 (cristobalite) VV7325000 (cristobalite)
15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7601, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
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OSHA: quartz (respirable) 10 mg/m³/(%SiO_2+2); cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m³; carcinogens
ACGIH: quartz (respirable) 0.1 mg/m³
cristobalite (respirable) 0.05 mg/m³
tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; d 2.65 g/cm³; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm cyclone, nylon or Higgins-Dewell (HD) + 0.8-µm MCE or 5-µm PVC)

FLOW RATE: HD cyclone: 2.2 L/min; nylon cyclone: 1.7 L/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied

BIAS: None known

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: Silicon complexes-silicomolybdate (420 nm) and molybdenum blue (820 nm)

DIGESTION: Phosphoric acid, to remove interfering silicon compounds

FILTRATION: To collect undigested material

DISSOLUTION: Crystalline silica in HF

CALIBRATION: NIST SRM 1878a quartz, NIST 1879a cristobalite, USGS 210-75-0043 dissolved in HF

RANGE: Silicomolybdate: 0.1 to 2.5 mg SiO_2; molybdenum blue: 0.02 to 0.15 mg SiO_2

ESTIMATED LOD: 10 µg SiO_2

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

APPLICABILITY: Determination of crystalline silica in respirable or total dust, settled dust and in biological samples [1,2]. The three crystalline polymorphs cannot be distinguished by this method. The working range is 0.04 to 5 mg/m³ for a 500-L air sample. Alternative XRD (e.g. NMAM 7500) and IR (e.g. NMAM 7602 and 7603) methods have better laboratory-to-laboratory agreement than visible absorption methods and therefore this method is recommended for research use only [3]. See also discussion of crystalline silica in Chapter R of this volume [4].

INTERFERENCES: Any silicon-containing compound which is soluble in HF will give a positive interference. See APPENDIX A.

OTHER METHODS: This is P&CAM 106 in a revised format [1]. X-ray diffraction (XRD; Method 7500) can distinguish the three main silica polymorphs and does not detect amorphous silica. Silicates interfere with XRD but are removed by phosphoric acid cleanup. Infrared spectrometry (IR; Methods 7602 and 7603) can determine the three polymorphs, although if two or more are present, a less sensitive peak must be used; however, amorphous silica and silicates, in large amounts, interfere with IR.

REAGENTS:

1. Silica Standards.
   a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, RM. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899; www.nist.gov.
   b. Tridymite* (210-75-0043), available from U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.
2. Hydrofluoric acid, 48% (HF).*
3. Orthophosphoric acid, 85% H_3PO_4.*
4. Silica-free water. All water used must be deionized and stored in polyethylene containers.
5. Hydrochloric acid (HCl),* 1:10 v/v conc. HCl in deionized water.
6. Sulfuric acid, 10 N.* Cautiously add 555 mL conc. H_2SO_4 to about 1.3 L of deionized water. Cool. Dilute to 2 L.
7. Nitric acid, conc.*
8. Perchloric acid, conc*. Use only if samples have been collected on PVC filters.
9. Boric acid solution, 5%. 200 g boric acid crystals in 4 L warm deionized water. Cool. Filter with vacuum through a 0.45-µm membrane filter. Store in a polyethylene container.
10. Molybdate reagent. Dissolve 50 g ammonium molybdate tetrahydrate in about 400 mL deionized water. Add 50 mL conc. sulfuric acid. Cool. Dilute to 500 mL. Store in dark.
11. Reducing solution. Dissolve 9 g sodium bisulfite in 80 mL deionized water. In 10 mL deionized water, dissolve 0.7 g anhydrous sodium sulfite and 0.15 g 1-amino-2-naphthol-4-sulfonic acid, in that order. Combine these solutions and dilute to 100 mL with deionized water. Stable about one month if stored in refrigerator.
12. Silica stock standard, 0.5 mg/mL. Dissolve 250 mg quartz in 10 mL 48% HF. Dilute to 500 mL with silica-free water. Store in a polyethylene container. Stable indefinitely.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter: Mixed cellulose ester (MCE) filter, 37-mm, 0.8-µm, or polyvinyl chloride (PVC) filter, 37-mm, 5.0-µm pore size, supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
      NOTE: If PVC filters are used, a perchloric acid fume hood, low-temperature radio-frequency plasma asher or muffle furnace will be needed to ash them (Appendix B).
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD).
   c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area Air Sampler: PVC membrane filter, 37-mm, 5-µm pore size in a two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Precision heater, 550-watt, 115-V, Type RH; 750-watt variable transformer with built-in voltmeter; variable speed clinical rotator, about 30 to 80 rpm range (can be achieved with a variable transformer).
5. Stopwatch or laboratory timer.
6. Phillips beakers, borosilicate glass, 250-mL; short-stemmed glass funnels with bent stems (must be done by laboratory); crucible tongs with tygon or rubber-padded tips; polyethylene stirring rods; polyethylene 50-mm discs.
7. Vacuum filtration assembly: MCE membrane filters, 0.45-µm pore size, 47-mm diameter; filter funnel, including membrane mount and flask assembly, 47-mm.
8. Buret, polypropylene, 10-mL; polyethylene reagent bottles for water, boric acid, and standard solutions.
9. Constant temperature bath, 40 °C.
10. Spectrophotometer, at 420 to 820 nm and 1-cm cuvettes.
11. Hotplate, 150 °C surface temperature.
12. Graduated cylinder or graduated pipet, 10- and 25-mL.
13. Polyethylene graduated cylinder or pipets, 25- and 5-mL.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [5]. Use personal protective equipment to prevent contact of acids with the skin. HF dissolves glass. Use plastic labware for all solutions containing HF. Concentrated acids are corrosive.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 2.2 ± 5% L/min with HD cyclone and 1.7 ± 5% L/min with nylon cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything other than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [6]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [5,7]

SAMPLE PREPARATION:

NOTE: Successful use of this method depends on close attention to details and uniformity in sample handling procedures.

3. Place a weighed sample containing no more than 2.5 mg SiO_2, or a membrane filter sample, in a 250-mL Phillips beaker. Add 3 to 4 mL conc. HNO_3 to ash membrane filters. Heat on a hotplate to absence of brown fumes.
4. Add an additional 2 mL conc. HNO_3 and heat to dryness. Repeat this step until any remaining residue is white.
   NOTE: Ash PVC filters using 2 mL conc. $HClO_4$. Heat slowly until the filter shrinks, turns brown and is dissolved. Add additional portions of $HClO_4$ if necessary. If a perchloric acid hood is not available, see APPENDIX B for alternate ashing procedures for PVC filters. Pretreatment procedures to remove various contaminants from bulk samples are outlined in reference [7].
5. Add 25 mL 85% H_3PO_4 to the beaker. Cover the beaker with a bent-stem funnel. Make sure that the tip of the funnel stem touches the wall of the flask. Start reagent blanks at this time.
   NOTE: The bent-stem funnel is used to prevent too rapid dehydration of the sample and to prevent spattering.
6. Place the 550-watt heater on the rotator in a fume hood. Preheat the heater and adjust to maintain a temperature of 240°C. Heat each sample and blank for exactly 8 min, swirling it by the action of the variable speed rotator.
   NOTE: The solution in the flask should reach 240°C during this procedure.
7. Remove the beaker from the heater with padded tongs and swirl it for 1 min. Allow the beaker to cool. Add about 125 mL warm (60 to 70°C) deionized water and swirl to mix completely.
8. Filter the sample with suction through a 47-mm filter. Wash thoroughly with 1:10 HCl.
9. Place the 47-mm filter in the bottom of a 150-mL polyethylene beaker. Add 0.5 mL 48% HF to the filter surface. Float a thin polyethylene disc of about 50-mm diameter over the 47-mm filter and cover the beaker. Allow to stand for 30 min.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a calibration graph for the silico-molybdate range.
    a. Dilute 1-, 2-, 3-, 4-, 5- and 6-mL aliquots of the silica stock standard (NIST SRM 1878a quartz) to 25 mL with silica-free water in polyethylene beakers.
    b. Analyze together with samples and blanks (steps 14 through 16).
    c. Plot absorbance vs. mg SiO_2.
11. Prepare a calibration graph in the molybdenum blue range.
    a. Dilute the working standards in step 10 1:25.
    b. Analyze the resulting standard solutions (steps 14 through 16).
    c. Plot absorbance vs. mg SiO_2.
12. Prepare control samples containing a silicate compound (about 50 mg $MgSiO_4$ sample) in addition to the quartz. Recovery of quartz is low and precision is much worse if quartz only is present during the phosphoric acid treatment.

    NOTE 1: Calibration standards are limited to specified NIST and USGS certified standards of known purity, particle size and sample-to-sample homogeneity. At least 12 materials including 5 µm Min-U-Sil previously used by laboratories throughout the United States and Canada have been evaluated. None have been found to be acceptable alternatives to the certified standards cited within this method [3]. Standard reference materials should be corrected for phase purity.

    NOTE 2: Crystalline silica methods require standards of known purity, specific particle size distribution, and sample-to-sample homogeneity. Establishing traceability of secondary standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used within the industrial hygiene field. In addition, particle size distribution measurements have considerable error. Therefore the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.

    NOTE 3: Some training (university or short course) in geology or mineralogy of the analyst or laboratory management is useful to provide a background in crystal structure and mineral transformation in order to answer the questions that laboratory clients may have and to understand any matrix effects.

MEASUREMENT:

13. Add 25 mL silica-free water to samples in polyethylene beakers.
14. Add 50 mL boric acid solution. Stir well. Cover. Heat the solution in a 40 °C waterbath for 10 min.
15. Add 4 mL molybdate reagent while stirring, staggering the addition at 2-min intervals between samples. Exactly 20 min after the addition of the molybdate reagent, add 20 mL 10 N H_2SO_4 and stir thoroughly.
16. Note the color of the solution.
    b. If a colorless solution results, allow it to stand for 2 to 5 min and add 1 mL 1-amino-2-naphthol-4-sulfonic acid reagent. Mix and read after 20 min at 820 nm against deionized water. This color is stable for several hours.
    c. Record the absorbances of the sample, A, and reagent blank, B.

CALCULATIONS:

17. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L), using the slope, m (μg^{-1}) of the appropriate calibration graph:

$$C = \frac{(A - B)}{m \cdot V}$$

EVALUATION OF METHOD:

This method is based on the well-characterized Talvitie method [1,8,9,10].

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METHOD REVISED BY:

Issue 1: Jensen Groff, NIOSH/DART

Issue 2: Rosa Key-Schwartz, Ph.D. and Paul Schlecht, NIOSH/DART.

APPENDIX A:

INTERFERENCES

Some silicates may be resistant to phosphoric acid digestion [8]. Any silicates not removed by the phosphoric acid treatment will give a positive interference. Amorphous silica, if not completely removed by phosphoric acid treatment, will give a positive interference. Phosphate ion complexes molybdic acid to produce a yellow phosphomolybdate color which is dissipated by lowering the pH of the solution with 10 N sulfuric acid. Excess ferric ion (more than 1 mg) will consume the reducing agent and inhibit the reduction of silicomolybdate to molybdenum blue. If more than 1 mg ferric ion is present, it should be removed by pretreatment with 10:1 HCl:HNO_3.

APPENDIX B:

ALTERNATE ASHING PROCEDURES FOR PVC FILTERS
If a perchloric acid fume hood is unavailable, ash PVC filters with one of the following methods.

1. **Muffle furnace ashing:** Wash the filters with 25% v/v HCl if the samples contain a significant amount of calcite (20% of the total dust loading); otherwise, proceed to next paragraph. Place a 0.5-µm, 47-mm PVC filter in the filtration apparatus. Center the sample filter on top of the first filter. Clamp the filter funnel over the frit so that the dust deposit is completely exposed. Add 10 mL HCl solution and 5 mL 2-propanol to the filter funnel; allow to stand for 5 min. Apply vacuum to aspirate the acid/alcohol solution from the filter. Wash with three 10-mL portions of deionized water. Release the vacuum.

   Place the filter samples in porcelain crucibles, cover loosely and ash in a muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL of 2-propanol to the ash, scrape the crucible to loosen all particles and transfer the residue to a 250-mL borosilicate glass Phillips beaker. Wash crucible several times and add wash to the beaker. Heat on a sparkless hotplate to evaporate the 2-propanol. When beaker is dry, proceed with step 4 of sample preparation.

2. **Low temperature ashing:** Place the filters in 50-mL glass beakers within the LTA so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, add 2-propanol to the beaker to transfer the residue to a 250-mL borosilicate Phillips beaker. Wash the beaker with 2-propanol several times, adding the washings to the Phillips beaker. Heat on a sparkless hotplate to remove the 2-propanol. When the beaker is dry, proceed to step 4 of sample preparation.

SILICA, CRYSTALLINE by IR (KBr pellet) 7602

SiO_2	MW: 60.08	CAS:14808-60-7	RTECS: VV7330000 (quartz)
		14464-46-1	VV7325000 (cristobalite)
		15468-32-3	VV335000 (tridymite)

METHOD: 7602, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 3: 15 March 2003

OSHA : quartz (respirable): 10 mg/ m^3 / (% SiO_2 + 2); cristobalite and tridymite (respirable): 1/2 the above
NIOSH: 0.05 mg/m^3 ; carcinogens
ACGIH: quartz (respirable) 0.1 mg/m^3 cristobalite and tridymite (respirable) 0.05 mg/m_3

PROPERTIES: solid; d 2.65 g/cm^3; crystalline transformation: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER: CYCLONE + FILTER (10-mm nylon or Higgins-Dewell (HD), and PVC filter, 37-mm, 5-µm) *see sampling section

FLOW RATE: Nylon cyclone: 1.7L/min
HD cyclone: 2.2 L/min

VOL-MIN: 400 L
-MAX: 800 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: High volume or settled dust to identify interferences

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: INFRARED ABSORPTION SPECTROPHOTOMETRY

ANALYTE: Quartz

ASH: Muffle furnace of RF plasma asher

PELLET: Mix residue with KBr; press 13-mm pellet

IR: Scan absorbance from 1000 to 600 cm^{-1}

CALIBRATION: NIST SRM 1878a quartz, NIST SRM 1879a cristobalite, USGS 210-75-0043 tridymite diluted in KBr

RANGE: 10 to 160 µg quartz

ESTIMATED LOD: 5 µg quartz

PRECISION ($\hat{S}_r$): < 0.15 @ 30 µg quartz per sample, in coal dust [1]

APPLICABILITY: The working range is 0.025 to 0.4 mg/m^3 for a 400-L air sample. Cristobalite and tridymite also have major absorbance peaks at 800 cm^{-1} which can be used for their determination [1-6]. IR methods can quantify quartz, cristobalite and tridymite if amorphous silica and silicates are not present in large amounts. However, sensitivity is reduced if multiple polymorphs are present and secondary peaks must be used. A potential for bias exists when correcting for matrix absorption effects, with an increasing risk of bias at lower quartz concentrations. See also discussion of crystalline silica in Chapter R of this volume [7].

INTERFERENCES: Amorphous silica, calcite, cristobalite, kaolinite and tridymite interfere; see APPENDIX.

OTHER METHODS: This is P&CAM 110 in a revised format [1]. It is similar to Method 7603, except for sample preparation (KBr pellet vs. redeposition). XRD (method 7500) can distinguish the three silica polymorphs and silica interferences can be eliminiated by phosphoric acid treatment. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., method 7601), but polymorphs cannot be distinguished. Visible absorption methods also have larger laboratory-to-laboratory variability than XRD and IR methods and therefore are recommended for research use only [8].

REAGENTS:

1. Silica Standards.
   a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, Rm 204, Bldg. 202, National Institute of Standards and Technology, Gaithersburg, MD 20899; www.nist.gov.
   b. Tridymite* (210-75-0043), available from U.S. Geological Survey, PO Box 25046, MS 973, Denver, CO 80225.
2. Potassium bromide (KBr), infrared quality.
3. Ethanol, 95% for cleaning sample handling equipment.*
4. Hydrochloric acid, 9% w/w.* Add 25 mL conc. HCl (37% w/w) to 70 mL with deionized water, cool, and bring to 100mL with deionized water.
5. Calibration stock standard, 0.5% w/w. Accurately weigh and thoroughly mix 5 g KBr (dried overnight at 110 °C) with 25 mg quartz. Store in a bottle in a desiccator.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Filter: 37-mm diameter, 5.0-µm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
   b. Cyclone: 10-mm nylon or Higgins-Dewell (HD).
   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-faced at 3 L/min.
3. Sampling pumps for HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/ min; and area sampler, 3 L/min.
4. Infrared spectrophotometer; laboratory press for preparing KBr pellets; 13-mm KBr pellet die (evacuable).
5. Low-temperature (RF Plasma) asher and aluminum weighing pan or muffle furnace and porcelain crucibles.
6. Mortar and pestle, 50-mm agate or mullite metal microspatula; non-serrate, non-magnetic forceps; desiccator, camel's hair brush, glassine paper.
7. Analytical balance (0.001 mg) for preparing standards.
8. Membrane filtration apparatus, 37-mm.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [9]. Ethanol is flammable. Keep away from flames. Use personal protective equipment to prevent contact of acids with the skin. Concentrated acids are corrosive.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with nylon cyclone, 2.2 ± 5% with HD cyclone, or 2.5 ± 5% with Al cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg total dust loading on the filter.
   NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
   NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is

currently used in the United States for the purpose of matching an earlier sampling convention [10]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [7].

SAMPLE PREPARATION:

3. Use one of the following methods to ash samples and blanks:
   a. Low temperature (RF Plasma) asher: Place the filters in labelled aluminum dishes (previously rinsed with distilled water, followed by ethanol, and air dried). Place the dishes in the low temperature asher so that sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. Carefully bring asher to atmospheric pressure and remove the dishes.
   b. Muffle furnace: For samples containing a significant amount of calcite (> 20% of the total dust loading), wash filters with 9% w/w hydrochloric aicd. Other samples proceed to step 3.b.ii.
      i. Place a 0.5-µm, 47-mm PVC filter in the filtration apparatus. Remove sample filter from cassette and center on top of first filter. Clamp funnel over the frit so that dust deposit is completely exposed. Add 10 mL 9% w/w HCl and 5 mL 2-propanol; allow to stand 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Wash with three successive 10-mL portions of distilled water. Release vacuum.
      ii. Place filter samples and blanks in porcelain crucibles, loosely cover, and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present).
4. Add approximately 300 mg KBr, weighed to 0.1 mg and dried overnight at 110 °C, directly to each sample. Mix the sample ash and KBr thoroughly with a pestle. Transfer to mortar to complete mixing if necessary. Transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Press a pellet using standard technique. Weigh the finished pellet to 0.1 mg. Calculate the ratio (weight of finished pellet/weight KBr initially added); it is usually about 0.98. Clean sample handling equipment with ethanol between samples.
   NOTE: A low relative humidity environment will facilitate sample handling when using KBr.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least 5 working standard pellets:
   NOTE 1: Calibration standards are limited to NIST and USGS certified standards of known purity, particle size, and sample-to-sample homogeneity. At least 12 materials, including 5 µm Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none has been found to be an acceptable alternative to the certified standards cited within this method [7]. Standard reference materials should be corrected for phase purity.
   NOTE 2: Establishing traceability of secondary calibration standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used in the industrial hygiene field can provide. In addition, particle size distribution measurements have considerable error. Therefore, the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.
   a. Weigh, to 0.001 mg, portions of NIST α-quartz SRM 1878a, NIST cristobalite SRM 1879a, USGS tridymite 210-75-00473 containing 10 to 200 µg standard.
   b. Add an accurately-weighed 300 mg KBr portion. Proceed as in step 4.
   c. Calculate the ratio (weight of finished pellet/weight of solids added); usually about 0.98.
   d. Determine the absorbance at 800 cm^{-1} for each standard pellet following the analytical procedure (step 8). Plot absorbances vs. µg SiO_2.
6. If samples were low temperature ashed (step 3.a.) and kaolinite is present, prepare pellets containing 100 to 600 µg kaolinite. Determine the absorbance at 800 cm^{-1} and at 915 cm^{-1} as abscissa. Prepare at least five different kaolinite concentrations. Use this curve to correct the absorbance value at 800 cm^{-1} for any sample containing kaolinite.
7. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures (steps 3 and 4) to monitor for contamination and losses.

NOTE: Some training (university or short course) in geology or mineralogy can be useful for the analyst and/or laboratory management. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret crystal structure, matrix interferences and mineral transformation for the laboratory client.

MEASUREMENT:

8. Set the infrared spectrophotometer to absorbance mode and to the appropriate settings for quantitative analysis. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1}. Rotate the pellet 45° and scan this diameter. Repeat twice more until 4 scans have been obtained. If the peak at 800 cm^{-1} is small, use 5X ordinate expansion to enhance the peak height. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1}. Measure the absorbance at 800 cm^{-1} from maximum to baseline in absorbance units. Average the four values for each sample.
9. If the sample was ashed at low temperature (step 3.a), the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw an appropriate baseline under this band from approximately 960 to 860 cm^{-1} and measure the absorbance at 915 cm^{-1} from this baseline to the maximum.

CALCULATIONS:

10. To correct for kaolinite, determine the sample absorbance at 915 cm^{-1} (step 9) and refer to the kaolinite curve (step 6) to find the absorbance at 800 cm^{-1}. Use this corrected value in step 11.
11. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} to find the weight of quartz, W_q (µg), from the calibration graph.
12. Calculate the concentration of silica, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{W_q}{V}, mg / m^3$$

13. If percent quartz, % Q, is required, divide the weight of quartz, W_q (µg), by the total sample weight, W_s (µg):

$$\%Q = \frac{W_q}{W_s} \cdot 100$$

EVALUATION OF METHOD:

This method is based on the well-characterized infrared method [1]. This method is particle size dependent. A mismatch of standards and sample particle sizes will result in an uncorrectable bias. Only NIST-certified standard reference materials (SRM) 1878a and 1879a and USGS 210-75-0043 have been found to have sufficient purity, sample-to-sample homogeneity in crystalline silica content and particle size necessary to ensure that results are similar to results obtained by other laboratories using other methods. A thorough study of the range of biases in IR methods has not been done.

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APPENDIX A:

INTERFERENCES

Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm^{-1} (quartz) and 625 cm^{-1} (cristobalite). Tridymite can only be determined in the absence of the other two polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [2].

Cristobalite and tridymite interfere positively at the 800 cm^{-1} peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.

Quartz is a common component of soil, rocks, sand, mortar, cement, fluxes, abrasives, glass, porcelain, paints and brick. Cristobalite is less common and found in volcanic rocks and soils, and can be formed in high temperature processes such as foundry processes, calcining diatomaceous earth, brick manufacturing, ceramic manufacturing and silicon carbide production. Tridymite is rarely encountered, but is present in some volcanic rocks and soils.

APPENDIX B:

DETERMINATION OF QUARTZ IN BULK SAMPLES

Additional equipment needed: Drying oven
Wilks Mini-Press, or other pellet press
Min-U-Sil 30

1. Homogenize the sample if necessary (e.g., by grinding using a large mortar and pestle) and dry it (e.g., in a vacuum oven at 110 °C for 2-4 hours).
2. Using a small aluminum weighing boat and a six-place analytical balance, weigh out 0.1 to 1 mg of the sample. The amount weighed out should contain a quantity of quartz which will produce an absorbance which is measurable, but which is not greater than about 0.9.
   NOTE: The weighed amount of sample and the amount of KBr (step 3) are specified for the Wilks Mini-press, which produces pellets approximately 8 mm in diameter. Adjust the amounts appropriately if another pellet press is used.
3. Quantitatively transfer the weighed sample to a small mortar and grind it thoroughly. Add between 75 and 100 mg dry KBr and mix it thoroughly with the ground sample.
4. Quantitatively transfer the mixture to the pellet press. Press the pellet according to the manufacturer's instructions.
   NOTE: Weighing paper and a camel's hair brush are helpful in making the transfer.
5. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1}, using a blank KBr pellet as background. Rotate the pellet 90 degrees and obtain another spectrum. Measure and record the mean peak absorbance at 798 cm^{-1} for the sample.
6. Calibration and Quality Control.
   a. Prepare calibration standards, using dry Min-U-Sil 30, in exactly the same manner as samples (steps 2-5) and plot peak absorbance vs. micrograms SiO_2.
   b. Analyze bulk sample of known quartz content and prepare a control chart of recovery for use with subsequent analyses.

1,1,2,2-TETRACHLOROETHANE 2562

$Cl_2CHCHCl_2$ MW: 167.85 CAS: 79-34-5 RTECS: KI8575000

METHOD: 2562, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: 5 ppm (skin)
NIOSH: 1 ppm; carcinogen; Group I Pesticide
ACGIH: 1 ppm

(1 ppm = 6.86 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.586 g/mL @ 25 °C; BP 146.5 °C; MP -44 °C; VP 0.8 kPa (6 mm Hg; 0.8% v/v) @ 25 °C; nonflammable

SYNONYMS: acetylene tetrachloride; bonoform; 1,1-dichloro-2,2-dichloroethane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb CMS; 100/50 mg)

FLOW RATE: 0.01-0.2 L/min

VOL-MIN: 3 L @ 5 ppm
-MAX: 30 L

SHIPMENT: Routine

SAMPLE STABILITY: 28 days at 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,2,2-tetrachloroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 40 °C (1 min), 10 °C/min to 175 °C

CARRIER GAS: He, 2.8 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID, 1.0-µm film, 100% dimethyl polysiloxane or equivalent

CALIBRATION: Standard solutions of analyte in CS_2

RANGE: 2.1 to 285.5 µg per sample [1]

ESTIMATED LOD: 0.6 µg per sample [1]

PRECISION ($\hat{S}_r$): 1.6% @ 38.1 to 253.8 µg per sample [1]

APPLICABILITY: The working range is 0.031 to 4.17 ppm (0.21 to 28.6 mg/m^3) for a 10-L air sample [1].

INTERFERENCES: Any compound with a similar retention time under these analytical conditions is considered to be an interference.

OTHER METHODS: This method updates NIOSH Method 1019 [2] through the use of a capillary column, incorporation of Anasorb CMS sorbent tubes, and lowered sampling and analytical range with accompanying lower LOD/LOQ values [1].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,2,2-Tetrachloroethane, reagent grade.*
3. Desorption efficiency (DE) stock solution, 12.7 mg/mL. Dilute 80 µL of 1,1,2,2-tetrachloroethane to 10 mL with CS_2.
4. Helium, purified
5. Hydrogen, prepurified
6. Air, filtered, compressed

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, glass-sealed ends with plastic caps, containing two sections of 100/50 Anasorb CMS (front = 100 mg; back = 50 mg) separated by a 2-mm glass wool plug. Another glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. (SKC 226-121, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column.
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-µL, readable to 0.1 µL, 25-µL, readable to 0.5 µL, and 1000-µL, readable to 1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: 1,1,2,2-Tetrachloroethane is a powerful narcotic, liver poison, and suspected carcinogen, and can be absorbed through the skin [3, 4]. Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = - 30 °C). Work with these substances only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 3 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10x the LOQ.
   a. Add a specific amount of 1,1,2,2-tetrachloroethane to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 1,1,2,2-tetrachloroethane concentrations in the range needed. Additional standards may be added to extend the calibration curve, if necessary.
   b. Analyze with calibration standards, samples, and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg 1,1,2,2-tetrachloroethane).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 25 µL) of DE stock solution, or a serial dilution thereof, directly onto the front sorbent section with a microliter syringe.

c. Cap the tube. Allow to stand for 24 hours.
d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. µg 1,1,2,2-tetrachloroethane recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are within the limits set by the quality assurance policy and are consistent with the results given in the section entitled "Evaluation of Method".

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2562-1. Inject sample aliquot manually using solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of 1,1,2,2-tetrachloroethane found in the sample front (W_f) and back (W_b) sorbent sections and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of 1,1,2,2-tetrachloroethane in the air volume sampled, V (L):

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

NMAM 1019, Issue 1 and Issue 2:

The 4th edition Method 1019 is 2nd edition NMAM Method S124 in the 4th edition format . Method S124 was issued on May 9, 1975 [5], and validated with generated atmospheres which were calibrated by gas chromatography [6]. Average recovery was 106% at 5 ppm. Breakthrough did not occur after sampling 4 h at 0.185 L/min from an atmosphere containing 101 mg/m^3 in dry air. Desorption efficiency for SKC Lot 104 petroleum-based charcoal was 0.83, 0.87, and 0.88 at 160, 320, and 640 µg 1,1,2,2-tetrachloroethane per sample, respectively. Lower recoveries were observed for coconut shell charcoal (SKC Lot 105). In subsequent work, 1,1,2,2-tetrachloroethane was observed to degrade rapidly into trichloroethylene during storage on Pittsburgh activated carbon: 19% converted during one day and 63% converted during eight days at ambient conditions [7]. Therefore, the analyte is sensitive to the sorbent type; only the recommended sorbent should be used. Breakthrough at high relative humidity was not tested, nor was sample stability.

NMAM 2562, Issue 1

Initial work to update the NMAM method 1019 resulted in an average recovery of 88.4% over a range of 38.1 to 253.8 µg from the petroleum charcoal [1]. In order to see if the overall desorption efficiency of 1,1,2,2-tetrachloroethane could be improved at these lower levels, the sorbent was changed from petroleum charcoal to Anasorb CMS. Desorption efficiency using Anasorb CMS (SKC Lot 1879) was 91, 85, 88, and 91% at 38, 76, 165, and 254 µg 1,1,2,2-tetrachloroethane per sample, respectively. The limit of detection was found to be 0.6 µg per sample. A recovery of 87% was obtained at a level of 165 µg after storage for 28 days at ambient conditions [1].

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METHOD WRITTEN BY:

Rebecca A. Bosse and Stephanie M. Pendergrass, NIOSH, DART

TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM CHLORIDE 5046

$P(CH_2OH)_4^+C1^-$ MW: 190.58 CAS: 124-64-1 RTECS: TA2450000

METHOD: 5046, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: None
NIOSH: None
ACGIH: None

PROPERTIES: hygroscopic, air sensitive solid; MP 151 °C; ionic; does not vaporize; soluble in water, methanol; insoluble in diethyl ether

SYNONYMS: tetramethylolphosphonium chloride, tetrahydroxymethylphosphonium chloride, THPC, Pyroset TKC, Proban CC, Retardol C, NCI-C55061, Tolcide THPC

SAMPLING

SAMPLER: 37-mm filter cassette (open-faced cassette containing two glass fiber filters coated with acidified 2,4-dinitrophenylhydrazine)

FLOW RATE: 1.0 to 1.7 L/min

VOL-MIN: 1 L @ 6.5 mg/m^3
-MAX: 480 L @ 0.15 mg/m^3

SHIPMENT: Ship on ice (0 °C).

SAMPLE STABILITY: 28 days @ 5 °C [1]

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

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC; UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone of formaldehyde

EXTRACTION: 4 mL acetonitrile; 60 °C, 1 hour

INJECTION VOLUME: 20 µL

MOBILE PHASE: 45:55 acetonitrile:water @ 1.3 mL/min

COLUMN: 3.9 x 150 mm stainless steel, packed with 5-µm C-18, Symmetry™ or equivalent

DETECTOR: UV @ 360 nm

CALIBRATION: DNPH-coated glass fiber filters fortified with THPC (media standards)

RANGE: 6.5 to 60 µg/sample (instrumental)[1]

ESTIMATED LOD: 2 µg/sample

PRECISION (S_r): 0.0585 for 8 to 31 µg per sample

APPLICABILITY: The theoretical working range is 0.43 to about 67 mg/m^3 for a 15-L air sample. This method may be applicable to other tetrakis(hydroxymethyl)phosphonium salts, such as the sulfate. However, evaluation of this method has been limited to THPC.

INTERFERENCES: Formaldehyde gas is an interference. Concentrations of THPC can be corrected for formaldehyde gas by sampling for formaldehyde gas with NMAM 2016 [2]. Ozone has been observed to consume DNPH and to degrade the DNPH derivative of formaldehyde [3]. However, use of an ozone scrubber is not recommended because this scrubber may trap THPC aerosol. Ketones and other aldehydes can react with DNPH; the derivatives produced, however, are separated chromatographically from the analyte of interest.

OTHER METHODS: Other methods for THPC in air are unknown. A microanalytical method for tetrakis(hydroxymethyl) phosphonium salts in solution involves ion chromatography, post-column reaction with an acetylacetone reagent to form a formaldehyde derivative, and detection at 425 nm [4].

REAGENTS:

1. Formaldehyde-2,4-dinitrophenylhydrazone, (formaldehyde-DNPH), 99% pure, Supelco, Bellefonte, PA, or Aldrich Chemical Co., Milwaukee, WI.
2. Tetrakis(hydroxymethyl)phosphonium chloride (THPC),* 80% aqueous solution. Aldrich Chemical Co., Milwaukee, WI.
   NOTE: Ascertain the correct percentage in solution by performing an assay [potentiometric titration of 0.22 g of 80% THPC solution (diluted with DI water and acidified with 10 mL of 25% sulfuric acid) with 0.1 *M* $AgNO_3$ and silver electrode] [1,8]. Density of 80% ± 2% aqueous solution: 1.30 to 1.40 g/mL @ 20 °C.
3. Acetonitrile,* high purity solvent for HPLC analysis, low carbonyl content.
   NOTE: Carbonyl content of acetonitrile can be determined by passing 10 mL of the solvent through a commerically available cartridge containing silica gel coated with acidified DNPH and analyzing for formaldehyde-DNPH by HPLC. The concentration of formaldehyde-DNPH should be below the LOD. [2]
4. Water, deionized (DI water).
5. Calibration stock solution. Accurately weigh 10 mg of formaldehyde-DNPH in a 10-mL volumetric flask. Add acetonitrile to the 10-mL mark.
6. Fortification stock solution, 10 mg/mL. Add 140 µL of 80% solution of THPC to 14.86 g of DI water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Samplers, 37-mm, three-piece, plastic cassettes containing two glass fiber filters, a front filter and a backup filter, separated by 1 cm of space by means of a center cassette piece (spacer). Each filter is coated with 2 mg of acidified 2,4-dinitrophenylhydrazine (commercially available from SKC, Eighty Four, PA, as glutaraldehyde sampler, catalogue number 225-9003.*
2. Personal sampling pump, 1.0 to 1.7 L/min, with flexible connecting tubing.
3. Vials, 4-mL, glass, PTFE-lined rubber septa in caps for airtight seals.
4. Liquid chromatograph with UV detector, recorder, integrator, and column (p. 5046-1).
5. Syringes, 100-µL, 500-µL, and 10-mL.
6. Volumetric flasks, 25-mL, 10-mL.
7. Water bath, 60 °C ± 3 °C.
8. Syringe filters, PTFE membrane, 0.45-µm porosity.
9. Forceps.
10. Equipment for NMAM 2016, Issue 2, for formaldehyde gas [2].

SPECIAL PRECAUTIONS: On heating, THPC will decompose to form chlorine, ammonia, and oxides of phosphorus. Avoid high temperatures for THPC and contact with alkalies or strong oxidizing agents. THPC causes eye burns and moderate skin irritation. Dermal studies have shown that tetrakis(hydroxymethyl)phosphonium salts are promotors of skin cancer but not initiators. There was no evidence of carcinogenicity of THPC in rats and mice [4]. The liver is a target organ.

DNPH is a suspect carcinogen and is light sensitive [7]. 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 at the desired sampling rate.
2. Remove inlet cassette piece from sampler for open-faced sampling. Remove cap from outlet of sampler. Open-faced sampling is recommended because excessive quantities of THPC will exhaust the quantity of DNPH in a small area of the filter during closed-face sampling.
3. Attach sampler to the sampling pump with flexible tubing.

4. In a similar fashion, prepare DNPH-coated silica gel samples for air sampling of formaldehyde gas [2]. NOTE: A frit or filter can be added in the inlet to trap THPC aerosol and separate the THPC from the formaldehyde gas. However, since the necessity of the frit or filter has not been determined, its use is optional.
5. Sample 1 to 480 liters of air at 1.0 to 1.7 L/min for THPC.
6. Conduct side-by-side air sampling for formaldehyde gas for the same period of time. Sample at 0.5 to 1.5 L/min for formaldehyde gas by NMAM 2016 [2].
7. Replace inlet cassette piece on the THPC sampler. Cap the outlet of the THPC sampler. Protect THPC samples from heat.
8. Place end caps onto the formaldehyde sampler and seal sampler in an envelope. Protect formaldehyde samples from heat.
9. Ship THPC and formaldehyde samples in separate containers on ice (0 °C).

SAMPLE PREPARATION:

10. Fold the front and back DNPH-coated filters using 2 pairs of forceps and place into separate 4-mL vials. Avoid finger contact.
11. Add 4.00 mL of carbonyl-free acetonitrile to each vial. Cap the vials tightly.
12. Place vials in water bath at 60 °C for 1 hour.
13. Remove vials from water bath and allow to cool to room temperature.
14. Filter the sample solutions with syringe filters. Collect filtrates in separate autosampler vials. Cap the autosampler vials.
    NOTE: Follow NMAM 2016, Issue 2, for the analysis of formaldehyde gas samples [2].

CALIBRATION AND QUALITY CONTROL:

15. Calibrate daily with at least six working (media) standards over the range of interest.
    a. Prepare a series of aqueous THPC solutions for fortification of blank DNPH-coated filters (media blanks) by dilution of THPC fortification stock solution (item 6) with DI water. Suggested concentrations of THPC in solution include 400 and 800 µg/mL. Media blanks and coated filters for actual air sampling should be from the same lot and should be handled and stored in the same manner.
    b. Place folded filters in 4-mL vials and fortify with known quantities of THPC solution in the range of 20 to 80 µL.
    c. Prepare the media standards (steps 11-14) and analyze (steps 17-19).
    d. Prepare a calibration graph (peak area or height vs. µg THPC per sample).
16. Determine percent yield of formaldehyde from THPC in the calibration range (step 15) at least once.
    a. Calculate the concentration of formaldehyde-DNPH derivative in the calibration stock solution (about 1000 µg/mL). Calculate the equivalent concentration of free formaldehyde in solution by multiplying the derivative concentration by 0.143 (molecular weight of formaldehyde divided by the molecular weight of formaldhyde-DNPH).
    b. Prepare a series of dilutions [working standards (liquid standards)] from 0.02 to about 1 µg/mL.
    c. Prepare six samples at the same level by fortifying six DNPH-coated filters with a known quantity of THPC (step 15).
    d. Analyze samples (steps 17-19).
    e. Calculate the molar quantity of formaldehyde found in each sample.
    f. Calculate the molar quantity of THPC applied to each DNPH-coated filter.
    g. Consider that one mole of THPC releases one mole of formaldehyde in the presence of DNPH. Calculate the percent yield of formaldehyde (yield should be 100%).

MEASUREMENT:

17. Set the liquid chromatograph according to manufacturer's recommendations and to conditions given on page 5046-1.
18. Inject a 20-µL aliquot of filtered sample solution.
19. Measure peak height or peak area. If sample peak is larger than the largest standard peak, dilute an

aliquot of the remaining sample solution, reanalyze, and apply appropriate dilution factor in the calculations.

20. To ensure validity of the samples, identify those samples which contain more than 1000 µg of THPC per sample. The capacity of the samplers may have been exceeded for these samples, and collection of smaller samples would be warranted.

CALCULATIONS:

21. Determine mass, µg, of THPC found on the front filter, W_F, on the backup filter, W_B, and on the average media blank, B, from the calibration graph.
22. Calculate concentration, C, of THPC in the air volume sample, V (L). This air concentration of THPC is uncorrected for formaldehyde gas present at the sampling site (if any).

$$C = \frac{W_F + W_B - 2B}{V}, mg/m^3$$

NOTE: µg/L = mg/m^3

23. Calculate the air concentration or average air concentration for formaldehyde gas, C_{form}, in mg/m^3 in side-by-side samples collected according to NMAM 2016 [2] (see steps 4 and 6 of NMAM 5046).
24. Calculate the corrected concentration, C', of THPC (corrected for the concentration of formaldehyde gas in the air). The value of 6.35 is found by dividing the molecular weight of THPC by the molecular weight of formaldehyde.

$$C' = C - 6.35(C_{form}), mg/m^3$$

EVALUATION OF METHOD:

THPC aerosol can be determined by measuring the formaldehyde which is released from THPC in the presence of DNPH and heat. However, formaldehyde gas, if present in the air, will be an interference in the measurement of THPC. This method attempts to measure THPC aerosol by correcting for the presence of formaldehyde gas in the air. The samplers for formaldehyde gas used in NMAM 2016 [2] conceptually would have frits or filters in the inlets to trap THPC aerosol and allow formaldehyde gas to pass through to the beds of DNPH-coated silica gel. However, since the necessity of the frit or filter has not been determined, use of frits or filters is optional. The degree of interference from THPC aerosol in measuring formaldehyde gas by NMAM 2016 has not been determined. This method has not been tested by air sampling for THPC aerosol or by air sampling for formaldehyde gas in a THPC aerosol environment.

This method was evaluated using 37-mm DNPH-coated glass fiber filters in three-piece cassettes and aqueous tetrakis(hydroxymethyl)phosphonium chloride. Average recoveries of 8-, 14-, 20- and 31-µg quantities of THPC from 37-mm DNPH-coated glass fiber filters ranged from 87% to 104% (23 samples, pooled RSD = 5.85%) [1]. Samples of THPC on DNPH-coated filters were stable during storage at 5 °C in the dark; average recoveries of 15.0-µg quantities of THPC from DNPH-coated filters ranged from 108% to 131% after 7 to 28 days of storage at 5 °C (n = 21 samples, RSD = 2.7% to 5.4%) [1].

The limit of detection and lower limit of quantitation of THPC were 2 and 6.5 µg per filter, respectively. These limits were found by least squares calculations based on six DNPH-coated filters fortified with known quantities of THPC.

The possibility of migration of formaldehyde from the front filter to the backup filter during storage at 5 °C in sealed three-piece cassettes was investigated. Front filters in six three-piece cassettes were fortified with 31.4-µg quantities of THPC, and the cassettes were sealed. The six cassettes were stored for 10 days at 5 °C in the dark and then front and backup filters were analyzed. Average recoveries of THPC from front and backup filters were 102% and 11%, respectively (RSDs were 5.7% and 23%, respectively). The average total recovery of THPC from front and backup filters was 113% (RSD = 5.0%). These data provide evidence that (a) formaldehyde from THPC can indeed migrate from one DNPH-coated filter to another and (b) one needs to analyze both the front and backup DNPH-coated filters for THPC in case there is migration.

Yields of formaldehyde from THPC were determined in order to study the stoichiometry of the breakdown of THPC. DNPH-coated glass fiber filters in 4-mL vials were fortified with known quantities of THPC at four levels (n = 23 samples). The samples were treated with acetonitrile and heat by the usual procedure and analyzed with liquid standards (standard solutions of formaldehyde-DNPH in acetonitrile). Theoretical quantities of formaldehyde were calculated on the basis that one mole of THPC releases one mole of formaldehyde in the presence of DNPH and heat. The average of the four average yields of formaldehyde was 100.3%.

The upper limit for collection of THPC on a filter is calculated at 1 mg. Since at 100% yield one mole of THPC releases one mole of formaldehyde in the presence of DNPH and heat, 1 mg of THPC would release 158 µg of formaldehyde, a quantity which theoretically would react with 1.04 mg of DNPH. One DNPH-coated filter contains 2 mg of DNPH, a quantity which allows for the presence of excess DNPH when 1 mg of THPC is collected.

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METHOD DEVELOPED BY:

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THIOPHANATE-METHYL IN AIR 5606

$C_{12}H_{14}N_4O_4S_2$ MW: 342.40 CAS: 23564-05-8 RTECS: BA3675000

METHOD: 5606, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: N/A
NIOSH: N/A
ACGIH: N/A

PROPERTIES: Colorless prisms, MP 181.5-182.5°, soluble in acetone, methanol, chloroform, acetonitrile, slightly soluble in other organics, insoluble in water

NAMES & SYNONYMS: Topsin-M; [1,2-phenylenebis(iminocarbonothioyl)]bisdimethyl ester carbamic acid

SAMPLING

SAMPLER: FILTER/SOLID SORBENT TUBE (OVS-2 Tube: 11 mm quartz fiber filter; XAD-2, 270 mg/140 mg)

FLOW RATE: 0.1 L/min - 1 L/min

VOL-MIN: 20 L @ 0.1 L/min [See Evaluation of Method, Note 1.]

-MAX: 480 L

SHIPMENT: 4°C

SAMPLE STABILITY: at least 28 days at 4°C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not determined

BIAS: Not determined

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

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC, UV detector

ANALYTE: Thiophanate-methyl

EXTRACTION: 2 mL 40% isopropanol:60% acetonitrile

INJECTION VOLUME: 5 µL

MOBILE PHASE: A=2% n-propanol in water, 0.02 M TEA-PO_4, pH adjusted to 7.0 +/- 0.1 using phosphoric acid
B=2% n-propanol in acetonitrile
Gradient from 20% B to 70% B (20 min.), decreasing to 20% B (2 min.), hold at 20% B (5 min.)

COLUMN: Reversed phase C-18, 4 µ, 250 x 2.00 mm (or equivalent).

DETECTOR: UV @200 nm [See Evaluation of Method, Note 2.]

CALIBRATION: Solutions prepared in extraction solvent

RANGE: 5-650 µg/sample

ESTIMATED LOD: 0.76 µg/sample

PRECISION ($\bar{S}_r$): 0.0318

APPLICABILITY: This method was developed for the determination of thiophanate-methyl in air samples for a fungicide field study of orchard workers, and was meant to be used in conjunction with NMAM 5601 for the determination of carbendazim and captan as well. Recoveries of thiophanate-methyl may be lower when carbendazim, thiophanate-methyl, and captan are present in the same sample due to chemical interactions. The working range for this method is 0.025-5.67 mg/m based on a 100 L sample.

INTERFERENCES: Potential interferences to the analysis of thiophanate-methyl include other organic compounds, in particular other pesticides or fungicides that have the same retention time on a C18 column. Positive identification may be confirmed by dual column chromatography using an appropriate alternative LC column. **NOTE:** It is possible to see a peak at the retention time for carbendazim, 9.8 minutes, since carbendazim is a decomposition product of thiophanate-methyl.

OTHER METHODS: This method is based in part on NMAM 5601 [1] for the development work. As such, several of the compounds listed in NMAM 5601can also be analyzed in conjunction with thiophanate-methyl using this method.

REAGENTS:

1. Isopropanol*, HPLC grade.
2. Acetonitrile*, HPLC grade.
3. Triethylamine (TEA)*, HPLC grade.
4. Water, deionized
5. Ortho-phosphoric acid*, >85% by weight, ACS grade or better grade.
6. Extraction solvent: 40% isopropanol / 60% acetonitrile (v/v).
7. Thiophanate-methyl stock solution, 10 mg/mL. Prepare in acetonitrile and store in refrigerator.
8. TEA-PO_4 Preservative. Dissolve 1.4 mL of TEA in 90 mL of deionized water in a 100 mL volumetric flask. Add phosphoric acid to lower pH to 7.0 ± 0.1 as indicated by a calibrated pH meter. Bring volume to 100 mL with water. Keep tightly capped and refrigerated. Solution stable for 12 months.
9. Mobile phase A. Combine 20 mL of n-propanol and 2.8 mL TEA in a 1-L volumetric flask and bring to volume using deionized water. Adjust pH to 7.0 (± 0.1) with phosphoric acid using a pH meter. Final concentrations: 2% n-propanol, 0.02 M TEA-PO_4. Degas prior to use.
10. Mobile phase B. Add 20 mL of n-propanol to acetonitrile in a 1-L volumetric flask and bring to volume with acetonitrile. Degas prior to use.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: OSHA Versatile Sampler (OVS-2 tube), 13 mm OD inlet, 6 mm OD outlet. Front section contains 270 mg 20/60 mesh XAD-2 sorbent held in place by an 11-mm diameter quartz fiber filter and Teflon® ring, separated from the back section of 140 mg XAD-2 sorbent by a short plug of polyurethane foam. The tube is available commercially.
2. Personal sampling pump: 1 L/min with flexible and inert connection tubing.
3. High Performance Liquid Chromatograph (HPLC) with UV detector.
4. Autosampler capable of 5-µL injections.
5. Analytical column: Phenomenex® Synergi™ 4 µ Hydro-RP 80A (250 x 2.00 mm) or equivalent [See Note 3].
6. Vials, 4-mL and 2-mL, glass with PTFE-lined caps.
7. Syringes, 50-µL ,1-mL and 5-mL.
8. Volumetric flasks, 5-mL, 100-mL, and 1-L.
9. Syringe filter, PTFE, 4-mm, 0.45-µm pore.
10. Forceps.
11. Small vial/tube rotator.
12. pH meter.
13. Graduated cylinder, 50-mL.
14. Pipettes, glass, disposable, 2-mL.
15. Funnel, plastic.
16. Bagged refrigerant.

SPECIAL PRECAUTIONS: Thiophanate-methyl: Avoid inhaling vapors or dust; avoid skin contact. Wear gloves and suitable clothing when handling pure material. Solvents: Avoid skin contact and open flame. Use in a hood. Phosphoric acid: Avoid skin contact. See Note 1.

SAMPLING:

1. Calibrate each personal sampling pump with representative sampler in line.
2. Connect the sampler to the personal sampling pump with flexible tubing. Place sampler vertically, with the large end down, in the breathing zone.
3. Sample at an accurately known flow rate between 0.1 and 1 L/min for a total sampling volume of up to 480 L. Record volume, and document presence of any known or potential interferences.
4. Cap both ends of the sampler with plastic caps and pack securely with bagged refrigerant for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end. Transfer PTFE retainer ring, filter, and front XAD-2 resin section to a 4 mL vial. Transfer the polyurethane foam divider plug along with the back-up XAD-2 resin bed to a second 4-mL vial.
6. Add 2 mL of extraction solvent to each vial and cap each vial using a PTFE-lined cap.
7. Mix by rotating the vials end-over-end for approximately one hour.
   NOTE: If this method is being combined with NMAM Method 5601 for Benomyl, then at the end of the mixing period allow the samples to sit at room temperature overnight. This will allow any possible residual benomyl to convert to carbendazim.
8. Filter an aliquot into a 2-mL autosampler vial through a 4-mm, 0.45-µm PTFE filter.

CALIBRATION AND QUALITY CONTROL:

9. Determine retention times for thiophanate-methyl using the column and chromatographic conditions as shown on pages 5606-1. The approximate retention time of thiophanate-methyl using the current chromatographic conditions is 14.1 minutes. (See Figures 1 - 3.)
10. Calibrate daily with at least six working standards covering the working range for thiophanate-methyl.
11. Determine desorption efficiency (DE) for each lot of OVS-2 tubes used for sampling in the calibration range. Prepare three tubes at each of five levels plus three media blanks.
    a. Remove cap and PTFE retainer ring from large end of sampler tube (to prevent wicking behind the ring). Apply known volume of calibration solution to face of quartz filter.
       NOTE: Spike no more than 30 µL at a time. If more must be applied, connect the sampler to a vacuum pump with a flow ≤1 L/min, then apply spiking solution in aliquots of 15-30 µL. Allow 15 minutes for the solvent to evaporate between each aliquot, to prevent wicking along the sides of the tube in the back-up section (5% or more may deposit on the walls of the tube).
    b. Cap and allow to stand a minimum of one hour.
    c. Include an unspiked sampler as a media blank.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 11 and 12).
    e. Prepare a graph of DE vs µg thiophanate-methyl recovered.
12. Prepare analyst spike samples when field samples are received and store them together. Analyze with the field samples, blanks, and the liquid standards.

MEASUREMENT:

13. Set the Liquid Chromatograph according to manufacturer's recommendations. Set the wavelength for detection at 200 nm and flow rate at 0.200 mL/min..
14. Inject a 5-µL sample aliquot with autosampler or sample injection valve.
    NOTE: If peak area of a sample is greater than the area of the highest standard, dilute with extraction solvent and reanalyze. Apply the appropriate dilution factor in the calculations.
15. Measure peak area of the analyte.

CALCULATIONS:

16. Determine the mass, µg, of thiophanate-methyl found in the sampler filter and front sorbent section (W_f), back-up sorbent section (W_b), and the media blank front (B_f) and back-up (B_b) sorbent sections from a standard curve.
17. Calculate concentration, C, of thiophanate-methyl 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 was evaluated with a recovery study over the range of 79.5-567 µg/sample, using spiked laboratory samples, with average recoveries in the range of 89.9-100%. The storage study was completed at 159 µg/sample with recovery averages of 91.6% to 99.8% over the 28 days of the study when the samples were stored at refrigerator temperatures.
Calibration standards have been prepared and evaluated up to a level of 324 µg/ml. This amount equates to 648 µg/sample for field samples.

This method was developed to be used in conjunction with NMAM 5601 for the analysis of thiophanate-methyl, carbendazim, and captan. In laboratory prepared samples, it was found that the recoveries of thiophanate-methyl may decrease and those of carbendazim may increase due to chemical interactions and the decomposition of thiophanate-methyl to carbendazim [2].

NOTES:

1. There are no established RELs or PELs for thiophanate-methyl. A REL of 5 mg/m^3 was assumed for the sampling requirements of this analyte. This method can comfortably measure thiophanate-methyl in solution at 5 µg/ml.

2. Thiophanate-methyl has an ultraviolet absorption maximum at 266 nm that may be a more appropriate wavelength for analysis. However, this method was developed to analyze several other fungicides concurrently with the thiophanate-methyl. One of these analytes has an absorption maximum at 195 - 200 nm, and 200 nanometers was selected as the wavelength of choice for this analysis. If it is known that the only analyte present in the sample is thiophanate-methyl, then it would be more advantageous to use a detector wavelength of 266 nm.

3. The major part of this work was performed on a Phenomenex® KingSorb™ C-18, 5 µm, 250 X 2 mm column. However, a direct replacement column, the Phenomenex® Synergi™, 4 µm, Hydro-RP, 250 X 2 mm column, was suggested by the manufacturer which would provide better separation and resolution. Retention times on the Synergi™ column are similar to those on the KingSorb™ column. (See Figures 1 & 2.) A small adjustment to the mobile phase gradient was all that was required to achieve the same separation and retention time. The Synergi™, Hydro-RP column was also able to resolve carbendazim (another fungicide included in the same overall project) from imidaclorpid, a potential interference in the field samples. The KingSorb™ column was not able to separate these two materials under any conditions that would not severely impact any of the other analytes.

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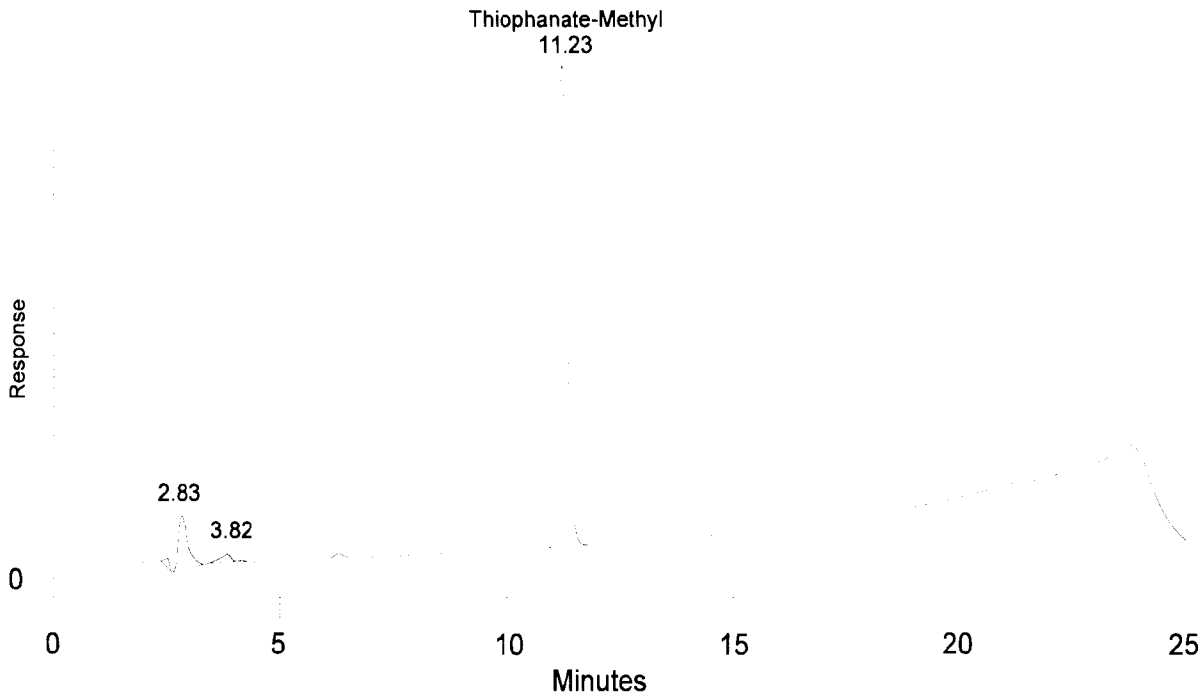

Figure 1. This is a typical chromatogram for a sample of thiophanate-methyl. This shows the response for a spike of 348 µg/sample of thiophanate-methyl on an OVS-2 tube, extracted and analyzed by this LC method using the Kingsorb™ column. On the Synergi™ column, the retention time for thiophanate-methyl is 14.1 minutes.

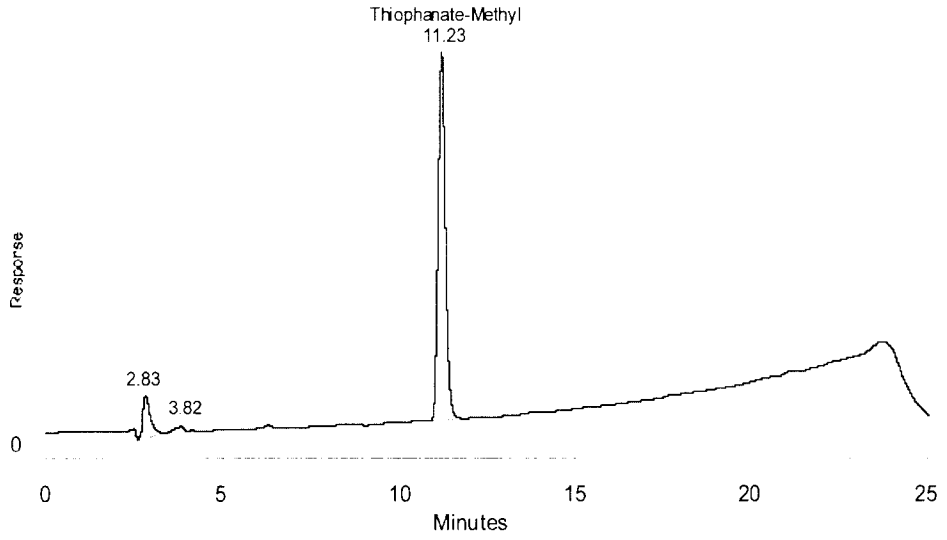

Figure 2. This is a typical chromatogram of a liquid calibration standard. This sample was analyzed with the Kingsorb™ column. The retention time on the Synergi™ column is 14.1 minutes.

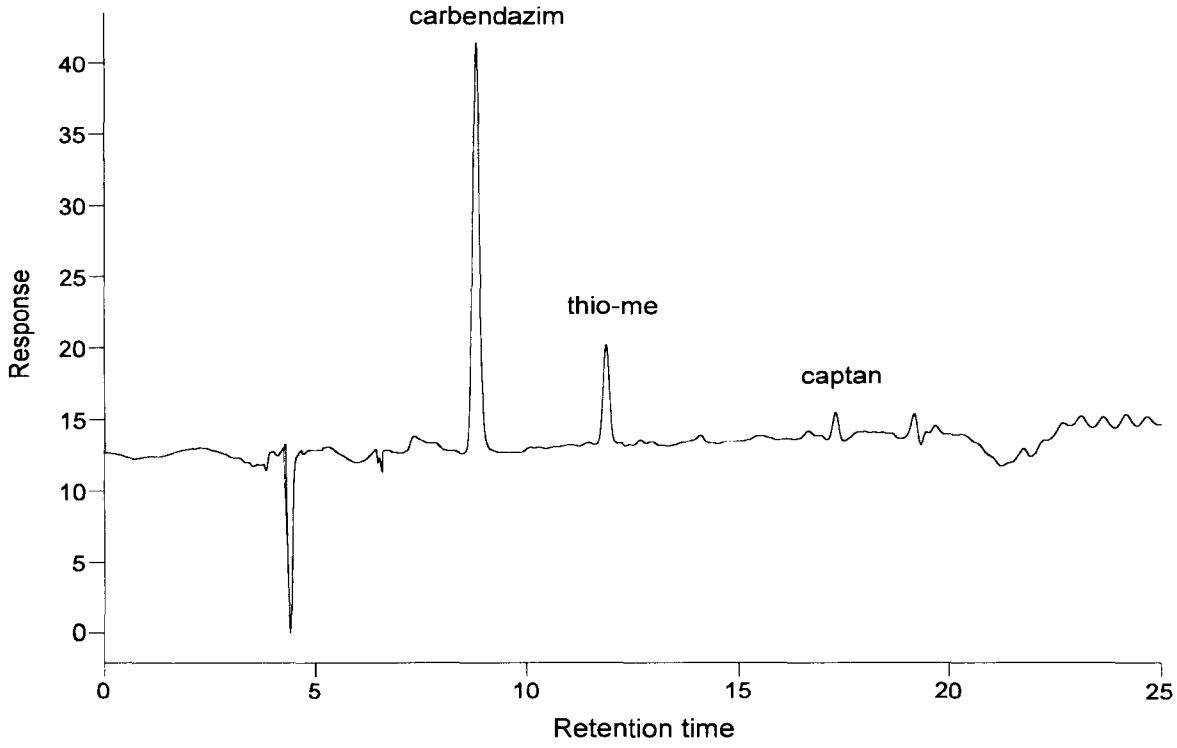

Figure 3. This chromatogram shows the three analytes of interest, carbendazim, thiophanate-methyl and captan, which were extracted from a spiked OVS-2 sampling tube. This chromatogram has been background corrected by subtracting an OVS-2 blank analysis.

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

METHOD: 8315, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

BIOLOGICAL INDICATOR OF: Exposure to triazine herbicides (1) - (4).

SYNONYMS: See TABLE 1

SAMPLING		MEASUREMENT	
SPECIMEN:	Urine	**TECHNIQUE:**	GAS CHROMATOGRAPHY, MASS SELECTIVE DETECTOR
VOLUME:	At least 15 mL of sample	**ANALYTE:**	s-Triazines (1) - (6)
PRESERVATIVE:	None	**EXTRACTION:**	Two liquid/liquid steps
SHIPMENT:	Frozen	**INJECTION VOLUME:**	1 µL
SAMPLE STABILITY:	Not established. Appear to be quite stable frozen for long (> one year) periods of time	**TEMPERATURE**	
		-INJECTION:	280 °C
		-DETECTOR:	285 °C
CONTROLS:	Urine from non-exposed persons.	**-COLUMN:**	50 °C hold for one minute, 50°C/min to 160 °C, 3.5 °C/min to 230 °C, 50°C/min to 280 °C, hold 2 minutes. Total run time, 26.20 min Solvent delay- 5.5 min
		ELECTRON MULTIPLIER VOLTAGE:	+153 mV from tune setting
		CARRIER GAS:	Helium, 1.5 mL/min
		COLUMN:	Capillary, fused silica, 30 m x 0.20-mm ID; 0.20 µm film SPB-5 or equivalent.
		CALIBRATION:	Standard solutions of analytes in ethyl acetate with internal standard.
		RANGE:	LOD to ~1900 nmol/L.
		ESTIMATED LOD:	20 - 47 nmol/L depending on compound
		PRECISION ($\bar{S}_r$):	~20% varies by compound

APPLICABILITY: Triazines are common agricultural herbicides. This method measures the parent compounds and two metabolites simultaneously and specifically. It is applicable to herbicide applicators, farmers, or other occupations with triazine exposure.

INTERFERENCES: None identified.

OTHER METHODS: This method is an adaptation of one published by Catenacci, et al. [2]

REAGENTS:

1. Sodium bicarbonate, Certified grade.
2. Ethyl acetate, HPLC grade.*
3. Ethyl ether, Spectranalyzed grade.*
4. Atrazine.
5. Cyanazine.
6. Propazine.
7. Simazine.
8. Desethyl atrazine.
9. Desisopropyl atrazine.
10. Internal standard solution, Phenanthrene-d_{10}, 100 µg/mL in methanol. Store in refrigerator.
11. Sodium sulfate, anhydrous, Certified ACS grade.
12. Sodium chloride, reagent grade.
13. Helium, zero grade.
14. Nitrogen, zero grade.
15. Methanol, HPLC grade.*
16. Deionized water.
17. A urine pool collected, frozen until use, and then thoroughly mixed

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Gas chromatograph with mass selective detector,SPB-5 or equivalent capillary column and autosampler (page 8315-1).
   NOTE: If large batches of samples are done, chilling the autosampler tray assures that there is no evaporation of the samples
2. Guard column, 1.5 meter x 0.4 mm ID, made of the same material (or SPB-1) as the analytical column and joined by a capillary column butt connector and polyamide/graphite ferrule.
   NOTE: This guard column and the injection port liner should be changed after every 35-40 samples.
3. Analytical balance.
4. Analytical evaporator/manifold fed with nitrogen gas.
5. Centrifuge.
6. "Roto-torque" rotator.
7. Disposable screw-top culture tubes, 16x125 mm, with PTFE-lined caps. NOTE: Caps with rubber liners will not work.
8. Disposable volumetric pipets, 5-mL.
9. Disposable transfer pipets, both short and long.
10. Volumetric flask, 25-mL.
11. Beakers, 50-mL, 5-mL.
12. Disposable centrifuge tubes, 15-mL, with caps.
13. Autosampler vials with 100-µL polypropylene inserts and caps.
14. Syringes, 10-µL and 100-µL.
15. Polypropylene bottles, 30-mL and 250-mL.
16. Disposable filtration columns, 10-mL with 20 µm pore frit.
17. Metal scoopula.
18. Repipet dispenser bottles, 1-L.

SPECIAL PRECAUTIONS: Universal precautions should always be used when dealing with bodily fluids or extracts thereof. Methanol, ethyl ether, and ethyl acetate are all highly flammable; handle with care and use in a hood. Reagents 4-10 come from the manufacturer with expiration dates on them. Be certain to heed these dates.

SAMPLING:

1. Collect the urine in a polyethylene bottle and cap.
2. Ship the sample in dry ice in an insulated container, store at -80°C upon arrival at lab. A reminder: commercial shippers have special labeling requirements for packages containing dry ice.

SAMPLE PREPARATION:

3. Weigh 0.7 g sodium chloride into screw-top culture tubes.
4. Weigh 0.5 g sodium bicarbonate into each of these tubes. Cap these tubes and then they can be stored for at least two weeks and most likely for as long as necessary.
5. Label two culture tubes (one empty and one containing the two salts) and one centrifuge tube with a unique number for each sample.
   NOTE: The labelling system is unimportant as long as there is no danger of the samples being mixed-up and so a record is kept of which sample corresponds to which tube number.
6. Thaw samples to room temperature. Using warm water is okay.
7. Mix thoroughly as urine becomes inhomogeneous upon freezing.
8. Transfer 5 mL of sample to its culture tube containing the salts. Leave the caps off the tubes until samples have been dispensed to every tube and any CO_2 evolved has dispersed.
9. Spin on Roto-torque for about one minute on setting 4 High to dissolve salt. Some salt will remain in the tube.
10. Dispense 5 mL ethyl ether into each of the urine tubes. Again leave caps off or on loosely to allow for gas to disperse.
11. Roto-torque for fifteen minutes on setting 4 High.
12. Centrifuge samples for five minutes at 3000 rpm.
13. Remove ether layer (top) with short transfer pipet to the second labelled culture tube. Remove all the ether; taking some aqueous phase does not appear to be detrimental to the analyses.
14. Dispense 5 mL ethyl acetate into each sample tube containing the remaining aqueous phase.
15. Roto-torque for fifteen minutes on setting 4 High.
16. Centrifuge samples for five minutes at 3000 rpm.
17. Remove organic layer (top) with short transfer pipet and add to the ether layer. Again, remove all the organic layer.
18. Fill the filtration columns about 3/4 full of anhydrous sodium sulfate.
19. Balance the column on top of the labelled 15-mL centrifuge tubes.
20. Using a transfer pipet, transfer the combined extract to the appropriate filtration column.
21. Wash the tube which held the organic phases with one pipetful ethyl ether and add this to the filtration column.
22. Wash the filtration column with another 2 mL ethyl ether.
23. Allow the filtration columns to drain completely.
24. Place the centrifuge tubes in the analytical evaporator and gently evaporate the solvent with a stream of nitrogen until the tube is dry.
    NOTE: A waterbath helps dissipate the cold, but it is important the bath be kept at room temperature. Raising the bath temperature to 30°C may cause marked decreases in the recoveries of analytes (5) and (6) and may well affect the other analytes as well.
25. Rinse the sides of the tubes with about 0.5 mL ethyl ether.
26. Evaporate to dryness again.
27. Add 10 µL internal standard solution to each centrifuge tube.
28. Add 90 µL ethyl acetate to each tube and mix well.
29. Let the extracts sit for at least thirty minutes.
30. Label autosampler vials and place an insert into each vial. Have the caps ready for the vials.
31. Transfer the entire extract to the correct autosampler vial with a long transfer pipet.
32. Cap the vial and place in appropriate tray position in the GC autosampler.

CALIBRATION AND QUALITY CONTROL:

33. The stock solution of the six analytes is prepared from the neat solids to about 240 µmol/L by accurately weighing 1.25 mg of each analyte into a 25 mL volumetric flask (larger flasks could be used with a concomitant increase in the amount of solid weighed out.) Fill the flask to the line with ethyl acetate. It is generally necessary to sonicate the flask for complete and quick dissolution, after which the analytes stay in solution. Aliquot into autosampler vials, cap, and store this solution in the refrigerator. Calculate the exact concentration of each analyte from the amount of solid weighed out. In ethyl acetate these analytes are quite stable for extended periods of time. At no point did degradation of the standard solutions become a problem, so they are stable for at least six months under these conditions.

34. The calibration standards are made the day of the analysis. Allow the stock solution and the internal standard solution to warm to room temperature before performing any pipetting. All the "pipetting" in this step is done using a 100 µL LC syringe. Prepare a diluted standard by adding 10 µL of the stock solution to 440 µL ethyl acetate to make a secondary solution. Prepare seven standards by first pipetting 10 µL of the internal standard solution into marked autosampler inserts/vials. Then add 10, 45, and 90 µL of the diluted standard to three vials and 10, 20, 50, and 90 µL of the stock solution to four of the vials. Make each vial contain 100 µL final volume by adding the correct amounts of ethyl acetate. This will make standards that are about 0.48, 2.4, 4.8, 24, 48, 120, and 216 µmol/L. Calculate the exact concentrations of each analyte in each standard from the stock solution concentrations. Insert these standards into the autosampler batch prepared in Step 32.
35. The two levels of quality control samples were made by adding 75 µL and 250 µL, of the stock solution to 250 mL of the pooled urine. Calculate the exact concentrations of each analyte in each quality control standard from the stock solution concentrations. Run enough QC samples so that they constitute ~10% of the batch and are equally divided between the two levels. Extract 5 mL of each QC (steps 3 through 32) and run with the samples.
36. Prepare calibration curves of Area std/Area IS vs conc std/conc IS for each of the six analytes.

MEASUREMENT:

37. Set gas chromatograph according to manufacturer's recommendations and to conditions on page 8315-1.
38. Set mass selective detector to the following SIM Parameters:

Compounds	Dwell (ms)	Start time*	Ions
Metabolites (5) & (6)	100	5.5	173, 158, 145, 172, 187
Parents (1) - (3)	100	14.1	201, 186, 200, 215, 214, 229
Phenanthrene-d_{10}	100	15.5	188
Cyanazine (4)	100	19.5	172, 225, 240

* These start times may change as necessary, and should be checked regularly, especially after replacing the guard column. A full-scan chromatogram should be performed on a standard to check the retention times and SIM windows.

39. Inject 1 µL ethyl acetate extract from step 32.
40. Measure the peak areas of the samples and internal standard. Divide the peak areas of the sample by the peak area of the internal standard in the same chromatogram. The following ions are used unless the mass selective detector is capable of adding areas of more than one ion:

Desisopropylatrazine	158
Desethylatrazine	172
Simazine	201
Atrazine	200
Propazine	214
Cyanazine	225

CALCULATIONS:

41. Determine the concentration (C_c) of the analytes in the extracts (in µmol/L) from the calibration curves.
42. The concentration (C_u) of the analytes in urine is calculated from the equation:

$$Cu = \frac{Cc}{50} x1000 \ , nmol / L$$

Where 50 is the concentration factorof going from 5 mL urine to 100 µL extracts, and 1000 is the factor for converting µmol/L to nmol/L.

Note: These concentrations could be corrected for creatinine level or sample density if desired and if those values were obtained.

GUIDES TO INTERPRETATION:

One of the limitations of this method is that different parent triazines are metabolized to the same compound. For example, de-alkylation of the isopropyl group on atrazine and cyanazine both give desisopropylatrazine, which can also be formed by the de-alkylation of one of the ethyl groups of simazine. Unless exposure is very high the parent compounds are not found in the urine, leaving the analyst with no way of knowing which parent the metabolite came from in the case of a mixed exposure which is very common in herbicide applicators. The metabolites and any parent compounds found can be summed and reported as total triazine level if desired.

There are very few biological monitoring studies of triazines and their metabolites found in the literature on which to develop a good reference range. And to our knowledge there have been no studies or reports on levels of these analytes in the general population.

1. Catenacci (1990) looking at parent atrazine in the urine found maximum excretion rates of 0.14 - 0.42 nmol/hr in workers at an atrazine manufacturing plant and very poor correlation between the concentration in the urine and the concentration in the air. These excretion rates dropped by an order of magnitude or more within twelve hours of the exposure.
2. Ikonen summed two metabolites (the desisopropyl atrazine and the bi-dealkylated atrazine, the latter of which was not investigated in this study) and found concentrations of 30-110 µmol/L in railway sprayers.
3. Catenacci (1993) returned to the atrazine manufacturing plant with an improved method that could measure all three of the de-alkylated metabolites of atrazine and found ranges of 1.1-1.6 µmol/24 hr for the bi-dealkylated metabolite, 0.13-0.21 for desisopropyl atrazine, 0.11-0.20 for desethyl atrazine, and 0.017-0.021 for parent atrazine. To convert to concentration it is possible to assume an average urinary output of 1.1 L/24 hr (Reference 4). Using that assumption and combining the metabolites gives average concentrations ranging from 1.2 - 1.8 µmol/L.
4. Hines (Reference 5) provides an overview of more recent metabolism studies and results for biomonitoring of the triazines as well as showing the utility of this method (and others) in a study of herbicide applicators.
5. There have been no human studies looking at cyanazine in which to obtain reference ranges of any kind.

EVALUATION OF METHOD:

The method was evaluated using 15 spiked urine samples ranging from 5.8 nmol/L - 1878 nmol/L and analyzing these samples on three different days. The recoveries for s-Triazines for compounds (1-5) ranged from 84-88% and for compound (6) it was 67%. Precisions and LOD were determined from this experiment and are listed on the first page of this method.

Sample stability was not exhaustively examined. There were, however, samples run after several months that had been stored at -20°C compared to splits of those samples stored at -80°C and no bias was found due to the different storage temperatures. This would lead one to believe that the samples would be very stable stored at -80°C for extended periods of time. The QC samples also tell something about sample stability. The first batch of these samples was stored at -20°C and the control chart shows no trend in these samples even when run over 18 months. There may be some loss of signal on samples that go through multiple freeze/thaw cycles, but conclusive experiments were not done and this may be a function of the amount of solids that form in the urine during this process and not because the analytes are breaking down. Because of this, it is a good idea to aliquot the QC samples out into containers that will only be thawed once or twice and then discarded.

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METHOD WRITTEN BY:

Dale A. Shoemaker, Ph.D., NIOSH/DART

TABLE 1. STRUCTURAL FORMULAS, MOLECULAR WEIGHTS, and PROPERTIES

Compound	Formula	Molecular Weight	CAS	RTECS	Synonyms
(1) Atrazine	$C_8H_{14}ClN_5$	215.72	1912-24-9	XY5600000	2-Chloro-4-ethylamino-6-isopropylamino-s-triazine; 2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine; 6-Chloro-N-ethyl-N'-(1- methylethyl)-1,3,5-triazine-2,4- diamine
(2) Simazine	$C_7H_{12}ClN_5$	201.69	122-34-9	XY5250000	2-Chloro-4,6-bis(ethylamino)-s-triazine
(3) Propazine	$C_9H_{16}ClN_5$	229.75	139-40-2	XY5300000	Chloro-4,6-bis(isopropylamino)- s-triazine; 2,4-Bis(isopropylamino)-6- chloro-1,3,5-triazine
(4) Cyanazine	$C_9H_{13}ClN_6$	240.73	21725-46-2	UG1490000	2-Chloro-4-ethylamino-6-(1- cyano-1-methyl)ethylamino-s- triazine; 2-[(4-chloro-6-ethylamino-s- triazin-2-yl)amino]-2- methylproprionitrile
(5) Desethylatrazine	$C_6H_{10}ClN_5$	187.66	6190-65-4		2-Amino-4-chloro-6- isopropylamino-s-triazine; 6-Chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine
(6) Desisopropylatrazine	$C_5H_8ClN_5$	173.67	1007-28-9		2-Amino-4-chloro-6-ethylamino- s-triazine; 6-Chloro-N-ethyl-1,3,5-triazine- 2,4-diamine

TRIPHENYL TIN CHLORIDE (as Sn) 5527

$C_{18}H_{15}ClSn$ MW: 385.46 CAS: 639-58-7 RTECS: WH6860000

METHOD: 5527, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA: 0.1 mg / m^3 as Sn
NIOSH: 0.1 mg / m^3 as Sn (skin)
ACGIH: 0.1 mg / m^3 as Sn

PROPERTIES: solid; MP 108 °C; BP 240 °C

SYNONYMS: Chlorotriphenylstannane, Chlorotriphenyltin, Fentin Chloride, Triphenylchlorostannane, Triphenylchlorotin

SAMPLING

SAMPLER: FILTER (37-mm, 5-µm polyvinyl chloride)

FLOW RATE: 1 to 4 L / min

VOL-MIN: 100 L
-MAX: 2000 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable at ambient temperature for 28 days

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: HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) / INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: Tin

FILTER DESORPTION: 5 mL tropolone/water/methanol (0.02:22:78)

SEPARATION: HPLC, reverse phase; C_{18}, 250 x 4.60-mm, 5-µm, Kingsorb 5 or equivalent

ICP: Operating under conditions for organic compounds.

DETECTOR WAVELENGTH: 189.9 nm

INJECTION VOLUME: 50 µL

CALIBRATION: Standard solutions of triphenyl tin chloride in methanol

RANGE: 10 µg to 225 µg per sample [1]

ESTIMATED LOD: 3 µg per sample (instrumental) [1]

PRECISION ($\bar{S}_r$): 0.034 [1]

APPLICABILITY: The working range of this method is 0.01 to 0.2 mg/m^3 as tin in a 1000 L air sample.

INTERFERENCES: Other organotin compounds with the same retention time as triphenyl tin chloride would interfere.

OTHER METHODS: There are no other NIOSH methods specifically for triphenyl tin chloride. Other organotin compounds have been determined by NIOSH Method 5504 [2] which uses the analytical technique of HPLC-atomic absorption spectroscopy.

REAGENTS:

1. Tropolone (2-Hydroxy-2,4,6-cycloheptatrienone) min. 99% pure.
2. Glacial Acetic Acid, Trace Metal Grade.*
3. Methanol, HPLC Grade.*
4. Triphenyl tin chloride*, 95% pure.
5. Deionized, distilled water.
6. Mobile Phase: 0.020%(w/v)tropolone, 22%(v/v) water, 6.0% (v/v) acetic acid, 72% (v/v) methanol [3].
7. Desorbing solution: 0.020%(w/v)tropolone, 22%(v/v) water, 78% (v/v) methanol.
8. Triphenyl tin chloride standard solution, 200 µg/mL (as tin) with methanol as solvent.
9. Calibration curve solutions: Pipet appropriate amounts of triphenyl tin chloride standard solution into 10-mL volumetric flasks to prepare solutions that are 1, 5, 15, 25, 35, and 45 µg/mL (as tin). Add desorbing solution to the mark.
10. Argon.
11. Oxygen.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: polyvinyl chloride filter with support pads (3-µm, 5-µm obtainable from SKC, Inc., Eighty Four, PA 15330, Cat. No. 225-8-01-1) in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC) with reverse phase column (Kingsorb 5 C_{18}, 250 x 4.60-mm, 5-micron, or equivalent), guard column (Alltima 10 mm X 4.60-mm C_{18}, 5-micron) and 50-µL sample loop injector.
4. Inductively coupled argon plasma-atomic emission spectrometer equipped for analysis of organic compounds (See APPENDIX).
5. Regulators for argon and for oxygen.
6. Beakers: Griffin, 50-mL. **
7. Volumetric flasks: 10-, 100- and 1000-mL.**
8. Syringe, 100-µL.
9. Ultrasonic bath.
10. Pipets, various sizes for standard preparation.
11. Polystyrene (8-mL) round bottom tubes with caps.
12. Plastic film.
13. Forceps.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Triphenyl tin chloride is highly toxic and readily absorbed through skin. Avoid breathing dust and wear gloves when working with it and its solutions. Concentrated acetic acid is corrive, and a skin and eye irritant. Methanol is flammable and toxic.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 100 to 1000 L.

SAMPLE PREPARATION:

3. Open the cassette filter holders and, with tweezers, transfer the samples and blanks to clean beakers.
4. Add 5 mL of desorbing solution. Cover with plastic film.
5. Agitate beakers in an ultrasonic bath for 5 min.
6. Transfer the solutions to polystyrene tubes. Cap.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate with six working standards in the range of 5 to 225 µg as tin per sample.
   a. Pipet known amounts of triphenyl tin chloride stock solution into 10-mL volumetric flasks. Dilute

with desorbing solution.
   b. Analyze samples and blanks (steps 10 and 11).
   c. Prepare a calibration graph (peak area vs µg Sn).
8. One day before analyzing samples, prepare three spiked media blanks. Desorb (steps 3 through 6) and analyze with standards and blanks.
9. Analyze three quality control blind spikes and three analyst spikes to check calibration graph.

MEASUREMENT:

10. Set ICP for analysis of organic compounds according to manufacturer's specifications.
11. Operate HPLC under the following conditions:
    a. C_{18} column
    b. Flush column with approximately 30 mL of mobile phase before connecting to ICP
    c. Mobile phase flow rate: 1 mL/min
    d. After ICP is ready for analysis, connect effluent from HPLC to ICP spray chamber.
12. Inject standards, samples, and blanks onto HPLC column and record chromatograms.

CALCULATIONS:

13. Analyze chromatograms using a convenient HPLC software program.
14. Construct a calibration graph (peak area versus µg of tin).
15. From calibration graph determine the mass in µg of tin for each sample (W) and for the average media blank (B). Calculate the concentration, C, of tin in the volume of air sampled, V (L):

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method was developed in response to an increased use of organotin compounds in the workplace and to test the applicability of the hyphenated technique of HPLC-ICP-AES for their analysis. Triphenyl tin chloride, the compound of this method, is a pesticide and an antifouling agent for paints.

ICP instruments are typically set up for the analysis of inorganic metal compounds. When one is used as a detector for organo-metal compounds in the effluent of an HPLC instrument, certain modifications of the operating conditions of the ICP must be considered. Its torch and spray chamber must be suited to the analysis of organic compounds and gas flow rates are different for analysis of solutions containing organic compounds. Such information can be obtained from the manufacturer of a specific ICP instrument. In addition, oxygen gas is introduced into the plasma to prevent the formation of carbon deposits.

This method was evaluated for limit of detection (LOD), linear range, and sample stability [1]. An instrumental LOD of 3 µg as tin per sample was determined. This corresponds to a Limit of Quantitation that is approximately 0.1 x the Permissible Exposure Limit (PEL). Calibration standards showed the method to be linear to an upper limit of approximately 240 µg per sample which is equivalent to 2.4 times the PEL. Samples with higher concentrations were not tested.

The method was further evaluated by a recovery study using spiked lab samples on polyvinyl chloride filters that contained triphenyl tin chloride at four levels in the range of 9.5 to 190 µg as tin per sample. This range is from approximately 0.1 to 2 x the PEL. At each level six filters were analyzed. Recoveries ranged from 97% to 100% with an average RSD of 0.034. Filters were also spiked at 95 µg/sample and stored at room temperature for 7, 14, and 28 days. Recoveries ranged from 96% to103% with an average RSD of 0.032.

REFERENCES:

[1] Hopkins BM [2002] Backup data report for Triphenyl Tin Chloride, August 15, 2002, (unpublished report). NIOSH/DART.
[2] NIOSH [1994]. NIOSH Manual of Analytical Methods, 4th ed., Method 5504, DHHS(NIOSH) Publication 94-113 (August 1994)
[3] Dauchy X, Cottier R, Batel A, Jeannot R, Borsier M, Astruc A, Astruc M [1993]. Mobile phase composition based on speciation of butyltin compounds by high-performance liquid chromatography with inductively coupled plasma mass spectrometry detection. J Chromatogr Sci *31*: 416-421.

METHOD WRITTEN BY: Barbara M. Hopkins, Ph.D. NIOSH/DART

APPENDIX: Operation of ICP-HPLC Instrument:

ICP conditions refer specifically to the Spectroflame EOP.

1. Install torch and spray chamber for analysis of organic compounds into ICP instrument.
2. Connect inlet tubing for organic analysis to spray chamber and direct ICP waste into a suitable waste container.
3. Once argon is flowing through instrument adjust gas pressures so that nebulizer pressure is 2.2 bar and auxiliary gas flow rate is 23 SKT.
4. Set valve for switching between pumping aqueous solutions and organic solvents to position for aqueous. Allow water to pump through system while following typical procedures for lighting the torch. Light torch and allow system to warm up for 30 minutes.
5. Start mobile phase pumping through HPLC instrument at a flow rate of 1 ml/min. Check for correct flow rate.
6. After warm-up period, profile the optics on the ICP using an aqueous solution that is 10 ppm Cd^{+2}, 10 ppm Li^{+1}, and 50 ppm Zn^{+2}.
7. Following successful profiling, open the valve on the oxygen tank and then change certain settings on the ICP under INSTRUMENT PARAMETERS (a subset of OPERATIONS) so that the following are applied:

GENERATOR PARAMETERS	
Plasma Power (W)	1500
Pump Step	2
Coolant Step	5
Auxiliary Step	1
Nebulizer Step	1
Heating	0
SPECIAL VALVE	
Flush Step	2

8. Change the position of the valve for switching between pumping aqueous solutions and organic solvents to the position for organic and connect the tubing from the ICP to the end of the HPLC column. Check the valve on the inside of the ICP side panel for leaks.
9. Allow mobile phase to run through ICP for about 10 min before injecting.
10. Plug in sample loop position controller being sure that it is in Position A.
11. In order to obtain a transient scan, select SCAN MANAGER, SCAN, TRANSIENT SCAN on ICP computer. Type in the name of the sample, the measure time (100), the interval time (600), and the number of points (999). Select the Sn line (189.9 nm).
12. Inject a sample of methanol (about 70 µL) into the 50 µL sample loop. Simultaneously push the button on the sample injector and the START button on the computer.
13. After the sample loop controller has moved from Position B back to Position A, remove the syringe.
14. Upon completion of the scan, save the scan on a floppy disc.
15. Inject standards and unknowns in triplicate following procedures 11-14.

16. After the last injection, disconnect HPLC column from ICP instrument, and allow water to run through the ICP for 15 min.
17. Flush HPLC column with a mixture of 70% methanol and 30% water and cap.
18. Close oxygen valve and change Flush Step setting on ICP to 1.
19. Turn off ICP following typical shut-down procedures.

V.a. INDEX OF THIRD AND FOURTH EDITION METHOD NUMBERS

XX = Discontinued Method

0500 PARTICULATES NOT OTHERWISE REGULATED, TOTAL (Grav)
0600 PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE (Grav)
0700 see 9100
0800 BIOAEROSOL SAMPLING (Indoor Air)
0801 AEROBIC BACTERIA BY GC-FAME
0900 MYCOBACTERIUM TUBERCULOSIS, AIRBORNE
1000 ALLYL CHLORIDE (GC)
1001 METHYL CHLORIDE (GC)
1002 CHLOROPRENE (GC)
1003 HYDROCARBONS, HALOGENATED (GC)
benzyl chloride
bromoform
carbon tetrachloride
chlorobenzene
chlorobromomethane
chloroform
o-dichlorobenzene
p-dichlorobenzene
1,1-dichloroethane
1,2-dichloroethylene
ethylene dichloride
hexachloroethane
tetrachloroethylene
1,1,1-trichloroethane
1,1,2-trichloroethane
1,2,3-trichloropropane
trichloroethylene
1004 DICHLOROETHYL ETHER (GC)
1005 METHYLENE CHLORIDE (GC)
1006 CLUOROTRICHLOROMETHANE (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)
1025 1-BROMOPROPANE, 2-BROMOPROPANE
1026 *p*-CHLOROBENZOTRIFLUORIDE
1300 KETONES I (GC)
acetone
cyclohexanone
diisobutyl ketone
2-hexanone
methyl isobutyl ketone
2-pentanone
1301 KETONES II (GC)
camphor
ethyl butyl ketone
mesityl oxide
5-methyl-3-heptanone
methyl-(*n*-amyl)-ketone
1302 *N*-METHYL-2-PYRROLIDINONE
1400 ALCOHOLS I (GC)
tert-butyl alcohol
isopropyl alcohol
ethanol
1401 ALCOHOLS II (GC)
n-butyl alcohol
sec-butyl alcohol
isobutyl alcohol
n-propyl alcohol
1402 ALCOHOLS III (GC)
allyl alcohol
cyclohexanol
isoamyl alcohol
diacetone alcohol
methyl isobutyl carbinol
1403 ALCOHOLS IV (GC)
2-butoxyethanol
2-ethoxyethanol
2-methoxyethanol
1404 METHYLCYCLOHEXANOL (GC)
1405 ALCOHOLS COMBINED
sec-butyl alcohol
isobutyl alcohol
n-butyl alcohol
n-propyl alcohol
allyl alcohol
diacetone alcohol
cyclohexanol
isoamyl alcohol
methyl isobutyl carbinol

1450 ESTERS I (GC)
n-amyl acetate
1-butyl acetate
n-butyl acetate
sec-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
1455 XX-Triphenyl phosphate
1456 see 5037
1458 METHYL ACETATE (GC)
1459 METHYL ACRYLATE (GC)
1460 ISOPROPYL ACETATE (GC)
1500 HYDROCARBONS, BP 36-126°C (GC)
cyclohexane
cyclohexene
n-decane
n-dodecane
n-heptane
n-hexane
methylcyclohexane
n-nonane
n-octane
n-pentane
n-undecane
1501 HYDROCARBONS, AROMATIC (GC)
benzene
p-*tert*-butyl toluene
cumene
ethylbenzene
α-methylstyrene
β-methylstyrene
styrene
toluene
o-,*m*-,*p*-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

2000 METHANOL (GC)
2001 XX Cresol - see 2546
2002 AMINES, AROMATIC (GC)
aniline
N,N-dimethyl aniline
N,N-dimethyl-*p*-toluidine
o-toluidine
2,4-xylidine
2003 1,1,2,2-TETRABROMOETHANE (GC)
2004 DIMETHYLACETAMIDE and
DIMETHYLFORMAMIDE (GC)
2005 NITROAROMATIC COMPOUNDS (GC)
4-chloronitrobenzene
nitrobenzene
nitrotoluene
2007 AMINOETHANOL COMPOUNDS I (GC)
2-aminoethanol
2-dibutylaminoethanol
2-diethylaminoethanol
2008 CHLOROACETIC ACID (IC)
2009 XX - see 2540
2010 AMINES, ALIPHATIC (GC)
diethylamine
dimethylamine

2011 FORMIC ACID (IC)
2012 *n*-BUTYLAMINE (GC)
2013 PHENYL ETHER & DIPHENYL (GC)
2014 *p*-CHLOROPHENOL (HPLC)
2015 CHLOROACETALDEHYDE
2016 FORMALDEHYDE
2017 ANILINE, *o*-TOLUIDINE, AND NITROBENZENE
2018 ALIPHATIC ALDEHYDES (HPLC)
acetaldehyde
propionaldehyde
valeraldehyde
isovaleraldehyde
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 and ETHYL METHACRYLATE (GC)
2538 ACETALDEHYDE (GC)
2539 ALDEHYDES, SCREENING (GC)
2540 ETHYLENEDIAMINE, DIETHYLENETRIAMINE, and TRIETHYLENETETRAMINE (HPLC)
2541 FORMALDEHYDE by GC
2542 MERCAPTANS, METHYL, ETHYL, *n*-BUTYL (GC)
2543 HEXACHLOROBUTADIENE (GC/ECD)
2544 NICOTINE (GC/NPD)
2545 ALLYL GLYCIDIL ETHER (GC)
2546 CRESOLS and PHENOL (GC)
2549 VOLATILE ORGANIC CPDS (SCREENING) (GC/MS)
2550 BENZOTHIAZOLE IN ASPHALT FUME
2551 NICOTINE
2552 METHYL ACRYLATE (GC)
2553 KETONES II (GC)
2-heptanone
3-heptanone
mesityl oxide
5-methyl-3-heptanone
camphor
2554 GLYCOL ETHERS (GC)
propylene glycol monomethyl ether
dipropylene glycol monomethyl ether
propylene glycol monomethyl ether acetate
2555 KETONES I (GC)
acetone
methyl ethyl ketone
2-pentanone
methyl isobutyl ketone
2-hexanone
diisobutyl ketone
cyclohexanone
2556 ISOPHORONE (GC)
2557 DIACETYL (GC)
2558 ACETOIN (GC)
2559 DECABROMODIPHENYL OXIDE (HPLC)
2560 1-NITROPYRENE in DIESEL PARTICULATES (GC)
2561 2-(DIMETHYLAMINO)ETHANOL
1-DIMETHYLAMINO-2-PROPANOL (GC)
2562 1,1,2,2-TETRACHLOROETHANE (GC)
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)
3600 MANEB (HPLC)
3601 MANEB (HPLC)
3700 BENZENE (portable GC)
3701 TRICHLOROETHYLENE (portable GC)
3702 ETHYLENE OXIDE (portable GC)
3703 XX Methylene chloride (portable GC)
3704 PERCHLOROETHYLENE (portable GC)
in exhaled breath and air
3800 ORGANIC and INORGANIC GASES by EXTRACTIVE FTIR SPECTROMETRY
benzene
o-xylene
m-xylene
p-xylene
styrene
toluene
n-hexane
acetone
2-butanone
methanol
methylene chloride
vinylidene fluoride
trichloroethylene
tetrafluoroethylene
formaldehyde
ethylene oxide
tetrahydrofuran
nitrous oxide
4000 TOLUENE, passive (GC)
5000 CARBON BLACK (Gray)
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
methylasonic acid
5023 XX Coal Tar Pitch Volatiles
5024 XX Tetryl
5025 CHLORINATED DIPHENYL ETHER (GC)
5026 OIL MIST, MINERAL (IR)
5027 RIBAVARIN (HPLC)
5028 XX Picric acid
5029 4,4'-METHYLENEDIANILINE (MDA)(HPLC)
5030 CYANURIC ACID (HPLC)
5031 ASPARTAME (HPLC)
5032 PENTAMIDINE ISETHIONATE (HPLC)
5033 *p*-NITROANILINE (HPLC)
5034 TRIBUTYL PHOSPHATE (GC)
5035 SUPER ABSORBENT POLYMER (ICP)
5036 TRIMELLITIC ANHYDRIDE (GC)
5037 TRIORTHOCRESYL PHOSPHATE (GC)
5038 TRIPHENYL PHOSPHATE (GC)
5039 CHLORINATED CAMPHENE (GC)
5040 ELEMENTAL CARBON (DIESEL EXHAUST) (EGA)
5041 CAPSAICIN & DIHYDROCAPSAICIN (HPLC/FL)
5042 BENZENE SOLUBLE FRACTION AND TOTAL PARTICULATE (ASPHALT FUME)
5043 *p*-TOLUENESULFONIC ACID
5044 ESTROGENIC COMPOUNDS (HPLC)
β-estradiol
estrone
progesterone
β-estradiol-3-benzoate
5046 TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE (HPLC)
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(isoctyl 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
info[1,2,3-cd]pyrene
naphghalene
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
naphghalene
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

5524 METALWORKING FLUIDS (MWF)
ALL CATEGORIES (Grav)

5525 ISOCYANATES, TOTAL (MAP) (HPLC)
toluene 2,6-diisocyanate (2,6-TDI)
toluene 2,4-diisocyanate (2,4-TDI)
4,4'-methylene-bis(phenyl isocyanate)(MDI)
1,6-hexamethylene diisocyanate (HDI)
isophorone diisocyanate (IPDI)
4,4'-methylene-bis(cyclo hexyl isocyanate) (HMDI)
1,5-naphthalene diisocyanate (NDI)

5526 METHYLTIN CHLORIDES (GC)
dimethyltin dichloride
trimethyltin chloride

5527 TRIPHENYLTIN CHLORIDES (GC)

5600 ORGANOPHOSPHOROUS PESTICIDES (GC/FPD)
azinphos methyl
chlorpyrifos
diazinon
dicrotophos
disulfoton
ethion
ethoprop
fenamiphos
fonofos
malathion
methamidophos
methyl parathion
mevinphos (E)
mevinphos (E&Z)
monocrotophos (E)
monocrotophos (Z)
parathion
phorate
ronnel
sulprophos
terbufos

5601 ORGANONITROGEN PESTICIDES
aldicarb
benomyl
captan
carbaryl
carbendazim
carbofuran
chloropropham
diuron
formetanate.HCl
methiocarb

methonyl
oxamyl
propham
propoxur
thiobencarb

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

5603 ALACHLOR in Air
5606 THIOPHENATE-METHYL in Air
5700 FORMALDEHYDE ON DUST/FIBERS (HPLC)
5701 RESORCINOL
5800 POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs)
6000 XX Mercury - see 6009
6001 ARSINE (GFAAS)
6002 PHOSPHINE (UV/VIS)
6003 XX Tellurium fluoride
6004 SUFUR DIOXIDE/SULFATE (IC)
6005 IODINE (IC)
6006 DIBORANE (PES)
6007 NICKEL CARBONYL (GFAAS)
6008 STIBINE (VIS)
6009 MERCURY (Hopcalite)(cold vapor AAS)
6010 HYDROGEN CYANIDE (VIS)
6011 CHLORINE and BROMINE (IC)
6012 SULFURYL FLUORIDE (GC)
6013 XX Hydrogen sulfide (IC)
6014 NITRIC OXIDE/NITROGEN DIOXIDE (VIS)
6015 AMMONIA (VIS)
6016 AMMONIA by IC
6017 HYDROGEN CYANIDE (IC)
6400 XX Hydrogen sulfide
6401 XX Phosphorus pentachloride
6402 PHOSPHORUS TRICHLORIDE (VIS)
6600 NITROUS OXIDE (portable IR)
6601 OXYGEN (EC sensor)
6602 SULFUR HEXAFLUORIDE (portable IR)
6603 CARBON DIOXIDE (portable GC)
6604 CARBON MONOXIDE (EC sensor)
6700 NITROGEN DIOXIDE
6701 XX Ammonia (pass)
7013 ALUMINUM (FAAS)
7020 CALCIUM (FAAS)
7024 CHROMIUM (FAAS)
7027 COBALT (FAAS)
7029 COPPER (FUME/DUST) (FAAS)
7030 ZINC (ICP)
7048 CADMIUM (FAAS)
7056 BARIUM, soluble (FAAS)
7074 TUNGSTEN, sol/insol (FAAS)
7082 LEAD (FAAS)
7101 XX Vanadium, sol/insol (ICP)
7102 BERYLLIUM (GFAAS)
7103 XX Rhodium - see 7300
7104 XX Platinum - see 7300
7105 LEAD (GFAAS)
7300 ELEMENTS (ICP)
7301 ELEMENTS by ICP (Aqua Regia Ashing)
7303 ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion)
7400 ASBESTOS and other FIBERS by PCM
7401 ALKALINE DUST (titration)
7402 ASBESTOS by TEM
7403 see 9002
7404 CELLULOSE INSULATION
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)
7605 CHROMIUM, HEXAVALENT by ION CHROMATOGRAPHY
7700 LEAD by Chemical Spot Test
7701 LEAD by ULTRASOUND/ASV
7702 LEAD by FIELDPORTABLE XRF
7703 CHROMIUM, HEXAVALENT by FIELD PORTABLE SPECTROPHOTOMETRY
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
8315 TRIAZINE HERBICIDES and their METABOLITES
atrazine
simazine
propazine
cyanazine
desethylatrazine
desisopropylatrazine
8316 BUTOXYACETIC ACID in urine
8317 ANALINE and *o*-TOLUDINE in urine
9000 ASBESTOS, CHRYSOTILE by XRD
9002 ASBESTOS (bulk) by PLM
9101 CHROMIUM (VI) in settled dust (Test Kit)
9102 ELEMENTS on WIPES (ICP)
9105 LEAD in DUST WIPES by Chemical Spot Test
9200 CHLORINATED and ORGANONITROGEN HERBICIDES (HAND WASH)
9201 CHLORINATED and ORGANONITROGEN HERBICIDES (DERMAL PATCH)
9202 CAPTAN and THIOPHENATEMETHYL (HAND RINSE)
9205 CAPTAN and THIOPHENATEMETHYL (DERMAL PATCH)

V.b. INDEX OF SECOND EDITION METHOD NUMBERS

(The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols. 1 through 7).
CRDT = Criteria Document
SDS = Sampling Data Sheet from NIOSH Publication 77-159
NRNR = Not revised and not recommended for use
NRIU = Not revised because of infrequent usage by NIOSH; the 2nd Ed. method recommended for use at present.

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	102	1	Lead in blood (Dithizone)	LEAD [7082]; LEAD [7105]; LEAD IN BLOOD OR URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	106	1	Silica (colorimetric)	SILICA, CRYSTALLINE [7601]
	107	1	Antimony in urine	NRIU
	108	1	Nitrogen oxides	NITRIC OXIDE and NITROGEN DIOXIDE [6014]; NITROGEN DIOXIDE [6700]
	109	1	Silica (XRD)	SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)	SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide	NRNR; see CARBON MONOXIDE [6604]
	113	1	Carbon monoxide in blood	NRIU
	114	1	Fluoride in urine	FLUORIDE IN URINE [8308]
	115	1	Hydrogen chloride	ACIDS, INORGANIC [7903]
	116	1	Cyanide	CYANIDES [7904]
	117	1	Hydrogen fluoride	ACIDS, INORGANIC [7903]
	118	1	Acrolein	ACROLEIN [2501]
	121	1	Beryllium	BERYLLIUM [7102]; ELEMENTS by ICP [7300]
	124	1	Selenium in urine	NRIU
	125	1	Formaldehyde	FORMALDEHYDE [2016, 2541, 3500, 3501]
	126	1	Hydrogen sulfide	see HYDROGEN SULFIDE [6013]
	127	1	Acetone	KETONES I [1300]
	127	1	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; BENZENE [3700]; HYDROCARBONS, AROMATIC [1501]
	127	1	2-Butanone	METHYL ETHYL KETONE [2500]
	127	1	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	*p*-Dioxane	DIOXANE [1602]
	127	1	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methylene chloride	METHYLENE CHLORIDE [1005]
	127	1	Styrene	HYDROCARBONS, AROMATIC [1501]
	127	1	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1300]
	127	1	Toluene	HYDROCARBONS, BP 35-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
	127	1	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1300]
	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; 7701; 7702]; ELEMENTS by ICP [7300]
	173	1,5	Lithium	ELEMENTS by ICP [7300]
	173	1,5	Magnesium	ELEMENTS by ICP [7300]
	173	1,5	Manganese	ELEMENTS by ICP [7300]
	173	1,5	Molybdenum	ELEMENTS by ICP [7300]
	173	1,5	Nickel	ELEMENTS by ICP [7300]
	173	1,5	Palladium	NRIU
	173	1,5	Potassium	NRIU
	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]

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

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

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
P&CAM	294	5	Cyclopentadiene	1,3-CYCLOPENTADIENE [2523]
	295	5	Dichlorovos	NRIU
	296	6	Hydrogen sulfide	NRIU
	297	5	Dibutyl phosphate	DIBUTYL PHOSPHATE [5017]
	298	5,7	Nickel	ELEMENTS BY ICP [7300]
	299	5	Dimethylnitrosamine	NITROSAMINES [2522]
	300	5	Ethylenimine (aziridine)	ETHYLENIMINE [3514]
	301	5	Dimethyl sulfate	NRIU
	302	5	Maleic anhydride	MALEIC ANHYDRIDE [3512]
	303	5	Styrene oxide	NRIU
	304	5	OCBM	NRIU
	305	5	Phosphorus trichloride	PHOSPHORUS TRICHLORIDE [6402]
	307	5	Hexachlorobutadiene	HEXACHLOROBUTADIENE [2543]
	308	5	Hexachlorocyclopentadiene	HEXACHLORO-1,3-CYCLOPENTADIENE [2518]
	309	5	Chrysotile asbestos (bulk)	ASBESTOS, CHRYSOTILE BY XRD [9000]
	310	5	Hydrogen chloride	ACIDS, INORGANIC [7903]
	313	6	Warfarin	WARFARIN [5002]
	314	5	Trichloroisocyanuric acid	NRIU
	315	5	Benzidine in urine	BENZIDINE IN URINE [8306]
	316	6	Silica, amorphous	SILICA, AMORPHOUS [7501]
	317	6	Diethylcarbamoyl chloride	NRIU
	318	6	Formaldehyde	FORMALDEHYDE [2541, 3500, 5700]
	319	6	Chromium (VI)	CHROMIUM, HEXAVALENT [7600, 7604]
	320	6	Arsenic, organo-	ARSENIC, ORGANO- [5022]
	321	6	1,2-Dichloroproane	1,2-DICHLOROPROPANE [1013]
	322	6	Trimellitic anhydride	TRIMELLITIC ANHYDRIDE [5036]
	323	6	Titanium diboride	NRIU
	324	6	Boron carbide	BORON CARBIDE [7506]
	325	6	Benzidine, o-anisidine, and *o*-Tolidine dyes	DYES [5013]
	326	6	TDI	NRNR; see TOLUENE-2,4-DIISOCYANATE [2535]; ISOCYANATES [5521, 5522]
	327	6	Hippuric acid in urine	HIPPURIC ACID IN URINE [8300]
	328	6	ALAD in blood	NRNR; see LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	329	6	PCB in blood	POLYCHLORINATED BIPHENYLS IN SERUM [8004]
	330	6	Phenol and Cresol in urine	PHENOL and p-CRESOL IN URINE [8305]
	331	6	Methyl ethyl ketone peroxide	METHYL ETHYL KETONE PEROXIDE [3508]
	332	6	Chloroacetic acid	CHLOROACETIC ACID [2008]
	333	6	Bisphenol A	NRIU
	335	6	Pentachloroethane	PENTACHLOROETHANE [2517]
	336	6	Tetraethyl pyrophosphate	TETRAETHYL PYROPHOSPHATE-TEPP [2504]
	337	7	*p*-Chlorophenol	β-CHLOROPHENOL [2014]
	338	7	Ethylene glycol	NRNR; see GLYCOLS [5523]
	339	7	Inorganic acids	ACIDS, INORGANIC [7903]

	2nd Ed. Method Number	Vol. Number	Substance	4th Ed. 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 [2016; 2541, 3500, 5700]
	355	--	Talc, respirable	NRIU
	357	--	*n*-Octanethiol	1-OCTANETHIOL [2510]
	358	--	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	359	--	Benzidine in urine	BENZIDINE IN URINE [8306]
	360	--	Hippuric Acid in urine	HIPPURIC ACID IN URINE [8300]; HIPPURIC and METHYL HIPPURIC ACIDS IN URINE [8301]
	361	--	2-Butanone, ethanol, and toluene in blood	METHYL ETHYL KETONE, ETHANOL, AND TOLUENE IN BLOOD [8002]
	362	--	Pentachlorophenol in blood	PENTACHLOROPHENOL IN BLOOD [8001]
	363	--	Polychlorinated terphenyls	CHLORINATED TERPHENYL [5014]
	364	--	Vanadium oxides	VANADIUM OXIDES [7504]
	365	--	2-Butanone	METHYL ETHYL KETONE [2500]
	368	--	Tin, organo-	ORGANOTIN COMPOUNDS [5504]
	374	--	Acrolein	ACROLEIN [2501]
	S1	2	Acetone	KETONES I [1300]
	S2	2	Antimony	NRIU
	S3	2	2-Butanone	METHYL ETHYL KETONE [2500]
	S4	2	Hydrogen sulfide	NRIU; see HYDROGEN SULFIDE [6013]
	S5	2	Manganese	ELEMENTS BY ICP [7300]
	S7	5	*p*-Nitroaniline	*p*-NITROANILINE [5033]
	S8	2	Ozone	NRIU
	S10	2	Camphor	KETONES II [1301]
	S11	5	Chloroacetaldehyde	CHLOROACETALDEHYDE [2015]
	S12	2	Mesityl oxide	KETONES II [1301]
	S13	2	5-Methyl-3-heptanone	KETONES II [1301]
	S15	2	Methyl (*n*-amyl) ketone	KETONES II [1301]
	S16	2	Ethyl butyl ketone	KETONES II [1301]
	S17	5	Furfural	FURFURAL [2529]
	S18	2	Hexone (MIBK)	KETONES I [1300]
	S19	2	Cyclohexanone	KETONES I [1300]
	S20	2	2-Pentanone	KETONES I [1300]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S22	2	*p-tert*-Butyltoluene	HYDROCARBONS, AROMATIC [1501]
S23	2	Cumene	HYDROCARBONS, AROMATIC [1501]
S24	4	Diphenyl	DIPHENYL [2530]
S25	2	Vinyl toluene	HYDROCARBONS, AROMATIC [1501]
S26	2	α-Methyl styrene	HYDROCARBONS, AROMATIC [1501]
S27	2	Terphenyl	*o*-TERPHENYL [1521]
S28	2	Cyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S29	2	Ethylbenzene	HYDROCARBONS, AROMATIC [1501]
S30	2	Styrene	HYDROCARBONS, AROMATIC [1501]
S31	2	*sec*-Amyl acetate	ESTERS I [1450]
S32	2	*tert*-Butyl acetate	ESTERS I [1450]
S33	2	Dibutyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
S35	2	Ethyl acrylate	ESTERS I [1450]
S36	2	Ethyl formate	ETHYL FORMATE [1452]
S37	2	Methyl isoamyl acetate	ESTERS I [1450]
S38	2	Methyl acrylate	METHYL ACRYLATE [1459]
S39	2	Methyl cellosolve acetate	METHYL CELLOSOLVE ACETATE [1451]
S40	2	Di-2-ethylhexyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
S41	2	2-Ethoxyethyl acetate	ESTERS I [1450]
S42	2	Methyl acetate	METHYL ACETATE [1458]
S43	6	Methyl methacrylate	METHYL METHACRYLATE [2537]
S44	2	Isobutyl acetate	ESTERS I [1450]
S45	2	Isoamyl acetate	ESTERS I [1450]
S46	2	*sec*-Butyl acetate	ESTERS I [1450]
S47	2	*n*-Butyl acetate	ESTERS I [1450]
S48	2	*n*-Propyl acetate	ESTERS I [1450]
S49	2	Ethyl acetate	ETHYL ACETATE [1457]
S50	2	Isopropyl acetate	ISOPROPYL ACETATE [1454]
S51	2	*n*-Amyl acetate	ESTERS I [1450]
S52	2	Allyl alcohol	ALCOHOLS III [1402]
S53	2	*sec*-Butyl alcohol	ALCOHOLS II [1401]
S54	2	Cyclohexanol	ALCOHOLS III [1402]
S55	2	Diacetone alcohol	ALCOHOLS III [1402]
S56	2	Ethanol	ALCOHOLS I [1400]
S57	2	Hydroquinone	HYDROQUINONE [5004]
S58	2	Isoamyl alcohol	ALCOHOLS III [1402]
S59	2	Methanol	METHANOL [2000]
S60	2	Methyl isobutyl carbinol	ALCOHOLS III [1402]
S62	2	*n*-Propyl alcohol	ALCOHOLS II [1401]
S63	2	*tert*-Butyl alcohol	ALCOHOLS I [1400]
S64	2	Isobutyl alcohol	ALCOHOLS II [1400]
S65	2	Isopropyl alcohol	ALCOHOLS I [1400]
S66	2	*n*-Butyl alcohol	ALCOHOLS II [1401]
S67	2	Chlorinated camphene	CHLORINATED CAMPHENE [5039]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S69	2	Dipropylene glycol methyl ether	NRIU
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	PHENYL ETHER [1617]
S73	2	Phenyl ether-biphenyl mixture	PHENYL ETHER-DIPHENYL MIXTURE [2013]
S74	2	Phenyl glycidyl ether	PHENYL GLYCIDYL ETHER [1619]
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	ISOPROPYL GLYCIDYL ETHER [1620]
S78	2	Tetrahydrofuran	TETRAHYDROFURAN [1609]
S79	2	2-Methoxyethanol	ALCOHOLS IV [1403]
S80	2	Ethyl ether	ETHYL ETHER [1610]
S81	2	*n*-Butyl glycidyl ether	*n*-BUTYL GLYCIDYL ETHER [1616]
S82	2	Cyclohexene	HYDROCARBONS, BP 36-126 °C [1500]
S84	5	Methyl acetylene (propyne)	NRIU
S85	6	Methyl acetylene/propadiene	NRIU
S86	2	Naphtha, coal tar	NAPHTHAS [1550]
S87	2	Propane	NRIU
S88	2	Turpentine	TURPENTINE [1551]
S89	2	Heptane	HYDROCARBONS, BP 36-126 °C [1500]
S90	2	Hexane	HYDROCARBONS, BP 36-126 °C [1500]
S91	2	Butadiene	1,3-BUTADIENE [1024]
S92	2	Ketene	NRIU
S93	2	LPG	NRIU
S94	2	Methylcyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S95	2	Propylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S96	2	Pentachloronaphthalene	NRIU
S97	2	Octachloronaphthalene	NRIU
S98	2	Methyl iodide	METHYL IODIDE [1014]
S99	4	Methyl chloride	METHYL CHLORIDE [1001]
S100	2	Hexachloronaphthalene	NRIU
S101	2	Hexachloroethane	HYDROCARBONS, HALOGENATED [1003]
S102	2	Fluorotrichloromethane	FLUOROTRICHLOROMETHANE [1006]
S103	2	Ethylene chlorohydrin	ETHYLENE CHLOROHYDRIN [2513]
S104	2	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
S105	4	Ethyl chloride	ETHYL CHLORIDE [2519]
S106	2	Ethyl bromide	ETHYL BROMIDE [1011]
S107	2	Dibromodifluoromethane	DIFLUORODIBROMOMETHANE [1012]
S108	2	Dichlorotetrafluoroethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]
S109	2	Dichlorofluoromethane	DICHLOROFLUOROMETHANE [2516]
S110	2	1,2-Dichloroethylene	HALOGENATED HYDROCARBONS [1003]
S111	2	Dichlorodifluoromethane	DICHLORODIFLUOROMETHANE, 1,2-DICHLORO-TETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE [1018]

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S112	2	Chloroprene	CHLOROPRENE [1002]
S113	2	Chlorobromomethane	HYDROCARBONS, HALOGENATED [1003]
S114	2	Bromoform	HYDROCARBONS, HALOGENATED [1003]
S115	2	Benzyl chloride	HYDROCARBONS, HALOGENATED [1003]
S116	2	Allyl chloride	ALLYL CHLORIDE [1000]
S117	2	Acetylene tetrabromide	1,1,2,2-TETRABROMOETHANE [2003]
S118	2	Epichlorohydrin	EPICHLOROHYDRIN [1010]
S119	2	Chlorinated diphenyl oxide	CHLORINATED DIPHENYL ETHER [5025]
S120	4	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S121	2	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S122	2	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S123	2	1,1-Dichloroethane	HYDROCARBONS, HALOGENATED [1003]
S124	2	1,1,2,2-Tetrachloroethane	1,1,2,2-TETRACHLOROETHANE [1019]
S125	2	Trifluorobromomethane	TRIFLUOROBROMOMETHANE [1017]
S126	2	1,2,3-Trichloropropane	HYDROCARBONS, HALOGENATED [1003]
S128	2	Trichloronaphthalene	NRIU
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE [1020]
S130	2	Tetrachloronaphthalene	NRIU
S131	2	1,1,1,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S132	2	1,1,2,2-Tetrachlorodifluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE & 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE [1016]
S133	2	Chlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S134	2	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1003]
S135	3	*o*-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S137	3	Diazomethane	DIAZOMETHANE [2515]
S138	4	*n*-Butylamine	*n*-BUTYLAMINE [2012]; AMINES, ALIPHATIC [2010]
S139	3	Diethylamine	AMINES, ALIPHATIC [2010]
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS I [2007]; AMINOETHANOL COMPOUNDS II [3509]
S141	4	Diisopropylamine	NRIU; see AMINES, ALIPHATIC [2010]
S142	3	Dimethylamine	AMINES, ALIPHATIC [2010]
S143	3	1,1-Dimethyl hydrazine	1,1-DIMETHYLHYDRAZINE [3515]
S144	3	Ethylamine	NRIU
S146	3	*N*-Ethyl morpholine	NRIU
S147	3	Isopropylamine	NRIU
S148	6	Methylamine	NRIU
S149	3	Methyl hydrazine	MONOMETHYLHYDRAZINE [3510]
S150	3	Morpholine	NRIU
S152	3	Triethylamine	NRIU
S153	3	Monomethylaniline	MONOMETHYLANILINE [3511]
S155	3	Tetramethylsuccinonitrile	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S156	3	Acrylonitrile	ACRYLONITRILE [1604]
S158	4	2-Aminopyridine	NRIU
S160	3	Phenyl hydrazine	PHENYLHYDRAZINE [3518]
S161	3	Pyridine	PYRIDINE [1613]
S162	3	2,4-Xylidine	AMINES, AROMATIC [2002]
S163	5	Anisidine (*o* and *p*-)	ANISIDINE [2514]
S164	3	Dimethylaniline	AMINES, AROMATIC [2002]
S165	3	Acetonitrile	ACETONITRILE [1606]
S166	5	Dinitro-*o*-cresol	NRIU
S167	3	Cresol	CRESOLS AND PHENOL [2546]
S168	3	*o*-Toluidine	AMINES, AROMATIC [2002]
S169	4	Acetic acid	ACETIC ACID [1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE [3506]
S173	5	Formic acid	FORMIC ACID [2011]
S174	3	Sulfuric acid	ACIDS, INORGANIC [7903]
S175	3	Hydrogen bromide	ACIDS, INORGANIC [7903]
S176	3	Hydrogen fluoride	FLUORIDES [7902, 7906]; ACIDS, INORGANIC [7903]
S178	3	2-Hexanone	KETONES I [1300]
S179	3	Phthalic anhydride	NRIU
S181	4	Quinone	NRIU
S182	5	Silver	ELEMENTS BY ICP [7300]
S183	3	Tin	ELEMENTS BY ICP [7300]
S185	3	Zirconium	ELEMENTS BY ICP [7300]
S186	3	Copper	COPPER [7029]; ELEMENTS BY ICP [7300]
S187	3	Tellurium hexafluoride	NRIU
S188	3	Rhodium, fume and dust	NRIU
S189	3	Rhodium, soluble	NRIU
S190	3,7	Selenium	ELEMENTS BY ICP [7300]
S191	3,7	Platinum	ELEMENTS BY ICP [7300]
S193	3	Molybdenum	ELEMENTS BY ICP [7300]
S194	5	Hafnium	NRIU
S198	3	Barium	BARIUM [7056]
S199	4	Mercury	NRIU; see MERCURY [6009]
S200	3	Yttrium	ELEMENTS BY ICP [7300]
S201	5	Tantalum	ELEMENTS BY ICP [7300]
S203	4	Cobalt	COBALT [7027]; ELEMENTS BY ICP [7300]
S204	3,7	Tellurium	ELEMENTS BY ICP [7300]
S205	3	Calcium	CALCIUM [7020]; ELEMENTS BY ICP [7300]
S206	3	Nickel	ELEMENTS BY ICP [7300]
S208	3	Tributyl phosphate	TRIBUTYL PHOSPHATE [5034]
S209	3	Triorthocresyl phosphate	TRIORTHOCRESYL PHOSPHATE [5037]
S210	3	Triphenyl phosphate	TRIPHENYL PHOSPHATE [5038]
S211	5	1-Chloro-1-nitropropane	NRIU
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S215	4	Dinitrotoluene	NRIU
S216	3	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
S217	3	Nitrobenzene	NITROBENZENES [2005]
S218	3	*p*-Nitrochlorobenzene	NITROBENZENES [2005]
S219	4,6	Nitroethane	NITROETHANE [2526]
S220	6	Nitromethane	NITROMETHANE [2527]
S223	3	Nitrotoluene	NITROBENZENES [2005]
S224	3	Tetranitromethane	NRIU
S225	3	Tetryl	NRIU
S227	3	*n*-Propyl nitrate	NRIU
S228	4	Picric acid	NRIU
S229	3	Arsine	ARSINE [6001]
S237	3	Hydrazine	HYDRAZINE [3503]
S243	4	Stibine	STIBINE [6008]
S244	5	Sulfur hexafluoride	NRIU
S245	6	Sulfuryl fluoride	SULFURYL FLUORIDE [6012]
S246	3	Hydrogen chloride	ACIDS, INORGANIC [7903]
S248	3	Carbon disulfide	CARBON DISULFIDE [1600]
S249	3	Carbon dioxide	CARBON DIOXIDE [6603]
S250	3	Cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S253	4	Benzoyl peroxide	BENZOYL PEROXIDE [5009]
S254	3	Dimethylacetamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S255	3	Dimethylformamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S256	5	Thiram	THIRAM [5005]
S257	5	Phosphorus pentachloride	NRIU
S262	3	Carbon black	CARBON BLACK [5000]
S264	3	Ethyl silicate	NRIU
S272	3	Oil mist	OIL MIST, MINERAL [5026]
S273	3	Carbaryl (Sevin)	CARBARYL [5006]
S274	3	DDT	NRIU
S275	3	Aldrin	ALDRIN and LINDANE [5502]
S276	5	ANTU	NRIU
S278	6	Chlordane	CHLORDANE [5510]
S279	5	2,4-D	2,4-D and 2,4,5-T [5001]; CHLORINATED AND ORGANONITROGEN PESTICIDES [5602]
S280	6	Demeton	DEMETON [5514]
S281	3	*p*-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S283	3	Dieldrin	NRIU
S284	6	Endrin	ENDRIN [5519]
S285	3	EPN	EPN [5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE [1607, 3702]
S287	5	Heptachlor	NRIU
S288	4	Hydrogen cyanide	CYANIDES [7904]; HYDROGEN CYANIDE [6010]
S290	3	Lindane	ALDRIN and LINDANE [5502]
S291	5	Methyl formate	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]
S293	3	Nicotine	NRIU; see NICOTINE [2544; 2551]
S294	5	Paraquat	PARAQUAT [5003]
S295	3	Parathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S296	6	Mevinphos (Phosdrin)	ORGANOPHOSPHORUS PESTICIDES [5600]
S297	4	Pentachlorophenol	PENTACHLOROPHENOL [5512]
S298	6	Pyrethrum	PYRETHRUM [5008]
S299	6	Ronnel	ORGANOPHOSPHORUS PESTICIDES [5600]
S300	5	Rotenone	ROTENONE [5007]
S301	5	Sodium fluoroacetate	NRIU
S302	5	Strychnine	STRYCHNINE [5016]
S303	5	2,4,5-T	2,4-D and 2,4,5-T [5001]
S306	3	Thallium	ELEMENTS BY ICP [7300]
S308	4	Sulfur dioxide	SULFUR DIOXIDE [6004]
S309	3	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS BY ICP [7300]
S310	3	Aniline	AMINES, AROMATIC [2002]
S311	3	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; BENZENE [3700]
S312	3	Cadmium	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S313	3	Cadmium fume	CADMIUM [7048]; ELEMENTS BY ICP [7300]
S314	3	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
S315	3	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
S316	4	Zinc oxide	ZINC OXIDE [7502]
S317	3	Chromium, hexavalent	CHROMIUM, HEXAVALENT [7600, 7604]
S318	3	Xylene	HYDROCARBONS, AROMATIC [1501]
S319	4	Nitric acid	ACIDS, INORGANIC [7903]
S320	4	Nitrogen dioxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]; NITROGEN DIOXIDE [6700]
S321	4	Nitric oxide	NITRIC OXIDE AND NITROGEN DIOXIDE [6014]
S323	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S327	4	Formaldehyde (Girard T)	NRNR; see FORMALDEHYDE [2542, 3500, 5700]
S328	3	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
S329	3	Methylene chloride	METHYLENE CHLORIDE [1005]
S330	3	Phenol	CRESOLS AND PHENOL [2546]
S332	5	Phosphine	PHOSPHINE [6002]
S333	3	Phosphoric acid	ACIDS, INORGANIC [7903]
S334	3	Phosphorus	PHOSPHORUS [7905]
S335	3	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]
S336	3	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
S339	3	Beryllium	BERYLLIUM [7102]; ELEMENTS BY ICP [7300]
S340	4	Carbon monoxide	NRNR; see CARBON MONOXIDE [6604]
S341	3,7	Lead	LEAD [7082, 7701, 7702]; ELEMENTS BY ICP [7300]
S342	6	Mercury, organo	NRIU

2nd Ed. Method Number	Vol. Number	Substance	4th Ed. Method [Number]
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
S345	5	Acetaldehyde	ACETALDEHYDE [3507]
S346	4	Allyl glycidyl ether	ALLYL GLYCIDYL ETHER [2545]
S347	5	Ammonia	see AMMONIA BY VIS [6015, 6016]
S348	5	Ammonium sulfamate	NRIU
S349	3	Boron oxide	PARTICULATES NOT OTHERWISE REGULATED, TOTAL [0500]
S350	4	*n*-Butyl mercaptan	*n*-BUTYL MERCAPTAN [2525]; MERCAPTANS, METHYL, ETHYL, and *n*-BUTYL [2542]
S351	3	Chloroform	HYDROCARBONS, HALOGENATED [1003]
S352	3	Chromium	CHROMIUM [7024]; ELEMENTS BY ICP [7300]
S354	4	Copper fume	COPPER [7029]; ELEMENTS BY ICP [7300]
S356	5	Crag herbicide I	NRIU
S357	3	*sym*-Dichloroethyl ether	DICHLOROETHYL ETHER [1004]
S358	3	Diisobutyl ketone	KETONES I [1300]
S360	3	Dioxane	DIOXANE [1602]
S361	5	2-Ethoxyethanol	ALCOHOLS IV [1403]
S365	4	Furfuryl alcohol	FURFURYL ALCOHOL [2505]
S366	4	Iron oxide fume	ELEMENTS BY ICP [7300]
S367	3	Isophorone	ISOPHORONE [2508]
S368	3	Isopropyl ether	ISOPROPYL ETHER [1618]
S369	3	Magnesium oxide fume	ELEMENTS BY ICP [7300]
S370	3	Malathion	ORGANOPHOSPHORUS PESTICIDES [5600]
S371	4	Methoxychlor	NRIU
S372	3	Methyl bromide	NRNR
S374	4	Methylcyclohexanol	METHYL CYCOHEXANOL [1404]
S375	4	Methylcyclohexanone	METHYL CYCLOHEXANONE [2521]
S376	3	Molybdenum	ELEMENTS BY ICP [7300]
S378	3	Octane	HYDROCARBONS, BP 36-126 °C [1500]
S379	3	Pentane	HYDROCARBONS, BP 36-126 °C [1500]
S380	3	Naphtha, petroleum	NAPHTHAS [1550]
S381	4	Sodium hydroxide	ALKALINE DUSTS [7401]
S382	3	Stoddard solvent	NAPHTHAS [1550]
S383	4	Tetraethyl lead	TETRAETHYL LEAD [2533]
S384	4	Tetramethyl lead	TETRAMETHYL LEAD [2534]
S385	3	Titanium dioxide	NRIU
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S391	3	Vanadium	ELEMENTS BY ICP [7300]
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1,1-DIMETHYLHYDRAZINE, 3515
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ETHYLENEDIAMINE (EDA), see ETHYLENEDIAMINE, DIETHYLENETRIAMINE, and TRIETHYLENETETRAMINE, 2540
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GLYCIDOL, 1608
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sec-Hexyl acetate, see ESTERS I, 1450
HF, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
HIPPURIC ACID in urine (VIS), 8300
HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC), 8301
Hi-sil, see SILICA, AMORPHOUS, 7501
Hydrated amorphous silica, see SILICA, AMORPHOUS, 7501
Hydrated lime, see CALCIUM, 7020
Hydraulic oils, see OIL MIST, MINERAL, 5026
HYDRAZINE, 3503
Hydrazinobenzene, see PHENYL ETHER, 3518
Hydrobromic acid, see ACIDS, INORGANIC, 7903
HYDROCARBONS, AROMATIC, 1501
HYDROCARBONS, BP 36-126°C, 1500
HYDROCARBONS, HALOGENATED, 1003
Hydrochloric acid, see ACIDS, INORGANIC, 7903
Hydrocyanic acid, see HYDROGEN CYANIDE, 6010; 6017; CYANIDES, 7904
Hydrofluoric acid, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
Hydrogen bromide, see ACIDS, INORGANIC, 7903
Hydrogen carboxylic acid, see FORMIC ACID, 2011
Hydrogen chloride, see ACIDS, INORGANIC, 7903
HYDROGEN CYANIDE, 6010; by IC, 6017; see CYANIDES, 7904
Hydrogen fluoride, see ACIDS, INORGANIC, 7903; FLUORIDES by ISE, 7902; 7906 (IC)
Hydroquinol, see HYDROQUINONE, 5004
HYDROQUINONE, 5004
Hydrosulfuric acid, see HYDROGEN SULFIDE, 6013
4-Hydroxychlorobenzene, see *p*-CHLOROPHENOL, 2014
Hydroxydimethylasine oxide, see ARSENIC, ORGANO-, 5022
2-Hydroxyethylamine, see AMINOETHANOL COMPOUNDS I, 2007
2-Hydroxyethyl ether, see GLYCOLS, 5523
Hydroxymethyl ethylene oxide, see GLYCIDOL, 1608
2-(Hydroxymethyl) furan, see FURFURYL ALCOHOL, 2505
2-(Hydroxymethyl)oxiran, see GLYCIDOL, 1608
4-Hydroxy-4-methyl-2-pentanone, see ALCOHOLS III, 1402
2-Hydroxy-2-methylpropanenitrile, see ACETONE CYANOHYDRIN, 2506
3-Hydroxypropylene oxide, see GLYCIDOL, 1608
2-Hydroxytriethylamine, see AMINOETHANOL COMPOUNDS I, 2007
Hyponitrous acid anhydride, see NITROUS OXIDE, 6600

ICN 1229, see RIBAVIRIN, 5027
IGE, see ISOPROPYL GLYCIDYL ETHER, 6020
2-Imidazolidinethione, see ETHYLENE THIOUREA, 5011
2,2'-Iminodiethanol, see AMINOETHANOL COMPOUNDS II, 3509
Indeno[1,2,3-cd]pyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
INDIUM, see ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion), 7303
IODINE, 6005
Iron, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102; ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion), 7303
Iodomethane, see METHYL IODIDE, 1014
Isoamyl acetate, see ESTERS I, 1450
Isoamyl alcohol, see ALCOHOLS III, 1402; ALCOHOLS COMBINED, 1405
Isobutyl acetate, see ESTERS I, 1450
Isobutyl alcohol, see ALCOHOLS II, 1401; ALCOHOLS COMBINED, 1405
Isobutyraldehyde, see ALDEHYDES, SCREENING, 2539
ISOCYANATES, MONOMER, 5521; see ISOCYANATES, 5522; 2,4-TOLUENEDIISOCYANATE, 2535
ISOCYANATES, 5522
Isocyanuric acid, see CYANURIC ACID, 5030

Isodiprene, see TERPENES, 1552
ISOPHORONE, 2508; 2556
Isopropenylbenzene, see HYDROCARBONS, AROMATIC, 1501
ISOPROPYL ACETATE, 1454; 1460
Isopropyl alcohol, see ALCOHOLS I, 1400; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
ISOPROPYL ETHER, 1618
Isopropyl epoxypropyl ether, see ISOPROPYL GLYCIDYL ETHER, 1620
ISOPROPYL GLYCIDYL ETHER, 1620
Isopropylbenzene, see HYDROCARBONS, AROMATIC, 1501
Isovaleraldehyde, see ALDEHYDES, SCREENING, 2539; ALIPHATIC ALDEHYDES, 2018

Jasmolin I, II, see PYRETHRUM, 5008

Kaolin, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
KEPONE, 5508
Kerosene, see NAPHTHAS, 1550
Kerosine, see NAPHTHAS, 1550
KETONES I, 1300
KETONES II, 1301

Lamp black, see CARBON BLACK, 5000
Lanthanum, see ELEMENTS in blood or tissue, 8005; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Lanthanum in blood, see ELEMENTS in blood or tissue, 8005
Lanthanum in tissue, see ELEMENTS in blood or tissue, 8005
Laughing gas, see NITROUS OXIDE, 6600
LEAD by ULTRASOUND/ASV, 7701
LEAD by FIELD PORTABLE XRF, 7702; LEAD by PORTABLE ULTRASONIC EXTRACTION/ASV, 7701
LEAD, 7082 (FAAS); 7105 (GFAAS); (Spot test), 7700; (ULTRASOUND/ASV), 7701; (Portable XRF), 7702; (Surface wipes), 9100; ELEMENTS by ICP, 7300; LEAD in blood and urine, 8003; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
LEAD in Air by chemical spot test, 7700
LEAD in DUST WIPES by Chemical Spot Test, 9105
LEAD in surface wipe samples, 9100; see ELEMENTS on WIPES, 9102
Lead oxide, see LEAD, 7082 (FAAS); 7105 (GFAAS)
LEAD SULFIDE, 7505
Lead tetraethyl, see TETRAETHYL LEAD (as Pb), 2533
Lead tetramethyl, see TETRAMETHYL LEAD (as Pb), 2534
Lepargylic acid, see AZELAIC ACID, 5019
Limestone, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
Limonene, see TERPENES, 1552; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Lindane, see ALDRIN and LINDANE, 5502
Lithium, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; ELEMENTS in blood or tissue, 8005
Lithium hydroxide, see ALKALINE DUSTS, 7401
Luteohormone, see ESTROGENIC COMPOUNDS, 5044
Lye, see ALKALINE DUSTS, 7401

Machine oil, see OIL MIST, MINERAL, 5026
Magnesite, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
Magnesium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; ELEMENTS by ICP (Hot Block/ Hcl/HNO_3 Digestion), 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Malathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
MALEIC ANHYDRIDE, 3512
MANEB, Hand Wash, 3601; Dermal Patch, 3600

Manganese, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102; ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion), 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Marble, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; CALCIUM, 7020
MBK, see KETONES I, 1300
MBOCA in urine, 8302
MDA, see 4,4'-METHYLENEDIANILINE, 5029
MDI, see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
MEA, see AMINOETHANOL COMPOUNDS II, 3509
MEK, see METHYL ETHYL KETONE, 2500
MEK, in blood, see 2-BUTANONE, ETHANOL and TOLUENE in blood, 8002
Mendrin, see ENDRIN, 5519
MERCAPTANS, Methyl, Ethyl, and *n*-Butyl, 2542
1-Mercaptobutane, see *n*-BUTYL MERCAPTAN, 2525; MERCAPTANS, Methyl, Ethyl, *n*-Butyl, 2542
1-Mercaptooctane, see 1-OCTANETHIOL, 2510
MERCURY, 6009
Mesityl oxide, see KETONES II, 1301; KETONES II, 2553
Metals in air, see ELEMENTS by ICP, 7300; or individual metals
METALS in urine (ICP), 8310
METALWORKING FLUIDS, 5524
Meta-phosphoric acid, see ACIDS, INORGANIC, 7903
Methacrylic acid methyl ester, see METHYL METHACRYLATE, 2537
Methamidophos, see ORGANOPHOSPHORUS PESTICIDES, 5600
Methanal, see FORMALDEHYDE (DNPH cartridge), 2016; FORMALDEHYDE (2-HMP), 2502; (chromotropic Acid), 3500; ALDEHYDES, SCREENING, 2539
Methanearsonic acid, see ARSENIC, ORGANO-, 5022
Methane carboxylic acid, see ACETIC ACID, 1603
Methanoic acid, see FORMIC ACID, 2011
METHANOL, 2000; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
Methiocarb, see ORGANONITROGEN PESTICIDES, 5601
Methomyl, see ORGANONITROGEN PESTICIDES, 5601
2-Methoxy-2-methyl propane, see METHYL *tert*-BUTYL ETHER, 1615
2-Methoxyacetate, see METHYL CELLOSOLVE ACETATE, 1451
2-Methoxybenzenamine, see ANISIDINE, 2514
4-Methoxybenzeamine, see ANISIDINE, 2514
Methoxycarbonylethylene, see METHYL ACRYLATE, 2552
2-Methoxyethanol, see ALCOHOLS IV, 1403
1-Methoxy-2-propanol, see GLYCOL ETHERS, 2554
1-Methoxy-2-propylacetate, see GLYCOL ETHERS, 2554
METHYLAL, 1611
METHYL ACETATE, 1458
METHYL ACRYLATE, 1459; 2552
Methyl alcohol, see METHANOL, 2000
4-methylbenzensulfonic acid, see *p*-TOLUENESULFONIC ACID, 5043
Methyl-(*n*-amyl)-ketone, see KETONES II, 1301; KETONES II, 2553
Methylarsonic acid, see ARSENIC, ORGANO-, 5022
Methylbenzene, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126°C, 1500; TOLUENE, 4000; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002
4-Methyl-1,3-benzenediamine, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
2-Methyl-1,3-benzenediamine, see 2,4- AND 2,6-TOLUENEDIAMINE, 5516
METHYL BROMIDE, 2520
3-Methyl-1-butanol, see ALCOHOLS III, 1402
Methyl *n*-butyl ketone, see KETONES I, 1300
Methyl cellosolve, see ALCOHOLS IV, 1403
METHYL CELLOSOLVE ACETATE, 1451
METHYL CHLORIDE, 1001
Methyl ethanoate, see METHYL ACETATE, 1458

Methylchloroform, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Methyl cyanide, see ACETONITRILE, 1606
Methylcyclohexane, see HYDROCARBONS, BP 36-126°C, 1500
METHYLCYCLOHEXANOL, 1404
METHYLCYCLOHEXANONE, 2521
2-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
3-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
4-Methylcyclohexanone, see METHYLCYCLOHEXANONE, 2521
4,4'-Methylenebis(2-chloroaniline) in urine, see MBOCA in urine, 8302
METHYLENE CHLORIDE, 1005; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
4,4'-METHYLENEDIANILINE, 5029
4,4'-Methylenediphenyldiisocyanate (MDI), see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
(1-Methylethenyl)-benzene, see HYDROCARBONS, AROMATIC, 1501
METHYL ETHYL KETONE, 2500; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002; KETONES I, 2555
METHYL ETHYL KETONE PEROXIDE, 3508
METHYL and ETHYL METHACRYLATE, 2537
5-Methyl-3-heptanone, see KETONES II, 1301; KETONES II, 2553
Methyl hippuric acid in urine, see HIPPURIC and METHYL HIPPURIC ACIDS in urine, 8301
METHYL IODIDE, 1014
Methyl isoamyl acetate, see ESTERS I, 1450
Methyl isobutyl acetate, see ISOPROPYL ACETATE, 1454
Methyl isobutyl carbinol, see ALCOHOLS III, 1402; ALCOHOLS COMBINED, 1405
Methyl isobutyl ketone, see KETONES I, 1300; 2555; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
2-Methyllactonitrile, see ACETONE CYANOHYDRIN, 2506
METHYL METHACRYLATE, 2537; see METHYL and ETHYL METHACRYLATE, 2537
Methyl-2-methyl-2-propeonate, see METHYL and ETHYL METHACRYLATE, 2537
Methyl parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
m-Methylnitrobenzene, see NITROAROMATIC COMPOUNDS, 2005
o-Methylnitrobenzene, see NITROAROMATIC COMPOUNDS, 2005
p-Methylnitrobenzene, see NITROAROMATIC COMPOUNDS, 2005
Methyloxirane, see PROPYLENE OXIDE, 1612
4-Methyl-2-pentanol, see ALCOHOLS III, 1402
4-Methyl-2-pentanone, see KETONES I, 1300
4-Methyl-3-penten-2-one, see KETONES II, 1301; KETONES II, 2553
2-Methylphenol, see CRESOLS and PHENOL, 2546; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
3-Methylphenol, see CRESOLS and PHENOL, 2546; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
4-Methylphenol, see CRESOLS and PHENOL, 2546; PHENOL and *p*-CRESOL in urine, 8305; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
2-Methyl-1-propanol, see ALCOHOLS II, 1401
Methyl hydrazine, see MONOMETHYL HYDRAZINE, 3510
Methyl propenoate, see METHYL ACRYLATE, 1459; 2552
2-Methyl-2-propanol, see ALCOHOLS I, 1400
Methyl propyl ketone, see KETONES I, 1300
METHYL *tert*-BUTYL ETHER, 1615
Methylstyrene, see HYDROCARBONS, AROMATIC, 1501
α-Methylstyrene, see HYDROCARBONS, AROMATIC, 1501
METHYLTIN CHLORIDES, 5526
Methyltin trichloride, see METHYLTIN CHLORIDES, 5526
Methylvinylbenzene, see HYDROCARBONS, AROMATIC, 1501
Methyl viologen, see PARAQUAT, 5003
Metolachlor, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201
Mevinphos, see ORGANOPHOSPHORUS PECTICIDES, 5600
MIBC, see ALCOHOLS III, 1402
MIBK, see KETONES I, 1300
Mineral oil mist, see OIL MIST, MINERAL, 5026

Mineral spirits, see NAPHTHAS, 1550
Mineral wool fiber, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; ASBESTOS and OTHER FIBERS by PCM, 7400
MOCA in urine, see MBOCA in urine, 8302
Molybdenum, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303
Monobromethane, see METHYL BROMIDE, 2520
Monochloracetic acid, see CHLORACETIC ACID, 2008
Monochlorobenzene, see HYDROCARBONS, HALOGENATED, 1003
Monoethanolamine (MEA), see AMINOETHANOL COMPOUNDS II, 3509
MONOMETHYLHYDRAZINE, 3510
MTBE, see METHYL *tert*-BUTYL ETHER, 1615
Muriatic acid, see ACIDS, INORGANIC, 7903
Muthmann's liquid, see 1,1,2,2-TETRABROMOETHANE, 2003
Mycobacterium, see MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900; AEROBIC BACTERIA by GC-FAME, 0801
MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900

Naphthalene, see HYDROCARBONS, AROMATIC, 1501; POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
1-Naphthalenol *N*-methylcarbamate, see CARBARYL, 5006
NAPHTHAS (refined petroleum solvents), 1550
Napthene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
NAPHTHYLAMINES, 5518
α-Naphthylamine, see NAPHTHYLAMINES, 5518
β-Naphthylamine, see NAPHTHYLAMINES, 5518
1-Naphthylamine, see NAPHTHYLAMINES, 5518
2-Naphthylamine, see NAPHTHYLAMINES, 5518
NEODYMIUM, see ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303
NG, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
Nickel, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310, ELEMENTS on WIPES, 9102; ELEMENTS by ICP (Hot Block/HCl/HNO_3 Digestion), 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
NICKEL CARBONYL, 6007
NICOTINE, 2544
NICOTINE, 2551
Nitric acid, see ACIDS, INORGANIC, 7903
NITRIC OXIDE and NITROGEN DIOXIDE, 6014
2,2',2"-Nitrilotriethanol, see AMINOETHANOL COMPOUNDS II, 3509
p-NITROANILINE, 5033
4-Nitroaniline, see *p*-NITROANILINE, 5033
NITROAROMATIC COMPOUNDS, 2005
Nitrobenzol, SEE ANILINE, *o*-TOLUIDINE, and NITROBENZENE, 2017; NITROAROMATIC COMPOUNDS, 2005
Nitrocarbol, see NITROMETHANE, 2527
p-Nitrochlorobenzene, see NITROAROMATIC COMPOUNDS, 2005
NITROETHANE, 2526
Nitrogen dioxide, see NITROGEN DIOXIDE (passive), 6700; NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen monoxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014
Nitrogen peroxide, see NITRIC OXIDE and NITROGEN DIOXIDE, 6014; NITROGEN DIOXIDE (passive), 6700
NITROGYLCERIN and ETHYLENE GLYCOL DINITRATE, 2507
NITROMETHANE, 2527
2-NITROPROPANE, 2528
1-NITROPYRENE in Diesel Particulates, 2560
NITROSAMINES, 2522
N-METHYL-2-PYRROLIDINONE, 1302
N-methyl-y-butyrolactone, see N-METHYL-2-PYRROLIDINONE, 1302
NMP, see *N*-METHYL-2-PYRROLIDINONE, 1302
N-Nitrosodibutylamine, see NITROSAMINES, 2522

N-Nitrosodiethylamine, see NITROSAMINES, 2522
N-Nitrosodimethylamine, see NITROSAMINES, 2522
N-Nitrosodiopropylamine, see NITROSAMINES, 2522
N-Nitrosomorpholine, see NITROSAMINES, 2522
N-Nitrosopiperidine, see NITROSAMINES, 2522
N-Nitrosopyrrolidine, see NITROSAMINES, 2522
Nitrotoluene, see NITROAROMATIC COMPOUNDS, 2005
NITROUS OXIDE, 6600; see ORGANIC and INORGANIC GASES, 3800
Nonanal, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Nonane, see HYDROCARBONS, BP 36-216°C, 1500
Nonanedioic acid, see AZELAIC ACID, 5019
Nuisance dust, respirable, see PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE, 0600
Nuisance dust, total, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500

Octalene, see ALDRIN and LINDANE, 5502
n-Octane, see HYDROCARBONS, BP 36-126°C, 1500; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Octachlor, see CHLORDANE, 5510
Octamethylcyclotetrasiloxane, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Octane, see HYDROCARBONS, BP 36-216°C, 1500
1-OCTANETHIOL, 2510
n-Octanethiol, see 1-OCTANETHIOL, 2510
Octylmercaptan, see 1-OCTANETHIOL, 2510
Octyl thiol, see 1-OCTANETHIOL, 2510
OIL MIST, MINERAL, 5026
Oil of turpentine, see TURPENTINE, 1551
Oil of vitriol, see ACIDS, INORGANIC, 7903
Oleum, see ACIDS, INORGANIC, 7903
ORGANIC and INORGANIC GASES, 3800
ORGANONITROGEN PESTICIDES, 5601
ORGANOPHOSPHORUS PESTICIDES, 5600
ORGANOTIN COMPOUNDS, 5504
ortho-Phosphoric acid, see ACIDS, INORGANIC, 7903
Oxamyl, see ORGANONITROGEN, 5601
Oxirane, see ETHYLENE OXIDE, 1614; ETHYLENE OXIDE, 3702
Oxiranemethanol, see GLYCIDOL, 1608
1,1'-Oxybisbenzene, see PHENYL ETHER, 1617
1,1'-Oxybis(2-chloroethane), see *sym*-DICHLOROETHYL ETHER, 1004
1,1'-Oxybisethane, see ETHYL ETHER, 1610
2,2'-Oxydiethanol, see GLYCOLS, 5523
OXYGEN, 6601

PAC, see POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs), 5800; POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
PAH, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
PALLADIUM, see ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303
PARAQUAT, 5003
Parathion, see ORGANOPHOSPHORUS PESTICIDES, 5600
Pb, see LEAD, 7082 (FAAS); 7105 (GFAAS); (Spot test), 7700; (ULTRASOUND/ASV), 7701; (Portable XRF), 7702; (Surface wipes), 9100; ELEMENTS by ICP, 7300; LEAD in blood and urine, 8003
PbB, see LEAD in blood and urine, 8003
PCB, see POLYCHLOROBIPHENYLS, 5503; POLYCHLOROBIPHENYLS in serum, 8004
PCP, see PENTACHLOROPHENOL, 5512; PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303
PCT, see CHLORINATED TERPHENYL, 5014
Pelargonic aldehyde, see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Pentabromophenyl ether, see DECABROMODIPHENYL OXIDE, 2559
Pentachlorobenzene, see POLYCHLOROBENZENES, 5517
PENTACHLOROETHANE, 2517
PENTACHLOROPHENOL, 5512

PENTACHLOROPHENOL in blood, 8001
PENTACHLOROPHENOL in urine, 8303
Pentaerythritol, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500; RESPIRABLE, 0600
Penta, see PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303
PENTACHLOROPHENOL, 5512, see also PENTACHLOROPHENOL in blood, 8001; PENTACHLOROPHENOL in urine, 8303
Pentanal, see VALERALDEHYDE, 2536; ALDEHYDES SCREENING, 2539
n-Pentane, see HYDROCARBONS, BP 36-126°C, 1500; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
2-Pentanone, see KETONES I, 1300; 2555
Perchlorobutadiene, see HEXACHLOROBUTADIENE, 2543
Perchlorocyclopentadiene, see HEXACHLORO-1,3-CYCLOPENTADIENE, 2518
Perchloroethane, see HYDROCARBONS, HALOGENATED, 1003
Perchloroethylene, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
PERCHLOROETHYLENE (portable GC) in exhaled breath and air, 3704
Petroleum ether, see NAPHTHAS, 1550
Petroleum naphtha, see NAPHTHAS, 1550
Phenanthrene, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
Phenol, see CRESOLS and PHENOL, 2546; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
PHENOL and *p*-CRESOL in urine, 8305
Phenyl chloride, see HYDROCARBONS, HALOGENATED, 1003
PHENYL ETHER, 1617
PHENYL ETHER - DIPHENYL MIXTURE, 2013
PHENYL GLYCIDYL ETHER, 1619
PHENYLHYDRAZINE, 3518
Phenoxypropane oxide, see PHENYL GLYCIDYL ETHER, 1619
2,3-Phenylenepyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Phenylphosphonothioic acid *O*-ethyl *O*-*p*-nitrophenyl ester, see EPN, 5012
Phorate, see ORGANOPHOSPHORUS PESTICIDES, 5600
Phosdrin, see ORGANOPHOSPHORUS PESTICIDES, 5600
Phosphoric acid, see ACIDS, INORGANIC, 7903
Phosphoric acid dibutyl ester, see DIBUTYL PHOSPHATE, 5017
Phosphoric acid tributyl ester, see TRIBUTYL PHOSPHATE, 5034
Phosphoric acid triorthocresyl ester, see TRIORTHOCRESYL PHOSPHATE, 5037
Phosphoric acid triphenyl phosphate, see TRIPHENYL PHOSPHATE, 5038
Phosphorothioic acid *O,O*-diethyl *O*-[2-(ethylthio)ethyl]ester mixture with *O,O*-diethyl-*S*-[2-ethylthio) ethyl]phosphorothioate, see DEMETON, 5514
Phosphorothioic acid *O,O*-diethyl *O*-(4-nitrophenyl)ester, see ORGANOPHOSPHORUS PESTICIDES, 5600
PHOSPHORUS, 7905; ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; Hot Block/HCl/HNO_3 Digestion, 7303; ELEMENTS on WIPES, 9102
PHOSPHORUS TRICHLORIDE, 6402
Phthalic acid dibutyl ester, see DIBUTYL PHTHALATE, 5020
Pinene, see TURPENTINE, 1551; TERPENES, 1552; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
Plaster of Paris, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Platinum, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303
Plictran, see ORGANOTIN COMPOUNDS, 5504
PNA (obsolete term), see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
POLYCHLORINATED BIPHENYLS in serum, 8004
POLYCHLOROBENZENES, 5517
POLYCHLOROBIPHENYLS, 5503
Polychloroterphenyl, see CHLORINATED TERPHENYL, 5014
POLYCYCLIC AROMATIC COMPOUNDS, TOTAL (PACs), 5800
POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
Portland cement, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
POTASSIUM, see ELEMENTS by ICP, Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; Hot Block/HCl/HNO_3 Digestion, 7303
Potassium cyanide, see CYANIDES, 7904
Potassium hydroxide, see ALKALINE DUSTS, 7401

Progesterone, see ESTROGENIC COMPOUNDS, 5044
1,2-Propanediol, see GLYCOLS, 5523
1,2,3-Propanetriol trinitrate, see NITROGLYCERIN and ETHYLENE GLYCOL DINITRATE, 2507
1-Propanol, see ALCOHOLS II, 1401
2-Propanol, see ALCOHOLS I, 1400
2-Propanone, see KETONES I, 1300
Propazine, see TRIAZINE HERBICIDES and their METABOLITES, 8315
2-Propenal, see ACROLEIN, 2501
2-Propenoic acid methyl ester, see METHYL ACRYLATE, 1459
Propham, see ORGANONITROGEN PESTICIDES, 5601
Propionaldehyde, see ALDEHYDES, SCREENING, 2539; ALIPHATIC ALDEHYDES, 2018
2-Propenenitrile, see ACRYLONITRILE, 1604
2-Propenoic acid ethyl ester, see ESTERS I, 1450
2-Propen-1-ol, see ALCOHOLS III, 1402
n-Propyl acetate, see ESTERS I, 1450
n-Propyl alcohol, see ALCOHOLS COMBINED, 1405
Propylene aldehyde, see CROTONALDEHYDE, 3516
PROPYLENE DICHLORIDE, 1013
Propylene glycol, see GLYCOLS, 5523
Propylene glycol monomethyl ether, see GLYCOL ETHERS, 2554
Propylene glycol monomethyl ether acetate, see GLYCOL ETHERS, 2554
Propoxur, see ORGANONITROGEN PESTICIDES, 5601
PROPYLENE OXIDE, 1612 Prussic acid, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904
Pyrene, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
Pyrethrin I, II, see PYRETHRUM, 5008
PYRETHRUM, 5008
PYRIDINE, 1613
Pyrophosphoric acid tetraethyl ester, see TETRAETHYL PYROPHOSPHATE, 2504

Quartz, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); QUARTZ in coal mine dust, 7603
Quicklime, see CALCIUM, 7020
Quicksilver, see MERCURY, 6009

Refrigerant 11, see FLUOROTRICHLOROMETHANE, 1006
Refrigerant 12, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, CHLORODIFLUOROMETHANE, 1018
Refrigerant 13B1, see TRIFLUOROBROMOMETHANE, 1017
Refrigerant 13B2, see DIFLUORODIBROMOMETHANE, 1012
Refrigerant 21, see DICHLOROFLUOROMETHANE, 2516
Refrigerant 112, see 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016
Refrigerant 112a, see 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016
Refrigerant 113, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Refrigerant 114, see DICHLORODIFLUOROMETHANE, 1,2-DICHLOROTETRAFLUOROETHANE, and CHLORODIFLUOROMETHANE, 1018
RESORCINOL, 5701
RIBAVIRIN, 5027
Ronnel, see ORGANOPHOSPHORUS PESTICIDES, 5600
ROTENONE, 5007
Rouge, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Rubber solvent, see NAPHTHAS, 1550

Selenium, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; Hot Block/HCl/HNO_3 Digestion, 7303; ELEMENTS on WIPES, 9102
Serpentine, see ASBESTOS (bulk) by PLM, 9002; ASBESTOS FIBERS by TEM, 7402; ASBESTOS and OTHER FIBERS by PCM, 7400
Sevin, see CARBARYL, 5006
SILICA, AMORPHOUS (XRD), 7501

SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); SILICA in coal mine dust, 7603 (IR); SILICA, CRYSTALLINE by XRD, 7500
Silica aerogel, see SILICA, AMORPHOUS, 7501
Silicic anhydride, see SILICA, AMORPHOUS, 7501
Silicon, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Silicon carbide, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Silicon dioxide, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR); SILICA in coal mine dust, 7603
Silver, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301, Nitric/Perchloric Acid Ashing, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102
Simazine, see CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING), 5602; (HAND WASH), 9200; (DERMAL PATCH), 9201; TRIAZINE HERBICIDES and their METABOLITES, 8315
Soda lime, see ALKALINE DUSTS, 7401
Sodium fluoride, see FLUORIDES by ISE, 7902; 7906 (IC)
Sodium hexafluoroaluminate, see FLUORIDES by ISE, 7902; 7906 (IC)
Sodium hydroxide, see ALKALINE DUSTS, 7401
Sodium, see ELEMENTS by ICP, 7300; Hot Block/HCl/HNO_3 Digestion, 7303
Stannane, chlorotributyl-, see ORGANOTIN COMPOUNDS, 5504
Stannane, tetrabutyl-, see ORGANOTIN COMPOUNDS, 5504
Stannane, tricyclohexylhydroxy-; see ORGANOTIN COMPOUNDS, 5504
Starch, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
STIBINE, 6008
Stoddard solvent, see NAPHTHAS, 1550
Strontium, see ELEMENTS by ICP, Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; Hot Block/HCl/HNO_3 Digestion, 7303; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102
Strychnidin-10-one, see STRYCHNINE, 5016
STRYCHNINE, 5016
Styrene, see HYDROCARBONS, AROMATIC, 1501
Sucrose, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
SULFUR DIOXIDE, 6004
Sulfuric acid, see ACIDS, INORGANIC, 7903
SULFURYL FLUORIDE, 6012
Systox, see DEMETON, 5514

2,4,5-T, see 2,4-D and 2,4,5-T, 5001
TB, see MYCOBACTERIUM TUBERCULOSIS, AIRBORNE, 0900
TC, see ORGANOTIN COMPOUNDS, 5504
TCHH, see ORGANOTIN COMPOUNDS, 5504
2,4-TDA, see 2,4- and 2,6-TOLUENEDIAMINE, 5516
2,6-TDA, see 2,4- and 2,6-TOLUENEDIAMINE, 5516
2,4-TDI, see TOLUENE-2,4-DIISOCYANATE, 2535; ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
2,6-TDI, see ISOCYANTES, MONOMER, 5521; ISOCYANATES, 5522
TEA, see AMINOETHANOL COMPOUNDS II, 3509
TeBT, see ORGANOTIN COMPOUNDS, 5504
TEG, see GLYCOLS, 5523
TEL, see TETRAETHYL LEAD (as Pb), 2534
Tellurium, see ELEMENTS by ICP, 7300; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
TEPP, see TETRAETHYL PYROPHOSPHATE, 2504
Terbufos, see ORGANOPHOSPHORUS PESTICIDES, 5600
TERPENES, 1552
o-TERPHENYL, 5021
Tetraboron carbide, see BORON CARBIDE, 7506
1,1,2,2-TETRABROMOETHANE, 2003
sym-Tetrabromoethane, see 1,1,2,2-TETRABROMOETHANE, 2003
Tetrabutyltin, see ORGANOTIN COMPOUNDS, 5504
1,2,4,5-Tetrachlorobenzene, see POLYCHLOROBENZENES, 5517
1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE, 1016

1,1,2,2-TETRACHLOROETHANE, 1019; 2562
Tetrachloroethylene, see HYDROCARBONS, HALOGENATED, 1003
Tetrachloroethylene; perc, see PERCHLOROETHYLENE (portable GC) in exhaled breath and air, 3704
Tetrachloromethane, see HYDROCARBONS, HALOGENATED, 1003
TETRAETHYL LEAD (as Pb), 2533
TETRAETHYL PYROPHOSPHATE, 2504
Tetrafluoroethylene, see ORGANIC and INORGANIC GASES, 3800
Tetrahydrobenzene, see HYDROCARBONS, BP 36-126°C, 1500
TETRAHYDROFURAN, 1609; see ORGANIC and INORGANIC GASES, 3800
TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM CHLORIDE, 5046
TETRAMETHYL LEAD (as Pb), 2534
TETRAMETHYL THIOUREA, 3505
Tetramethylthioperoxydicarbonic diamide, see THIRAM, 5005
Tetramethylthiuram disulfide, see THIRAM, 5005
Tetraphene, see POLYNUCLEAR AROMATIC HYDROCARBONS, 5506 (HPLC); 5515 (GC)
Thallium, see ELEMENTS, 7300; ELEMENTS in blood or tissue, 8005; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
THF, see TETRAHYDROFURAN, 1609
Thiobencarb, see ORGANONITROGEN PESTICIDES, 5601
Thiophenate methyl, see CAPTAN and THIOPHENATE METHYL on Dermal Patch, 9205; Handrinse, 9202; in Air, 5606
THIRAM, 5005
Tin, see METALS in urine, 8310; ORGANOTIN COMPOUNDS, 5504; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Titanium, see ELEMENTS, 7300; METALS in urine, 8310, ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Titanium dioxide, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
TML, see TETRAMETHYL LEAD (as Pb), 2534
o-Tolidine, see DYES, 5013
p-TOLUENESULFONIC ACID, 5043
TOLUENE, 4000; see HYDROCARBONS, BP 36-126°C, 1500; HYDROCARBONS, AROMATIC, 1501; METHYL ETHYL KETONE, ETHANOL, and TOLUENE in blood, 8002; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
2,4- and 2,6-TOLUENEDIAMINE, 5516
TOLUENE-2,4-DIISOCYANATE, 2535; see ISOCYANATES MONOMER, 5521; ISOCYANATES, 5522
Toluene 2,6-TDI, see ISOCYANATES, MONOMER, 5521; ISOCYANATES, 5522
o-Toluidine, see AMINES, AROMATIC, 2002
o-Tolyl phosphate, see TRIORTHOCRESYL PHOSPHATE, 5037
Topsin-M, see CAPTAN and THIOPHENATE-METHYL, 9205
Toxaphene, see CHLORINATED CAMPHENE, 5039
Toxilis anhydride, see MALEIC ANHYDRIDE, 3512
Toxichlor, see CHLORDANE, 5510
Transformer oil, see OIL MIST, MINERAL, 5026
Tremolite, see ASBESTOS and OTHER FIBERS, 7400; ASBESTOS FIBERS by TEM, 7402; ASBESTOS (bulk) by PLM, 9002
TRIAZINE HERBICIDES and their METABOLITES in urine, 8315
Tribromomethane, see HYDROCARBONS, HALOGENATED, 1003
Tributyltin chloride, see ORGANOTIN COMPOUNDS, 5504
TRIBUTYL PHOSPHATE, 5034
1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
1,2,4-Trichlorobenzene, see POLYCHLOROBENZENES, 5517
1,1,1-Trichloroethane, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
1,1,2-Trichloroethane, see HYDROCARBONS, HALOGENATED, 1003
Trichloroethene, see TRICHLOROETHYLENE, 1022; 3701 (portable GC)
TRICHLOROETHYLENE, 1022; 3701 (portable GC); see ORGANIC and INORGANIC GASES, 3800
Trichlorofluoromethane, see FLUOROTRICHLOROMETHANE, 1006
Trichloromethane, see HYDROCARBONS, HALOGENATED, 1003

Trichloromethylstannane, see METHYLTIN CHLORIDES, 5526
(2,4,5-Trichlorophenoxy) acetic acid, see 2,4-D and 2,4,5-T, 5001
1,2,3-Trichloropropane, see HYDROCARBONS, HALOGENATED, 1003
Tricyclohexyltin hydroxide, see ORGANOTIN COMPOUNDS, 5504
Tridymite, see SILICA, CRYSTALLINE (XRD), 7500; 7601 (VIS); 7602 (IR)
Triethanolamine, see AMINOETHANOL COMPOUNDS II, 3509
Triethylene glycol, see GLYCOLS, 5523
TRIETHYLENETETRAMINE, see ETHYLENEDIAMINE, DIETHYLENETRIAMINE and TRIETHYLENETERAMINE, 2540
TRIFLUOROBROMOMETHANE, 1017
Trimellitic acid-1,2-anhydride, see TRIMELLITIC ANHYDRIDE, 5036
TRIMELLITIC ANHYDRIDE, 5036
3,3,5-Trimethyl-2-cyclohexen-1-one, see ISOPHORONE, 2508; 2556
Trimethyltin chloride, see METHYLTIN CHLORIDES, 5526
2,4,7-TRINITROFLUOREN-9-ONE, 5018
TRIORTHOCRESYL PHOSPHATE, 5037
o-Triphenyl, see *o*-TERPHENYL, 5021
TRIPHENYL PHOSPHATE, 5038
TRIPHENYLTIN CHLORIDE, 5527
Trolene, see ORGANOPHOSPHORUS PESTICIDES, 5600
TTE, see 1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE, 1020
Tubatoxin, see ROTENONE, 5007
TUNGSTEN (soluble and insoluble), 7404; see ELEMENTS by ICP, Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
TURPENTINE, 1551; see VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549

Undecane, see HYDROCARBONS, BP 36-126°C, 1500

VALERALDEHYDE, 2536; see ALDEHYDES, SCREENING, 2539; ALIPHATIC ALDEHYDES, 2018
Vanadic anhydride, see VANADIUM OXIDES, 7504
Vanadic oxide, see VANADIUM OXIDES, 7504
Vanadium, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
VANADIUM OXIDES, 7504
Vanadium pentoxide, see VANADIUM OXIDES, 7504
Vanadium sesquioxide, see VANADIUM OXIDES, 7504
Vanadium trioxide, see VANADIUM OXIDES, 7504
Vegetable oil mists (except castor, cashew nut or similar irritant oils), see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Vikane, see SULFURYL FLUORIDE, 6012
VINYL ACETATE, 1453
Vinylbenzene, see HYDROCARBONS, AROMATIC, 1501
VINYL BROMIDE, 1009
VINYL CHLORIDE, 1007
Vinyl cyanide, see ACRYLONITRILE, 1604
VINYLIDENE CHLORIDE, 1015
Vinylidene fluoride, see ORGANIC and INORGANIC GASES, 3800
Vinyl trichloride, see HYDROCARBONS, HALOGENATED, 1003
Vinyltoluene, see HYDROCARBONS, AROMATIC, 1501
VM&P naphta, see NAPHTHAS, 1550
Virazole, see RIBAVIRIN, 5027
VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549

WARFARIN, 5002
Wolfram, see TUNGSTEN, 7074
Wood alcohol, see METHANOL, 2000
Wood turpentine, see TURPENTINE, 1551

Xylene, see HYDROCARBONS, AROMATIC, 1501; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
2,4-Xylidene, see AMINES, AROMATIC, 2002

Yttrium, see ELEMENTS by ICP, 7300; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300

ZINC, 7030, see ELEMENTS by ICP, 7300; ELEMENTS in blood or tissue, 8005; METALS in urine, 8310; ELEMENTS on WIPES, 9102; ELEMENTS by ICP, Hot Block/HCl/HNO_3 Digestion, 7303; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300
Zincite, see ZINC OXIDE (XRD), 7502
ZINC OXIDE, 7502, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600; ZINC (FAAS), 7030
Zinc stearate, see PARTICULATES NOT OTHERWISE REGULATED, TOTAL, 0500; RESPIRABLE, 0600
Zinc white, see ZINC OXIDE (XRD), 7502
Zirconium, see ELEMENTS by ICP, 7300; Aqua Regia Ashing, 7301; Nitric/Perchloric Acid Ashing, 7300; ELEMENTS in blood or tissue, 8005; ELEMENTS on WIPES, 9102

CAS # 50-00-0, see ORGANIC and INORGANIC GASES, 3800; see FORMALDEHYDE (DNPH Cartridge), 2016; FORMALDEHYDE (2-HMP), 2541; (chromotropic acid), 3500; ALDEHYDES, SCREENING, 2539
CAS # 50-28-2, see ESTROGENIC COMPOUNDS, 5044
CAS # 50-32-8, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 50-50-0, see ESTROGENIC COMPOUNDS, 5044
CAS # 53-16-7, see ESTROGENIC COMPOUNDS, 5044
CAS # 53-70-3, see POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC), 5506; 5515 (GC)
CAS # 54-11-5, see NICOTINE, 2551; NICOTINE, 2544
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 # 57-83-0, see ESTROGENIC COMPOUNDS, 5044
CAS # 58-89-9, see ALDRIN and LINDANE, 5502
CAS # 59-89-2, see NITROSAMINES, 2522
CAS # 60-29-7, see ETHYL ETHER, 1610
CAS # 60-34-4, see MONOMETHYL HYDRAZINE, 3510
CAS # 62-53-3, see AMINES, AROMATIC, 2002
CAS # 62-75-9, see NITROSAMINES, 2522
CAS # 63-25-2, see CARBARYL, 5006; ORGANONITROGEN PESTICIDES, 5601
CAS # 64-17-5, see ALCOHOLS I, 1400; 2-BUTANONE, ETHANOL, and TOLUENE in blood, 8002; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS # 64-18-6, see FORMIC ACID, 2011
CAS # 64-19-7, see ACETIC ACID, 1603
CAS # 66-25-1, see ALDEHYDES, SCREENING, 2539; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS # 67-56-1, see METHANOL, 2000; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
CAS # 67-63-0, see ALCOHOLS I, 1400; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS # 67-64-1, see KETONES I, 1300; 2555; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
CAS # 67-66-3, see HYDROCARBONS, HALOGENATED, 1003
CAS # 67-72-1, see HYDROCARBONS, HALOGENATED, 1003
CAS # 68-12-2, see DIMETHYLFORMAMIDE, 2004
CAS # 71-23-8, see ALCOHOLS II, 1401; ALCOHOLS COMBINED, 1405
CAS # 71-36-3, see ALCOHOLS II, 1401; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ALCOHOLS COMBINED, 1405

CAS # 71-43-2, see HYDROCARBONS, AROMATIC, 1501; HYDROCARBONS, BP 36-126°C, 1500; BENZENE by portable GC, 3700; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549; ORGANIC and INORGANIC GASES, 3800
CAS # 71-55-6, see HYDROCARBONS, HALOGENATED, 1003; VOLATILE ORGANIC COMPOUNDS (SCREENING), 2549
CAS # 72-20-8, see ENDRIN, 5519
CAS # 74-83-9, see METHYL BROMIDE, 2520
CAS # 74-87-3, see METHYL CHLORIDE, 1001
CAS # 74-88-4, see METHYL IODIDE, 1014
CAS # 74-90-8, see HYDROGEN CYANIDE, 6010; CYANIDES, 7904; HYDROGEN CYANIDE, 6017
CAS # 74-93-1, see MERCAPTANS, METHYL-, ETHYL- and *n*-BUTYL, 2542
CAS # 74-96-4, see ETHYL BROMIDE, 1011
CAS # 74-97-5, see HYDROCARBONS, HALOGENATED, 1003
CAS # 75-00-3, see ETHYL CHLORIDE, 2519
CAS # 75-01-4, see VINYL CHLORIDE, 1007
CAS # 75-05-8, see ACETONITRILE, 1606
CAS # 75-07-0, see ACETALDEHYDE, (GC), 2538; (SCREENING), 2539; 3507 (HPLC); ALIPHATIC ALDEHYDES, 2018
CAS # 75-08-1, see MERCAPTANS, METHYL-, ETHYL, and *n*-BUTYL, 2542
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