TABLE 2

EXAMPLE LOWER LIMITS OF QUANTITATION FOR SEMIVOLATILE ORGANICS

	Lower Limits of Quantitation[a]	
Compound	Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Lower Limits of Quantitation[a] Low Soil/Sediment[b] (µg/kg)
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND

TABLE 2
(continued)

	Lower Limits of Quantitation[a]	
Compound	Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND

TABLE 2
(continued)

	Lower Limits of Quantitation[a]	
Compound	Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-Methylcholanthrene	10	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Lower Limits of Quantitation[a] Low Soil/Sediment[b] (µg/kg)
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND

TABLE 2
(continued)

[a] Sample lower limits of quantitation are highly matrix-dependent and those listed here are provided for guidance and may not always be achievable.

[b] Lower limits of quantitation listed for soil/sediment are based on wet weight. When data are reported on a dry weight basis, the lower limits will be higher based on the % dry weight of each sample. These lower limits are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined

NA = Not Applicable

<u>Other Matrices</u>	<u>Factor</u>[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c] Lower limit of quantitation = (Lower limit of quantitation for low soil/sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	10-80% of Base Peak
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of Base Peak
197	< 2% of mass 198
198	Base peak, or > 50% of Mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	> 1% of mass 198
441	present but < 24% of mass 442
442	Base Peak, or > 50% of mass 198
443	15-24% of mass 442

[a] The majority of the data are taken from Reference 13 (Method 525.2).

[b] The criteria in this table are intended to be used as default criteria for quadrupole instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 4

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION USING THE SUGGESTED IONS FROM TABLE 1

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethylphenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
Fluoranthene	p-Dimethyl aminoazobenzene	7,12-Dimethylbenz(a) anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylcholanthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr) = surrogate

TABLE 6

EXAMPLE SINGLE LABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	$\bar{x}$ of 5 replicates (µg/L)	% Recovery of Avg.
Acenaphthene	50	46.7	93.4
Acenaphthylene	50	46.1	92.2
Aniline	50	8.3	16.7
Anthracene	50	48.4	96.8
Benzoic acid	50	43.7	87.4
Benz(a)anthracene	50	49.6	99.2
Benzo(b)fluoranthene	50	49.8	99.6
Benzo(k)fluoranthene	50	50.6	101
Benzo(a)pyrene	50	47.7	95.5
Benzo(g,h,i)perylene	50	52.6	105
Benzyl alcohol	50	44.4	88.8
Bis(2-chloroethyl) ether	50	44.2	88.4
Bis(2-chloroethoxy)methane	50	46.6	93.1
Bis(2-chloroisopropyl) ether	50	43.4	86.8
Bis(2-ethylhexyl) phthalate	50	50.2	100
4-Bromophenyl phenyl ether	50	48.6	97.2
Butyl benzyl phthalate	50	49.6	99.3
Carbazole	50	52.1	104
2-Chloroaniline	50	38.9	77.7
4-Chloro-3-methylphenol	50	47.3	94.6
2-Chloronaphthalene	50	45.3	90.8
2-Chlorophenol	50	43.1	86.2
4-Chlorophenyl phenyl ether	50	47.3	94.6
Chrysene	50	50.3	101
Dibenzofuran	50	47.4	94.7
Dibenz(a,h)anthracene	50	51.6	103
Di-n-butyl phthalate	50	50.5	101
1,2-Dichlorobenzene	50	35.8	71.6
1,3-Dichlorobenzene	50	33.3	66.7
1,4-Dichlorobenzene	50	34.4	68.7
3,3'-Dichlorobenzidine	50	32.0	64.0
2,4-Dichlorophenol	50	47.4	94.8
Diethyl phthalate	50	50.0	99.9
Dimethyl phthalate	50	48.5	97.0
2,4-Dimethylphenol	50	31.2	62.3
4,6-Dinitro-2-methylphenol	50	57.6	115
2,4-Dinitrophenol	50	58.7	117
2,4-Dinitrotoluene	50	51.3	103

TABLE 6
(continued)

Compound	Test conc. (μg/L)	$\bar{x}$ of 5 replicates (μg/L)	% Recovery of Avg.
2,6-Dinitrotoluene	50	50.2	100
Di-n-octyl phthalate	50	51.1	102
Fluoranthene	50	51.0	102
Fluorene	50	48.5	97.0
Hexachlorobenzene	50	49.0	97.9
Hexachlorobutadiene	50	34.7	69.5
Hexachlorocyclopentadiene	50	1.9	3.8
Hexachloroethane	50	29.9	58.8
Indeno(1,2,3-cd)pyrene	50	51.7	103
Isophorone	50	47.1	94.3
2-Methylnaphthalene	50	44.7	89.4
2-Methylphenol	50	41.7	83.4
4-Methylphenol	50	42.6	85.2
Naphthalene	50	43.4	86.8
2-Nitroaniline	50	48.4	96.7
3-Nitroaniline	50	46.8	93.6
4-Nitroaniline	50	56.1	112
Nitrobenzene	50	47.1	94.1
2-Nitrophenol	50	47.3	94.6
4-Nitrophenol	50	55.4	111
N-Nitrosodiphenylamine	50	46.7	93.4
N-Nitroso-di-propylamine	50	44.6	89.3
Pentachlorophenol	50	56.9	114
Phenanthrene	50	49.7	99.4
Phenol	50	40.9	81.8
Pyrene	50	49.2	98.4
1,2,4-Trichlorobenzene	50	39.1	78.2
2,4,5-Trichlorophenol	50	47.7	95.4
2,4,6-Trichlorophenol	50	49.2	98.4

$\bar{x}$ = Average recovery for five initial demonstration of capability measurements, in μg/L

[a] Extraction using acidic pH only with a modified continuous liquid-liquid extractor with hydrophobic membrane according to Method 3520. <u>These values are for guidance only. Appropriate derivation of acceptance criteria for similar extraction conditions may result in much different recovery ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.</u>

TABLE 7

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

	Percent Recovery, Day 0		Percent Recovery, Day 7	
Compound	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 8

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANIC FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

	Clay Soil		Topsoil	
Compound	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

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[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 9

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8

Compound	Mean Recovery	RSD
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenz(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 10

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	% RSD
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 10 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 11

PRESSURIZED FLUID EXTRACTION (METHOD 3545) RECOVERY VALUES AS PERCENT OF SOXTEC™

	Clay			Loam			Sand			Mean
Compound	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	102.0
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	101.9
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	101.6
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	120.6
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	119.2
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	112.5
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	104.7
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	100.2
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	110.3
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	98.1
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	118.6
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	100.2
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	101.7
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	109.8
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	96.3
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	97.2
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	98.6
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	104.2
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	106.1
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	108.1
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	104.7
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	99.7
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	102.1
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	75.8
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	95.9
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	94.1
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	96.2
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	92.6
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	90.3
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	101.7
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	92.9
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	98.4
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	75.6
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	90.7

TABLE 11
(continued)

	Clay			Loam			Sand			Mean
Compound	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	98.8
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	94.4
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	95.4
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	99.1
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	96.8
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	95.8
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	93.7
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	81.2
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	100.6
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	101.2
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	99.1
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	102.7
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	105.2
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	116.5
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	101.5
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	102.9
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	99.0
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	103.1
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	99.9
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	102.7
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	98.6
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	66.4
Mean	95.1	94.3	101.0	95.5	96.5	104.1	113.0	100.9	92.5	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 12

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4 ± 8.2	29.55	91	10.5
2-Methylnaphthalene	62.1 ± 11.5	76.13	122	2.0
Acenaphthene	632 ± 105	577.28	91	2.9
Dibenzofuran	307 ± 49	302.25	98	4.1
Fluorene	492 ± 78	427.15	87	3.0
Phenanthrene	1618 ± 340	1278.03	79	3.4
Anthracene	422 ± 49	400.80	95	2.6
Fluoranthene	1280 ± 220	1019.13	80	4.5
Pyrene	1033 ± 285	911.82	88	3.1
Benz(a)anthracene	252 ± 8	225.50	89	4.8
Chrysene	297 ± 26	283.00	95	3.8
Benzo(a)pyrene	97.2 ± 17.1	58.28	60	6.5
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153 ± 22	130.88	86	10.7

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

TABLE 15

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS LOW SPIKE LEVEL

Analyte	Spike Level (μg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	3,750	63	10	63	9
Hexachloroethane	1,500	55	6	77	4
Nitrobenzene	1,000	82	10	100	5
Hexachlorobutadiene	250	65	3	56	4
2,4-Dinitrotoluene	65	89	4	101	5
Hexachlorobenzene	65	98	5	95	6
o-Cresol	100,000	83	10	85	5
m-Cresol*	100,000	86	8	85	3
p-Cresol*	100,000	*	*	*	*
2,4,6-Trichlorophenol	1,000	84	12	95	12
2,4,5-Trichlorophenol	200,000	83	11	88	3
Pentachlorophenol	50,000	82	9	78	9

Results from seven replicate spiked buffer samples.

* In this study, m-cresol and p-cresol co-eluted and were quantitated as a mixture of both isomers.

Data from Reference 12.

TABLE 16

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS HIGH SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	15,000	63	10	63	9
Hexachloroethane	6,000	54	7	46	7
Nitrobenzene	4,000	81	4	81	13
Hexachlorobutadiene	1,000	81	5	70	11
2,4-Dinitrotoluene	260	99	8	98	3
Hexachlorobenzene	260	89	8	91	9
o-Cresol*	400,000	92	15	90	4
m-Cresol*	400,000	95	8	82	6
p-Cresol*	400,000	82	14	84	7
2,4,6-Trichlorophenol	4,000	93	12	104	12
2,4,5-Trichlorophenol	800,000	93	14	97	23
Pentachlorophenol	200,000	84	9	73	8

Results from seven replicate spiked buffer samples.

* In this study, recoveries of these compounds were determined from triplicate spikes of the individual compounds into separate buffer solutions.

Data from Reference 12.

TABLE 17

RECOVERY DATA FROM THREE LABORATORIES FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP LEACHATES FROM SOIL SAMPLES

Buffer 1 pH = 2.886		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,000	86	8	7	35.3	0.7	3	7.6	6	3
m-Cresol**	--	77	8	7	--	--	--	--	--	--
p-Cresol**	--	--	--	--	--	--	--	7.7	11	3
2,4,6-Trichlorophenol	2,000	106	6	7	96.3	3.9	3	44.8	5	3
2,4,5-Trichlorophenol	400,000	93	3	7	80.5	4.5	3	63.3	11	3
Pentachlorophenol	100,000	79	2	7	33.8	12.2	3	29.2	13	3
1,4-Dichlorobenzene	7,500	51	5	7	81.3	5.3	3	19.2	7	3
Hexachloroethane	3,000	50	5	7	66.2	2.1	3	12.6	11	3
Nitrobenzene	2,000	80	8	7	76.3	5.3	3	63.9	12	3
Hexachlorobutadiene	500	53	8	7	63.3	4.8	3	9.6	9	3
2,4-Dinitrotoluene	130	89	8	7	35.7	2.6	3	58.2	17	3
Hexachlorobenzene	130	84	21	7	92.3	1.6	3	71.7	9	3

(continued)

TABLE 17
(continued)

Buffer 2 pH = 4.937		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,00	97	13	7	37.8	4.5	3	6.1	24	3
m-Cresol**	--	83	4	7	--	--	--	6.0	25	3
p-Cresol**	--	--	--	--	--	--	--	--	--	--
2,4,6-Trichlorophenol	2,000	104	4	7	91.7	8.0	3	37.7	25	3
2,4,5-Trichlorophenol	400,000	94	4	7	85.2	0.4	3	64.4	10	3
Pentachlorophenol	100,000	109	11	7	41.9	28.2	3	36.6	32	3
1,4-Dichlorobenzene	7,500	50	5	7	79.7	1.0	3	26.5	68	3
Hexachloroethane	3,000	51	3	7	64.9	2.0	3	20.3	90	3
Nitrobenzene	2,000	80	4	7	79.0	2.3	3	59.4	6	3
Hexachlorobutadiene	500	57	5	7	60	3.3	3	16.6	107	3
2,4-Dinitrotoluene	130	86	6	7	38.5	5.2	3	62.2	6	3
Hexachlorobenzene	130	86	7	7	91.3	0.9	3	75.5	5	3

* 250-mL aliquots of leachate were spiked. Lab 1 spiked at one-half these levels.

** m-Cresol and p-Cresol coelute. Lab 1 and Lab 3 reported o-Cresol and the sum of — and p-Cresol. Lab 2 reported the sum of all three isomers of Cresol.

Data from Reference 12.

TABLE 18

SINGLE-LABORATORY PAH ANALYSIS DATA FROM A REAL SOIL CONTAMINATED WITH CREOSOTE, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Concentration (µg/kg)	RSD (%)	REAC values (µg/kg)
Naphthalene	2,170	12.4	710,000
2-Methylnaphthalene	28,710	3.1	N/R
1-Methylnaphthalene	33,180	2.4	N/R
Biphenyl	13,440	6.0	N/R
2,6-Dimethylnaphthalene	52,990	3.8	N/R
Acenaphthylene	16,320	3.1	21,000
Acenaphthene	801,210	6.0	1,700,000
Fluorene	789,980	3.4	990,000
Phenanthrene	1,627,480	0.7	3,300,000
Anthracene	346,010	4.0	360,000
Benzo(a)anthracene	300,380	2.7	310,000
Fluoranthene	1,331,690	1.6	1,600,000
Pyrene	1,037,710	3.0	1,100,000
Chrysene	293,200	3.4	320,000
Benzo(b)fluoranthene	152,000	3.8	140,000
Benzo(k)fluoranthene	127,740	3.6	130,000
Benzo(e)pyrene	87,610	3.9	N/R
Benzo(a)pyrene	128,330	3.9	110,000
Perylene	35,260	4.3	N/R
Indeno(123-cd)pyrene	63,900	5.0	25,000
Dibenz(a,h)anthracene	17,290	6.9	N/R
Benzo(ghi)perylene	42,720	6.9	20,000

*n = 4

Soil samples obtained from US EPA Emergency Response Center archive bank through their contract laboratory REAC (Edison, NJ). The standard Soxhlet extraction procedures were performed by REAC three years earlier; this long storage period is believed to account for the low naphthalene recovery data in the present study

REAC data labeled N/R = not reported

TABLE 19

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-5 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	250	180 - 320	76
Acenaphthylene	150	*	107
Acenaphthene	230	130 - 330	61
Fluorene	400	300 - 500	63
Phenanthrene	5,200	4,200 - 6,200	72
Anthracene	380	230 - 530	84
Fluoranthene	8,400	5,800 - 10,000	81
Pyrene	5,800	4,000 - 7,600	69
Benzo(a)anthracene	2,900	1,700 - 4,100	53
Chrysene	2,800	1,900 - 3,700	76
Benzo(b)fluoranthene	2,000	1,000 - 3,000	84
Benzo(k)fluoranthene	1,000	600 - 1,400	137
Benzo(a)pyrene	1,700	900 - 2,500	52
Indeno(123-cd) pyrene	1,300	600 - 2,000	63
Dibenz(a,h)anthracene	200	100 - 300	125
Benzo(ghi)perylene	1,300	1000 - 1600	64

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 20

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-4 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (μg/kg)	Confidence Interval (μg/kg)	Recovery (%)
Naphthalene	150	*	54
Acenaphthylene	150	*	82
Acenaphthene	150	*	63
Fluorene	150	*	81
Phenanthrene	680	600 - 760	81
Anthracene	140	70 - 210	108
Fluoranthene	1250	1,150 - 1,350	84
Pyrene	940	820 - 1,060	85
Benzo(a)anthracene	530	470 - 580	78
Chrysene	650	570 - 730	84
Benzo(b)fluoranthene	700	550 - 850	84
Benzo(k)fluoranthene	360	310 - 410	156
Benzo(a)pyrene	650	570 - 730	73
Indeno(123-cd) pyrene	510	360 - 660	88
Dibenz(a,h)anthracene	120	70 - 170	117
Benzo(ghi)perylene	580	360 - 800	91

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 21

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-3 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	9,000	8300 - 9,700	61
Acenaphthylene	300	200 - 400	199
Acenaphthene	4,500	3,000 - 6,000	80
Fluorene	13,300	10,200 -16,400	58
Phenanthrene	85,000	65000 -105,000	87
Anthracene	13,400	12,900 -13,900	48
Fluoranthene	60,000	51,000-69,000	91
Pyrene	39,000	30,000-48,000	86
Benzo(a)anthracene	14,600	12,600-16,600	78
Chrysene	14,100	12,100-16,100	91
Benzo(b)fluoranthene	7,700	6,500-8,900	101
Benzo(k)fluoranthene	2,800	800-4,800	275
Benzo(a)pyrene	7,400	3,000-7,000	74
Indeno(123-cd)pyrene	5,400	4,100-6,700	100
Dibenz(a,h)anthracene	1,300	800-1,800	118
Benzo(ghi)perylene	5,000	3,000-7,000	99

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 22

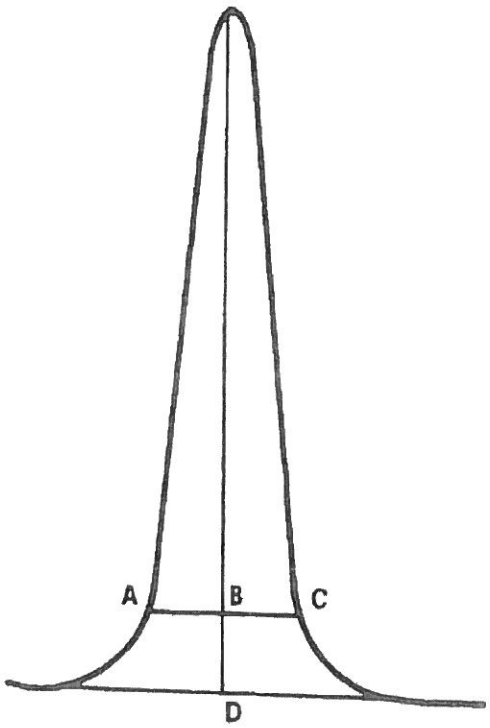
SINGLE-LABORATORY PAH RECOVERY DATA FROM SRM 1941 MARINE SEDIMENT, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Recovery (%)
Naphthalene	1010	97.4
Fluorene	100	100.0
Phenanthrene	490	102.0
Fluoranthene	980	116.7
Pyrene	810	97.3
Benz(a)anthracene	430	89.8
Chrysene	380	130.3
Benzo(b)fluoranthene	740	95.8
Benzo(k)fluoranthene	360	130.2
Benz(e)pyrene	550	81.0
Benzo(a)pyrene	630	76.0
Perylene	450	72.4
Indeno(123-cd)pyrene	500	126.0
Dibenz(a,h)anthracene	110	78.7
Benz(ghi)perylene	530	85.2

n = 3

All RSDs < 10%

FIGURE 1
TAILING FACTOR CALCULATION



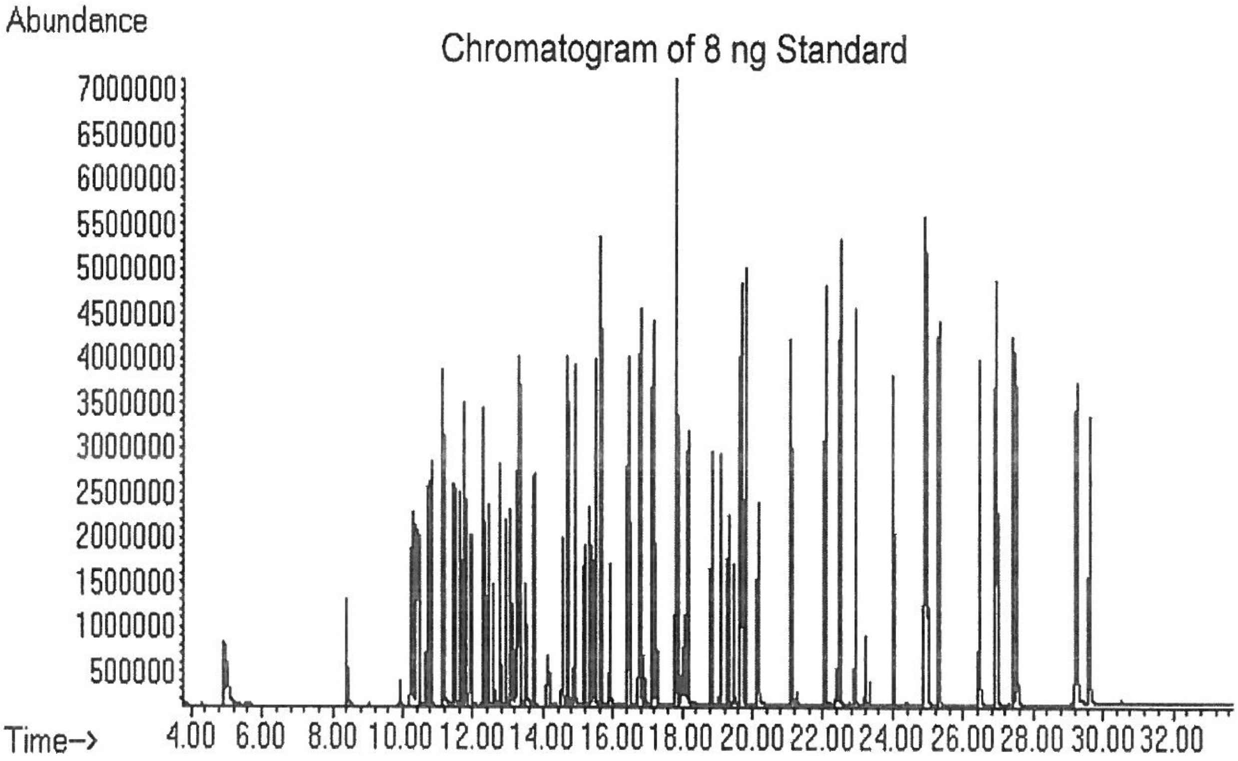
$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

FIGURE 2

GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



METHOD 6020A

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests (Refs. 1 and 2). When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-soluble) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of this method in a multi-laboratory study on solid and aqueous wastes are listed below.

Element		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0

Element		CASRN[a]
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a] Chemical Abstract Service Registry Number

Acceptability of this method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Sec. 13.0. The lower limit of quantitation and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, quantitation limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If this method is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Sec. 9.0). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{74}Ge, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

1.5 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel, including spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples should be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and extracted through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be applicable to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.3 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature (Refs. 3 and 4). Examples include $^{75}ArCl^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature (Ref. 5), the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals <u>observed</u> for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z.

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [Ref. 6]).

Similarly:

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =
(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any $^{114}Sn^+$ or $^{114}MoO^+$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting precision.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found (Ref. 7) to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported (Ref. 7) for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that the lower limits of quantitation, accuracy, and precision requirements for analysis of the samples can be met.

4.4 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to Methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The method also provides a method for preconcentration to enhance quantitation limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (Refs. 13 through 15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.5 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) are recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.5).

4.6 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of observed memory interferences. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer -- A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.2 Argon gas supply -- High-purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used (Refs. 3 and 4). Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

7.3 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.4 Standard stock solutions for each analyte may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010 for instructions on preparing standard solutions from solids.

7.4.1 Bismuth internal standard stock solution (1 mL = 100 µg of Bi) -- Dissolve 0.1115 g of Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.2 Germanium internal standard stock solution (1 mL = 100 µg of Ge) -- Dissolve 0.2954 g of $GeCl_4$ in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.3 Holmium internal standard stock solution (1 mL = 100 µg of Ho) -- Dissolve 0.1757 g of $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.4 Indium internal standard stock solution (1 mL = 100 µg of In) -- Dissolve 0.1000 g of indium metal in 10 mL of conc. HNO_3. Dilute to 1,000 mL with reagent water.

7.4.5 Lithium internal standard stock solution (1 mL = 100 µg of ^{6}Li) -- Dissolve 0.6312 g of 95-atom-% ^{6}Li, Li_2CO_3 in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.6 Rhodium internal standard stock solution (1 mL = 100 µg of Rh) -- Dissolve 0.3593 g of ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL of conc. HCl and dilute to 1,000 mL with reagent water.

7.4.7 Scandium internal standard stock solution (1 mL = 100 µg of Sc) -- Dissolve 0.15343 g of Sc_2O_3 in 10 mL (1+1) of hot HNO_3. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.8 Terbium internal standard stock solution (1 mL = 100 µg of Tb) -- Dissolve 0.1828 g of $Tb_2(CO_3)_3 \bullet 5H_2O$ in 10 mL (1+1) of HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.9 Yttrium internal standard stock solution (1 mL = 100 µg of Y) -- Dissolve 0.2316 g of $Y_2(CO_3)_3 \bullet 3H_2O$ in 10 mL (1+1) of HNO_3. Add 5 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.10 Titanium interference stock solution (1 mL = 100 µg of Ti) -- Dissolve 0.4133 g of $(NH_4)_2TiF_6$ in reagent water. Add 2 drops of conc. HF and dilute to 1,000 mL with reagent water.

7.4.11 Molybdenum interference stock solution (1 mL = 100 µg of Mo) -- Dissolve 0.2043 g of $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

7.4.12 Gold preservative stock solution for mercury (1 mL = 100 µg) -- Recommend purchasing as high purity prepared solution of $AuCl_3$ in dilute hydrochloric acid matrix.

7.5 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{74}Ge and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.)

7.6 Blanks -- Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration. The rinse blank is used to flush the system between all samples and standards.

7.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Sec. 7.2.

7.6.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.9).

7.6.3 The rinse blank consists of 1 to 2% of HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL (ppm) of $AuCl_3$ solution.

7.7 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If this method is used to determine an element not listed in Sec. 1.2, the analyst should modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Sec. 9.7).

7.7.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

7.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g of $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g of $CaCO_3$ (dried at 180 •C for 1 hr before weighing), 1.000 g of Fe, 1.658 g of MgO, 2.305 g of Na_2CO_3, and 1.767 g of K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g of 85 % H_3PO_4, 6.373 g of 96% H_2SO_4, 40.024 g of 37% HCl, and 10.664 g of citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.7.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL of reagent water. Add 2.0 mL of concentrated HNO_3, and dilute to 100.0 mL with reagent water.

7.7.1.4 Working ICS solutions

7.7.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), and 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.7.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2), and 2.0 mL of mixed ICS solution III (Sec. 7.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.8 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.4.3 for use). This standard may also be purchased.

7.9 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.4.4 for use).

7.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Sec. 10.2). This solution is also used to verify that the instrument has reached thermal stability (see Sec. 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material in Chapter Three, "Inorganic Analytes."

8.2 Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to a 3000 series method (Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are a useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limits of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.2.3.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 70% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. As an example, if the initial calibration internal standard response is 100,000 cps, anything below 70,000 cps in the sample would be unacceptable. Under these conditions, the established lower limit of quantitation has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed -- First, make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Sec. 7.6.1). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum 70% limit. Reported results must be corrected for all dilutions.

9.7 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Sec. 4.2) for each instrument system are acceptable corrections for use in Method 6020.

9.8 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process, as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.9 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and, if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 - 120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.10 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.11 should be conducted.

9.10.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$\mathrm{RPD} = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where:

RPD = relative percent difference.