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Analytical Methods for the National Sewage Sludge Survey

ANALYTICAL METHODS FOR THE NATIONAL SEWAGE SLUDGE SURVEY

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INTRODUCTION

This document is a compilation of the analytical methods that the USEPA Office of Water Regulations and Standards (OWRS) will use in the National Sewage Sludge Survey.

These methods have been compiled from three sources other than OWRS, they are:

1) "Methods for Chemical Analysis of Water and Wastes," USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-79-020 (Revised March 1983).
Note: This document is currently available from National Technical Information Service, Springfield, VA 22161, PB84-128677.

2) "Test Methods for Evaluating Solid Waste," USEPA, OSW, Washington, DC 20460, SW-846, (November 1986).
Note: This document is currently available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

3) Method 8290 is included in draft form and was developed by :

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EPA METHOD 1624C
VOLATILE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GCMS

EPA METHOD 1625C
SEMIVOLATILE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GCMS

Introduction

Methods 1624 and 1625 were developed by the Industrial Technology Division (ITD) within EPA's Office of Water Regulations and Standards to provide improved precision and accuracy of analysis of pollutants in aqueous and solid matrices. The ITD is responsible for development and promulgation of nationwide standards setting limits on pollutant levels in industrial discharges.

Methods 1624 and 1625 are isotope dilution, gas chromatography-mass spectrometry methods for analysis of the volatile and semi-volatile, organic "priority" pollutants, and other organic pollutants amenable to gas chromatography-mass spectrometry. Isotope dilution is a technique which employs stable, isotopically labeled analogs of the compounds of interest as internal standards in the analysis.

Questions concerning the Methods or their application should be addressed to:

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METHOD 1624 15 February 1988 Revision C

Volatile Organic Compounds by Isotope Dilution GCMS

1 SCOPE AND APPLICATION

1.1 This method is designed to determine the volatile toxic organic pollutants associated with the 1976 Consent Decree; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liabilities Act; and other compounds amenable to purge and trap gas chromatography-mass spectrometry (GCMS).

Table 1

VOLATILE ORGANIC COMPOUNDS DETERMINED BY CALIBRATED GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

	Pollutant				Labeled Compound		EPA-
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EGD
acetone	81552	67-64-1	516 V		d_6	666-52-4	616 V
acrolein	34210	107-02-8	002 V	001 V	d_4	33984-05-3	202 V
acrylonitrile	34215	107-13-1	003 V	002 V	d_3	53807-26-4	203 V
benzene	34030	71-43-2	004 V	003 V	d_6	1076-43-3	204 V
bromodichloromethane	32101	75-27-4	048 V	012 V	^{13}C	93952-10-4	248 V
bromoform	32104	75-25-2	047 V	005 V	^{13}C	72802-81-4	247 V
bromomethane	34413	74-83-9	046 V	020 V	d_3	1111-88-2	246 V
carbon tetrachloride	32102	56-23-5	006 V	006 V	^{13}C	32488-50-9	206 V
chlorobenzene	34301	108-90-7	007 V	007 V	d_5	3114-55-4	207 V
chloroethane	34311	75-00-3	016 V	009 V	d_5	19199-91-8	216 V
2-chloroethylvinyl ether	34576	110-75-8	019 V	010 V			
chloroform	32106	67-66-3	023 V	011 V	^{13}C	31717-44-9	223 V
chloromethane	34418	74-87-3	045 V	021 V	d_3	1111-89-3	245 V
dibromochloromethane	32105	124-48-1	051 V	008 V	^{13}C	93951-99-6	251 V
1,1-dichloroethane	34496	75-34-3	013 V	014 V	d_3	56912-77-7	213 V
1,2-dichloroethane	32103	107-06-2	010 V	015 V	d_4	17070-07-0	210 V
1,1-dichloroethene	34501	75-35-4	029 V	016 V	d_2	22280-73-5	229 V
trans-1,2-dichlorethene	34546	156-60-5	030 V	026 V	d_2	42366-47-2	230 V
1,2-dichloropropane	34541	78-87-5	032 V	017 V	d_6	93952-08-0	232 V
trans-1,3-dichloropropene	34699	10061-02-6	033 V		d_4	93951-86-1	233 V
diethyl ether	81576	60-29-7	515 V		d_{10}	2679-89-2	615 V
p-dioxane	81582	123-91-1	527 V		d_8	17647-74-4	627 V
ethylbenzene	34371	100-41-4	038 V	019 V	d_{10}	25837-05-2	238 V
methylene chloride	34423	75-09-2	044 V	022 V	d_2	1665-00-5	244 V
methyl ethyl ketone	81595	78-93-3	514 V		d_3	53389-26-7	614 V
1,1,2,2-tetrachloroethane	34516	79-34-5	015 V	023 V	d_2	33685-54-0	215 V
tetrachlorethene	34475	127-18-4	085 V	024 V	$^{13}C_2$	32488-49-6	285 V
toluene	34010	108-88-3	086 V	025 V	d_8	2037-26-5	286 V
1,1,1-trichloroethane	34506	71-55-6	011 V	027 V	d_3	2747-58-2	211 V
1,1,2-trichloroethane	34511	79-00-5	014 V	028 V	$^{13}C_2$	93952-09-1	214 V
trichloroethene	39180	79-01-6	087 V	029 V	$^{13}C_2$	93952-00-2	287 V
vinyl chloride	39175	75-01-4	088 V	031 V	d_3	6745-35-3	288 V

1.2 The chemical compounds listed in tables 1 and 2 may be determined in waters, soils, and municipal sludges by this method. The method is designed to meet the survey requirements of the Environmental Protection Agency.

Table 2

VOLATILE ORGANIC COMPOUNDS TO BE DETERMINED BY REVERSE SEARCH AND QUANTITATION USING KNOWN RETENTION TIMES, RESPONSE FACTORS, REFERENCE COMPOUNDS, AND MASS SPECTRA

EGD No.	Compound	CAS Registry
532	allyl alcohol*	107-18-6
533	carbon disulfide	75-15-0
534	2-chloro-1,3-butadiene (chloroprene)	126-99-8
535	chloroacetonitrile*	107-14-2
536	3-chloropropene	107-05-1
537	crotonaldehyde*	123-73-9
538	1,2-dibromoethane (EDB)	106-93-4
539	dibromomethane	74-95-3
540	trans-1,4-dichloro-2-butene	110-57-6
541	1,3-dichloropropane	142-28-9
542	cis-1,3-dichloropropene	10061-01-5
543	ethyl cyanide*	107-12-0
544	ethyl methacrylate	97-63-2
545	2-hexanone	591-78-6
546	iodomethane	74-88-4
547	isobutyl alcohol*	78-83-1
548	methacrylonitrile	126-98-7
549	methyl methacrylate	78-83-1
550	4-methyl-2-pentanone	108-10-1
551	1,1,1,2-tetrachloroethane	630-20-6
552	trichlorofluoromethane	75-69-4
553	1,2,3-trichloropropane	96-18-4
554	vinyl acetate	108-05-4
951	m-xylene	108-38-3
952	o- + p-xylene	

* determined at a purge temperature of 75 - 85 °C

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The levels in table 3 typify the minimum quantity that can be detected with no interferences present.

1.4 The GCMS portions of this method are for use only by analysts experienced with GCMS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GCMS should run the performance tests in reference 1 before beginning.

2 SUMMARY OF METHOD

2.1 The percent solids content of the sample is determined. If the solids content is known or determined to be less than one percent, stable isotopically labeled analogs of the compounds of interest are added to a 5 mL sample and the sample is purged with an inert gas at 20 - 25 °C in a chamber designed for soil or water samples.

If the solids content is greater than one percent, five mL of reagent water and the labeled compounds are added to a 5 gram aliquot of sample and the mixture is purged at 40 °C. Compounds that will not purge at 20 - 25 °C or at 40 °C are purged at 75 - 85 °C. In the purging process, the volatile compounds are transferred from the aqueous phase into the gaseous phase where they are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS) (references 2 and 3). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a pollutant (qualitative analysis) is performed in one of three ways: (1) For compounds listed in table 1 and other compounds for which authentic standards are available, the GCMS system is calibrated and the mass spectrum and retention time for each standard are

stored in a user created library. A compound is identified when its retention time and mass spectrum agree with the library retention time and spectrum. (2) For compounds listed in table 2 and other compounds for which standards are not available, a compound is identified when the retention time and mass spectrum agree with those specified in this method. (3) For chromatographic peaks which are not identified by (1) and (2) above, the background corrected spectrum at the peak maximum is compared with spectra in the EPA/NIH Mass Spectral File (reference 4). Tentative identification is established when the spectrum agrees.

2.3 Quantitative analysis is performed in one of four ways by GCMS using extracted ion current profile (EICP) areas: (1) For compounds listed in table 1 and other compounds for which standards and labeled analogs are available, the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique. (2) For compounds listed in table 1 and for other compounds for which authentic standards but no labeled compounds are available, the GCMS system is calibrated and the compound concentration is determined using an internal standard technique. (3) For compounds listed in table 2 and other compounds for which standards are not available, compound concentrations are determined using known response factors. (4) For compounds for which neither standards nor known response factors are available, compound concentration is determined using the sum of the EICP areas relative to the sum of the EICP areas of the nearest eluted internal standard.

2.4 Quality is assured through reproducible calibration and testing of the purge and trap and GCMS systems.

3 CONTAMINATION AND INTERFERENCES

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from interferences under conditions of the

Table 3

GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Relative (2)	Minimum level (ug/L)	Method Detection Limit (4) Low solids (ug/kg)	Method Detection Limit (4) High solids (ug/kg)
245	chloromethane-d_3	147	181	0.141 - 0.270	50		
345	chloromethane	148	245	0.922 - 1.210	50	207*	13
246	bromomethane-d_3	243	181	0.233 - 0.423	50		
346	bromomethane	246	246	0.898 - 1.195	50	148*	11
288	vinyl chloride-d_3	301	181	0.286 - 0.501	50		
388	vinyl chloride	304	288	0.946 - 1.023	10	190*	11
216	chloroethane-d_5	378	181	0.373 - 0.620	50		
316	chloroethane	386	216	0.999 - 1.060	50	789*	24
244	methylene chloride-d_2	512	181	0.582 - 0.813	10		
344	methylene chloride	517	244	0.999 - 1.017	10	566*	280*
546	iodomethane	498	181	0.68			
616	acetone-d_6	554	181	0.628 - 0.889	50		
716	acetone	565	616	0.984 - 1.019	50	3561*	322*

202	acrolein-d_4	564	181	0.641 - 0.903(5)	50		
302	acrolein	566	202	0.984 - 1.018(5)	50	377*	18
203	acrylonitrile-d_3	606	181	0.735 - 0.926	50		
303	acrylonitrile	612	203	0.985 - 1.030	50	360*	9
533	carbon disulfide	631	181	0.86			
552	trichlorofluoromethane	663	181	0.91			
543	ethyl cyanide	672	181	0.92			
229	1,1-dichloroethene-d_2	696	181	0.903 - 0.976	10		
329	1,1-dichloroethene	696	229	0.999 - 1.011	10	31	5
536	3-chloropropene	696	181	0.95			
532	allyl alcohol	703	181	0.96			
181	bromochloromethane (I.S.)	730	181	1.000 - 1.000	10		
213	1,1-dichloroethane-d_3	778	181	1.031 - 1.119	10		
313	1,1-dichloroethane	786	213	0.999 - 1.014	10	16	1
615	diethyl ether-d_{10}	804	181	1.067 - 1.254	50		
715	diethyl ether	820	615	1.010 - 1.048	50	63	12
230	trans-1,2-dichloroethene-d_2	821	181	1.056 - 1.228	10		
330	trans-1,2-dichloroethene	821	230	0.996 - 1.011	10	41	3
614	methyl ethyl ketone-d_3	840	181	0.646 - 1.202	50		
714	methyl ethyl ketone	848	614	0.992 - 1.055	50	241*	80*
223	chloroform-$^{13}C_1$	861	181	1.092 - 1.322	10		
323	chloroform	861	223	0.961 - 1.009	10	21	2
535	chloroacetonitrile	884	181	1.21			
210	1,2-dichloroethane-d_4	901	181	1.187 - 1.416	10		
310	1,2-dichloroethane	910	210	0.973 - 1.032	10	23	3
539	dibromomethane	910	181	1.25			
548	methacrylonitrile	921	181	1.26			
547	isobutyl alcohol	962	181	1.32			
211	1,1,1-trichloroethane-$^{13}C_2$	989	181	1.293 - 1.598	10		
311	1,1,1-trichloroethane	999	211	0.989 - 1.044	10	16	4
627	p-dioxane-d_8	982	181	1.262 - 1.448(5)	10		
727	p-dioxane	1001	627	1.008 - 1.040(5)	10	--	140*
206	carbon tetrachloride-$^{13}C_1$	1018	182	0.754 - 0.805	10		
306	carbon tetrachloride	1018	206	0.938 - 1.005	10	87	9
554	vinyl acetate	1031	182	0.79			
248	bromodichloromethane-$^{13}C_1$	1045	182	0.766 - 0.825	10		
348	bromodichloromethane	1045	248	0.978 - 1.013	10	28	3
534	2-chloro-1,3-butadiene	1084	182	0.83			
537	crotonaldehyde	1098	182	0.84			
232	1,2-dichloropropane-d_6	1123	182	0.830 - 0.880	10		
332	1,2-dichloropropane	1134	232	0.984 - 1.018	10	29	5
542	cis-1,3-dichloropropene	1138	182	0.87			
287	trichloroethene-$^{13}C_2$	1172	182	0.897 - 0.917	10		
387	trichloroethene	1187	287	0.991 - 1.037	10	41	2
541	1,3-dichloropropane	1196	182	0.92			
204	benzene-d_6	1200	182	0.888 - 0.952	10		
304	benzene	1212	204	1.002 - 1.026	10	23	8
251	chlorodibromomethane-$^{13}C_1$	1222	182	0.915 - 0.949	10		
351	chlorodibromomethane	1222	251	0.989 - 1.030	10	15	2
214	1,1,2-trichloroethane-$^{13}C_2$	1224	182	0.922 - 0.953	10		
314	1,1,2-trichloroethane	1224	214	0.975 - 1.027	10	26	1
233	trans-1,3-dichloropropene-d_4	1226	182	0.922 - 0.959	10		
333	trans-1,3-dichloropropene	1226	233	0.993 - 1.016	10	(6)*	(6)*

019	2-chloroethylvinyl ether	1278	182	0.983 - 1.026	10	122	21
538	1,2-dibromoethane	1279	182	0.98			
182	2-bromo-1-chloropropane (I.S.)	1306	182	1.000 - 1.000	10		
549	methyl methacrylate	1379	182	1.06			
247	bromoform-$^{13}C_1$	1386	182	1.048 - 1.087	10		
347	bromoform	1386	247	0.992 - 1.003	10	91	7
551	1,1,1,2-tetrachloroethane	1408	182	1.08			
550	4-methyl-2-pentanone	1435	183	0.92			
553	1,2,3-trichloropropane	1520	183	0.98			
215	1,1,2,2-tetrachloroethane-d_2	1525	183	0.969 - 0.996	10		
315	1,1,2,2-tetrachloroethane	1525	215	0.890 - 1.016	10	20	6
545	2-hexanone	1525	183	0.98			
285	tetrachloroethene-$^{13}C_2$	1528	183	0.966 - 0.996	10		
385	tetrachloroethene	1528	285	0.997 - 1.003	10	106	10
540	trans-1,4-dichloro-2-butene	1551	183	1.00			
183	1,4-dichlorobutane (int std)	1555	183	1.000 - 1.000	10		
544	ethyl methacrylate	1594	183	1.03			
286	toluene-d_8	1603	183	1.016 - 1.054	10		
386	toluene	1619	286	1.001 - 1.019	10	27	4
207	chlorobenzene-d_5	1679	183	1.066 - 1.135	10		
307	chlorobenzene	1679	207	0.914 - 1.019	10	21	58*
238	ethylbenzene-d_{10}	1802	183	1.144 - 1.293	10		
338	ethylbenzene	1820	238	0.981 - 1.018	10	28	4
185	bromofluorobenzene	1985	183	1.255 - 1.290	10		
951	m-xylene	2348	183	1.51	10		
952	o- + p-xylene	2446	183	1.57	10		

(1) Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) The retention time limits in this column are based on data from four wastewater laboratories. The single values for retention times in this column are based on data from one wastewater laboratory.

(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points when calibrated using reagent water. The concentration in the aqueous or solid phase is determined using the equations in section 13.

(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).

(5) Specification derived from related compound.

(6) An unknown interference in the particular sludge studied precluded measurement of the Method Detection Limit (MDL) for this compound.

*Background levels of these compounds were present in the sludge resulting in higher than expected MDL's. The MDL for these compounds is expected to be approximately 20 ug/kg (100 - 200 for the gases and water soluble compounds) for the low solids method and 5 - 10 ug/kg (25 - 50 for the gases and water soluble compounds) for the high solids method, with no interferences present.

Column: 2.4 m (8 ft) x 2 mm i.d. glass, packed with one percent SP-1000 coated on 60/80 Carbopak B.

Carrier gas: helium at 40 mL/min.

Temperature program: 3 min at 45 °C, 8 °C per min to 240 °C, hold at 240 °C for 15 minutes.

analysis by analyzing reagent water blanks initially and with each sample batch (samples analyzed on the same 8 hr shift), as described in section 8.5.

3.2 Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

3.3 Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. To reduce carry-over, the purging device (figure 1 for samples containing less than one percent solids; figure 2 for samples containing one percent solids or greater) is cleaned or replaced with a clean purging device after each sample is analyzed. When an unusually concentrated sample is encountered, it is followed by analysis of a reagent water blank to check for carry-over. Purging devices are cleaned by washing with soap solution, rinsing with tap and distilled water, and drying in an oven at 100-125 °C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

3.4 Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

4 SAFETY

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard.

Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 5 - 7.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 APPARATUS AND MATERIALS

5.1 Sample bottles for discrete sampling

5.1.1 Bottle--25 to 40 mL with screw cap (Pierce 13075, or equivalent). Detergent wash, rinse with tap and distilled water, and dry at >105 °C for one hr minimum before use.

5.1.2 Septum--Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100 - 200 °C for one hour minimum.

5.2 Purge and trap device--consists of purging device, trap, and desorber.

5.2.1 Purging devices for water and soil samples

5.2.1.1 Purging device for water samples--designed to accept 5 mL samples with water column at least 3 cm deep. The volume of the gaseous head space between the water and trap shall be less than 15 mL. The purge gas shall be introduced less than 5 mm from the base of the water column and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shown in figure 1 meets these criteria.

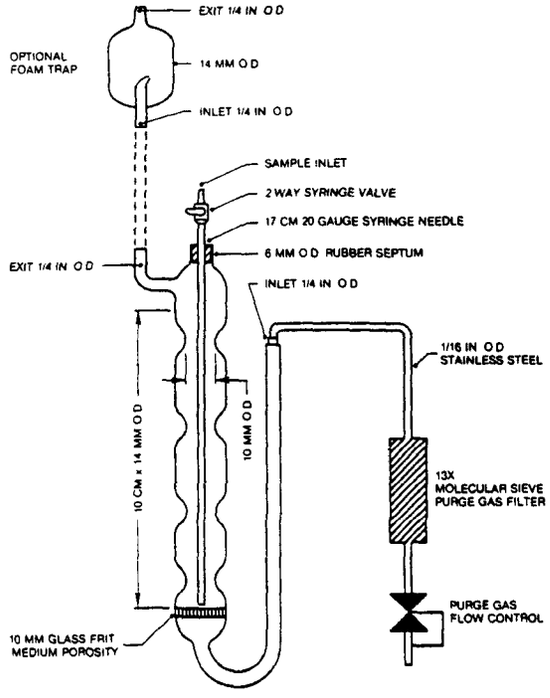

FIGURE 1 Purging Device for Waters

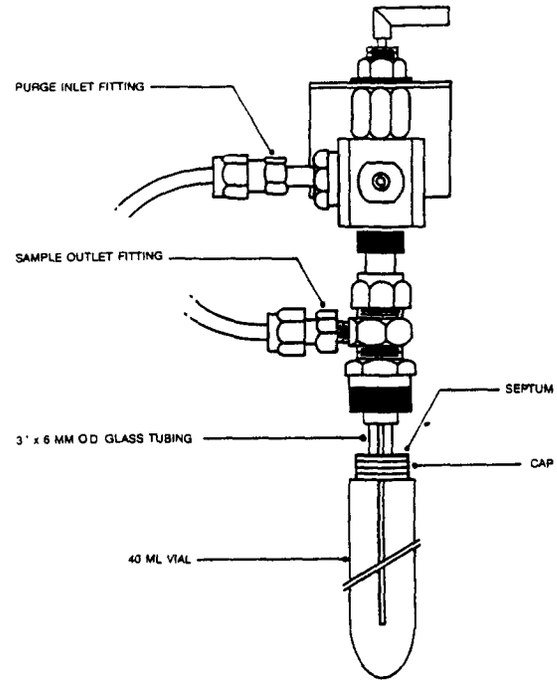

FIGURE 2 Purging Device for Soils or Waters

5.2.1.2 Purging device for solid samples--designed to accept 5 grams of solids plus 5 mL of water. The volume of the gaseous head space between the water and trap shall be less than 25 mL. The purge gas shall be introduced less than 5 mm from the base of the sample and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shall be capable of operating at ambient temperature (20 - 25 °C) and of being controlled at temperatures of 40 ± 2 °C and 80 ± 5 °C while the sample is being purged. The purging device shown in figure 2 meets these criteria.

5.2.2 Trap--25 to 30 cm x 2.5 mm i.d. minimum, containing the following:

5.2.2.1 Methyl silicone packing--one ± 0.2 cm, 3 percent OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.2.2.2 Porous polymer--15 ± 1.0 cm, Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.2.2.3 Silica gel--8 ± 1.0 cm, Davison Chemical, 35/60 mesh, grade 15, or equivalent. The trap shown in figure 3 meets these specifications.

5.2.4 Desorber--shall heat the trap to 175 ± 5 °C in 45 seconds or less. The polymer section of the trap shall not exceed a temperature of 180 °C and the remaining sections shall not exceed 220 °C during desorb, and no portion of the trap shall exceed 225 °C during bakeout. The desorber shown in figure 3 meets these specifications.

5.2.5 The purge and trap device may be a separate unit or coupled to a GC as shown in figures 4 and 5.

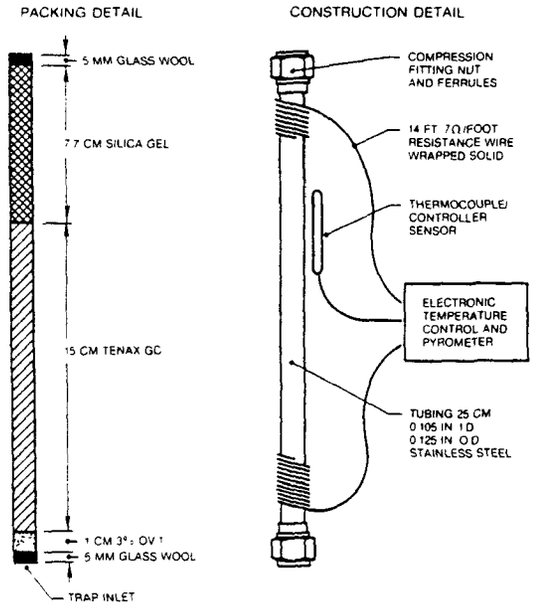

FIGURE 3 Trap Construction and Packings

5.3 Gas chromatograph--shall be linearly temperature programmable with initial and final holds, shall contain a glass jet separator as the MS interface, and shall produce results which meet the calibration (section 7), quality assurance (section 8), and performance tests (section 11) of this method.

5.3.1 Column--2.8 ± 0.4 m x 2 ± 0.5 mm i.d. glass, packed with one percent SP-1000 on Carbopak B, 60/80 mesh, or equivalent.

5.4 Mass spectrometer--70 eV electron impact ionization; shall repetitively scan from 20 to 250 amu every 2-3 seconds, and produce a unit resolution (valleys between m/z 174-176 less than 10 percent of the height of the m/z 175 peak), background corrected mass spectrum from 50 ng 4-bromofluorobenzene (BFB) injected into the GC. The BFB spectrum shall meet the mass-intensity criteria in table 4. All portions of the GC column, transfer lines, and separator which connect the GC column to the ion source shall remain at or above the column temperature during analysis to

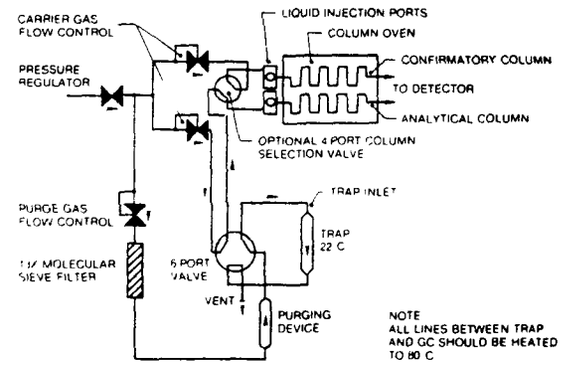

FIGURE 4 Schematic of Purge and Trap Device--Purge Mode

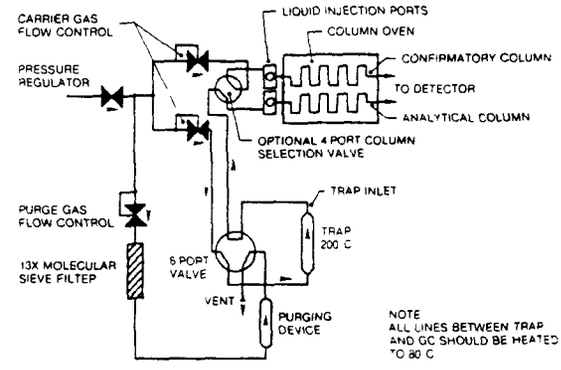

FIGURE 5 Schematic of Purge and Trap Device--Desorb Mode

preclude condensation of less volatile compounds.

Table 4

BFB MASS-INTENSITY SPECIFICATIONS

M/z	Intensity Required
50	15 to 40 percent of m/z 95
75	30 to 60 percent of m/z 95
95	base peak, 100 percent
96	5 to 9 percent of m/z 95
173	less than 2 percent of m/z 174
174	greater than 50 percent of m/z 95
175	5 to 9 percent of m/z
176	95 to 101 percent of m/z 174
177	5 to 9 percent of m/z 176

5.5 Data system--shall collect and record MS data, store mass-intensity data in spectral libraries, process GCMS data and generate reports, and shall calculate and record response factors.

5.5.1 Data acquisition--mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.5.2 Mass spectral libraries--user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GCMS runs for the compounds of interest (section 7.2).

5.5.3 Data processing--the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GCMS analysis. Software routines shall be employed to compute retention times and EICP areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.5.4 Response factors and multipoint calibrations--the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and on-going performance shall be maintained (sections 8 and 11).

5.6 Syringes--5 mL glass hypodermic, with Luer-lok tips.

5.7 Micro syringes--10, 25, and 100 uL.

5.8 Syringe valves--2-way, with Luer ends (Teflon or Kel-F).

5.9 Syringe--5 mL, gas-tight, with shut-off valve.

5.10 Bottles--15 mL, screw-cap with Teflon liner.

5.11 Balances

5.11.1 Analytical, capable of weighing 0.1 mg.

5.11.2 Top loading, capable of weighing 10 mg.

5.12 Equipment for determining percent moisture

5.12.1 Oven, capable of being temperature controlled at 110 ± 5 °C.

5.12.2 Dessicator.

5.12.3 Beakers--50 - 100 mL.

6 REAGENTS AND STANDARDS

6.1 Reagent water--water in which the compounds of interest and interfering compounds are not detected by this method (section 11.7). It may be generated by any of the following methods:

6.1.1 Activated carbon--pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

6.1.2 Water purifier--pass tap water through a purifier (Millipore Super Q, or equivalent).

6.1.3 Boil and purge--heat tap water to 90-100 °C and bubble contaminant free inert gas through it for approximately one hour. While still hot, transfer the water to screw-cap bottles and seal with a Teflon-lined cap.

6.2 Sodium thiosulfate--ACS granular.

6.3 Methanol--pesticide quality or equivalent.

6.4 Standard solutions--purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the standard.

6.5 Preparation of stock solutions--prepare in methanol using liquid or gaseous standards

per the steps below. Observe the safety precautions given in section 4.

6.5.1 Place approximately 9.8 mL of methanol in a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 minutes or until all methanol wetted surfaces have dried.

In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids--using a 100 uL syringe, permit 2 drops of liquid to fall into the methanol without contacting the neck of the flask.

Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride)--fill a valved 5 mL gas-tight syringe with the compound.

Lower the needle to approximately 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

6.5.2 Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (ug/uL) from the weight gain (or density if a known volume was injected).

6.5.3 Transfer the stock solution to a Teflon sealed screw-cap bottle.

Store, with minimal headspace, in the dark at -10 to -20 °C.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

6.6 Labeled compound spiking solution--from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5-10 uL spike into each 5 mL sample, blank, or aqueous standard analyzed will result in a concentration of 20 ug/L of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, and MEK), a concentration of 100 ug/L may be used. Include the internal standards (section 7.5) in this solution so that a concentration of 20 ug/L in each sample, blank, or aqueous standard will be produced.

6.7 Secondary standards--using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 500 ug/mL. For the gases and water soluble compounds (section 6.6), a concentration of 2.5 mg/mL may be used.

6.7.1 Aqueous calibration standards--using a 25 uL syringe, add 20 uL of the secondary standard (section 6.7) to 50, 100, 200, 500, and 1000 mL of reagent water to produce concentrations of 200, 100, 50, 20, and 10 ug/L, respectively. If the higher concentration standard for the gases and water soluble compounds was chosen (section 6.6), these compounds will be at concentrations of 1000, 500, 250, 100, and 50 ug/L in the aqueous calibration standards.

6.7.2 Aqueous performance standard--an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (section 11). This standard shall contain either 20 or 100 ug/L of the labeled and pollutant gases and water soluble compounds, 10 ug/L BFB, and 20 ug/L of all

other pollutants, labeled compounds, and internal standards. It may be the nominal 20 ug/L aqueous calibration standard (section 6.7.1).

6.7.3 A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge and trap analyses are compared.

This standard shall contain either 100 ug/mL or 500 ug/mL of the gases and water soluble compounds, and 100 ug/mL of the remaining pollutants and internal standards (consistent with the amounts in the aqueous performance standard in 6.7.2).

6.7.4 Other standards which may be needed are those for test of BFB performance (section 7.1) and for collection of mass spectra for storage in spectral libraries (section 7.2).

7 CALIBRATION

Calibration of the GCMS system is performed by purging the compounds of interest and their labeled analogs from reagent water at the temperature to be used for analysis of samples.

7.1 Assemble the gas chromatographic apparatus and establish operating conditions given in table 3. By injecting standards into the GC, demonstrate that the analytical system meets the minimum levels in table 3 for the compounds for which calibration is to be performed, and the mass-intensity criteria in table 4 for 50 ng BFB.

7.2 Mass spectral libraries--detection and identification of the compounds of interest are dependent upon the spectra stored in user created libraries.

7.2.1 For the compounds in table 1 and other compounds for which the GCMS is to be calibrated, obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic m/z's or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under BFB tuning conditions (section 7.1 and table 4) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. The spectrum may be further edited to remove common interfering masses. If 5 mass spectral peaks cannot be obtained under the scan conditions given in section 5.4, the mass spectrometer may be scanned to an m/z lower than 20 to gain additional spectral information. The spectrum obtained is stored for reverse search and for compound confirmation.

7.2.5 For the compounds in table 2 and other compounds for which the mass spectra, quantitation m/z's, and retention times are known but the instrument is not to be calibrated, add the retention time and reference compound (table 3); the response factor and the quantitation m/z (table 5); and spectrum (Appendix A) to the reverse search library. Edit the spectrum per section 7.2.4, if necessary.

7.3 Assemble the purge and trap device. Pack the trap as shown in figure 3 and

Table 5

VOLATILE ORGANIC COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled analog	Primary m/z's	Reference compound (1)	Response factor at purge temp. of 20 °C	80 °C
acetone	d_6	58/64			
acrolein	d_4	56/60			
acrylonitrile	d_3	53/56			
allyl alcohol		57	181	(2)	0.20
benzene	d_6	78/84			
2-bromo-1-chloropropane (3)		77			
bromochloromethane (3)		128			
bromodichloromethane	^{13}C	83/86			
bromoform	^{13}C	173/176			
bromomethane	d_3	96/99			
carbon disulfide		76	181	1.93	2.02
carbon tetrachloride	^{13}C	47/48			
2-chloro-1,3-butadiene		53	182	0.29	0.50
chloroacetonitrile		75	181	(2)	1.12
chlorobenzene	d_5	112/117			
chloroethane	d_5	64/71			
2-chloroethylvinyl ether	d_7	106/113			
chloroform	^{13}C	85/86			
chloromethane	d_3	50/52			
3-chloropropene		76	181	0.43	0.63
crotonaldehyde		70	182	(2)	0.090
dibromochloromethane	^{13}C	129/130			
1,2-dibromoethane		107	182	0.86	0.68
dibromomethane		93	181	1.35	1.91
1,4-dichlorobutane (3)		55			
trans-1,4-dichloro-2-butene		75	183	0.093	0.14
1,1-dichloroethane	d_3	63/66			
1,2-dichloroethane	d_4	62/67			
1,1-dichloroethene	d_2	61/65			
trans-1,2-dichlorethene	d_2	61/65			
1,2-dichloropropane	d_6	63/67			
1,3-dichloropropane		76	182	0.89	0.88
cis-1,3-dichloropropene		75	182	0.29	0.41
trans-1,3-dichloropropene	d_4	75/79			
diethyl ether	d_{10}	74/84			
p-dioxane	d_8	88/96			
ethyl cyanide		54	181	(2)	1.26
ethyl methacrylate		69	183	0.69	0.52
ethylbenzene	d_{10}	106/116			
2-hexanone		58	183	0.076	0.33
iodomethane		142	181	4.55	2.55
isobutyl alcohol		74	181	(2)	0.22
methylene chloride	d_2	84/88			
methyl ethyl ketone	d_3	72/75			
methyl methacrylate		69	182	0.23	0.79
4-methyl-2-pentanone		58	183	0.15	0.29

methacrylonitrile		67	181	0.25	0.79
1,1,1,2-tetrachloroethane		131	182	0.20	0.25
1,1,2,2-tetrachloroethane	$^{13}C_2$	83/84			
tetrachlorethene	d_2	166/172			
toluene	d_8	92/99			
1,1,1-trichloroethane	$^{13}C_2$	97/102			
1,1,2-trichloroethane	$^{13}C_2$	83/84			
trichloroethene		95/136			
trichlorofluoromethane		101	181	2.31	2.19
1,2,3-trichloropropane		75	183	0.89	0.72
vinyl acetate		86	182	0.054	0.19
vinyl chloride	d_3	62/65			
m-xylene		106	183	1.69	-
o- + p-xylene		106	183	3.33	-

(1) 181 = bromochloromethane 182 = 2-bromo-1-chloropropane 183 = 1,4-dichlorobutane

(2) not detected at a purge temperature of 25 °C

(3) internal standard

condition overnight at 170 - 180 °C by backflushing with an inert gas at a flow rate of 20 - 30 mL/min. Condition traps daily for a minimum of 10 minutes prior to use.

7.3.1 Analyze the aqueous performance standard (section 6.7.2) according to the purge and trap procedure in section 10. Compute the area at the primary m/z (table 5) for each compound. Compare these areas to those obtained by injecting one uL of the methanolic standard (section 6.7.3) to determine compound recovery. The recovery shall be greater than 20 percent for the water soluble compounds (section 6.6), and 60 - 110 percent for all other compounds. This recovery is demonstrated initially for each purge and trap GCMS system. The test is repeated only if the purge and trap or GCMS systems are modified in any way that might result in a change in recovery.

7.3.2 Demonstrate that 100 ng toluene (or toluene-d_8) produces an area at m/z 91 (or 99) approximately one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required.

7.4 Calibration by isotope dilution--the isotope dilution approach is used for the purgeable organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available, or interferences are present, the internal standard method (section 7.5) is used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) vs concentration (ug/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d_8 is given in figure 6. Also shown are the ± 10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration (section 7.4.4).

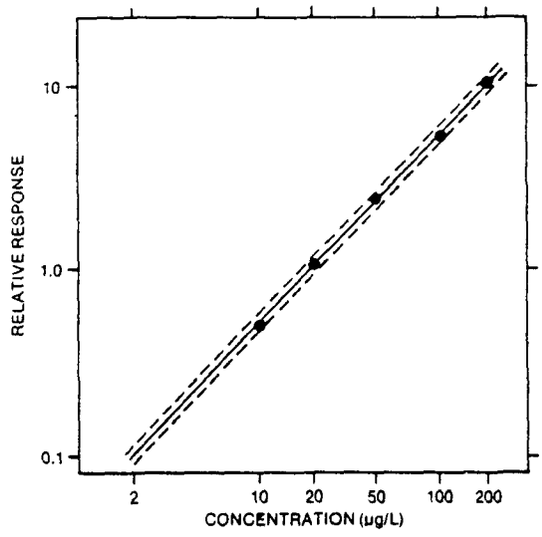

FIGURE 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window

7.4.1 The relative response (RR) of pollutant to labeled compound is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured in the pure pollutant (figure 7A).

R_y = the isotope ratio of pure labeled compound (figure 7B).

R_m = the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (figure 7C).

The correct way to calculate RR is:

$$RR = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method (section 7.5).

7.4.2 In most cases, the retention times of the pollutant and labeled compound are the same and isotope ratios (R's) can be calculated from the EICP areas, where:

$$R = \frac{(\text{area at } m_1/z)}{(\text{area at } m_2/z)}$$

If either of the areas is zero, it is assigned a value of one in the calculations; that is, if:

area of m_1/z = 50721, and
area of m_2/z = 0, then

$$R = \frac{50721}{1} = 50720$$

The m/z's are always selected such that $R_x > R_y$. When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios.

R_x, R_y, and R_m are defined as follows:

$$R_x = \frac{[\text{area } m_1/z \text{ (at } RT_1)]}{1}$$

$$R_y = \frac{1}{[\text{area } m_2/z \text{ (at } RT_2)]}$$

$$R_m = \frac{[\text{area } m_1/z \text{ (at } RT_1)]}{[\text{area } m_2/z \text{ (at } RT_2)]}$$

7.4.3 An example of the above calculations can be taken from the data plotted in figure 7 for toluene and toluene-d_8. For these data,

$$R_x = \frac{168920}{1} = 168900$$

$$R_y = \frac{1}{60960} = 0.00001640$$

$$R_m = \frac{96868}{82508} = 1.174$$

The RR for the above data is then calculated using the equation given in section 7.4.1. For the example, RR = 1.174. Not all labeled compounds elute before their pollutant analogs.

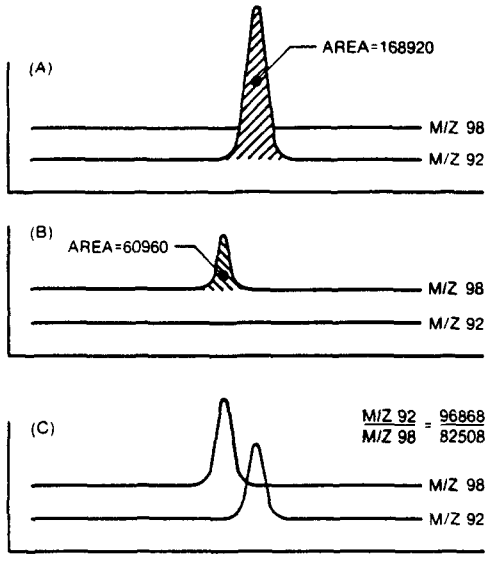

FIGURE 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-d_8, and (C) a Mixture of Toluene and Toluene-d_8

7.4.4 To calibrate the analytical system by isotope dilution, analyze a 5 mL aliquot of each of the aqueous calibration standards (section 6.7.1) spiked with an appropriate constant amount of the labeled compound spiking solution (section 6.6), using the purge and trap procedure in section 10. Compute the RR at each concentration.

7.4.5 Linearity--if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard--used when criteria for isotope dilution (section 7.4) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds.

The internal standards used for volatiles analyses are bromochloro methane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluted internal standard, as shown in tables 3 and 5.

7.5.1 Response factors--calibration requires the determination of response factors (RF) which are defined by the following equation:

$$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)}, \text{ where}$$

A_s is the EICP area at the characteristic m/z for the compound in the daily standard.

A_{is} is the EICP area at the characteristic m/z for the internal standard.

C_{is} is the concentration (ug/L) of the internal standard.

C_s is the concentration of the pollutant in the daily standard.

7.5.2 The response factor is determined at 10, 20, 50, 100, and 200 ug/L for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants--see section 6.7), in a way analogous to that for calibration by isotope dilution (section 7.4.4). The RF is plotted against concentration for each compound in the standard (C_s) to produce a calibration curve.

7.5.3 Linearity--if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration--by adding the isotopically labeled compounds and

internal standards (section 6.6) to the aqueous calibration standards (section 6.7.1), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 11.5) by purging the aqueous performance standard (section 6.7.2).

Recalibration is required only if calibration and on-going performance (section 11.5) criteria cannot be met.

7.7 Elevated purge temperature calibration--samples containing greater than one percent solids are analyzed at a temperature of 40 ± 2 °C (section 10). For these samples, the analytical system may be calibrated using a purge temperature of 40 ± 2 °C in order to more closely approximate the behavior of the compounds of interest in high solids samples.

8 QUALITY ASSURANCE/QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (reference 8). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method.

This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis (section 3). The procedures and criteria for analysis of a blank are described in sections 8.5.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3.

When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 14.2).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through the analysis of the aqueous performance standard (section 6.7.2) that the analysis system is in control. This procedure is described in sections 11.1 and 11.5.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in sections 8.4 and 11.5.2.

8.2 Initial precision and accuracy--to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations for compounds to be calibrated:

8.2.1 Analyze two sets of four 5-mL aliquots (8 aliquots total) of the aqueous performance standard (section 6.7.2) according to the method beginning in section 10.

8.2.2 Using results of the first set of four analyses in section 8.2.1, compute the average recovery (X) in ug/L and the standard deviation of the recovery (s) in ug/L for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy found in table 6. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 6 present a substantial probability that one or more will fail one of the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for the compound (s) in question. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Spike and analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the percent recovery for each compound with the corresponding labeled compound recovery limit in table 6. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample.

Therefore, the sample matrix is complex and the sample is to be diluted and reanalyzed, per section 14.2.

8.4 As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in section 8.3.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if $P = 90\%$ and $s_p = 10\%$, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound on a regular basis (e.g. after each 5 - 10 new accuracy measurements).

8.5 Blanks--reagent water blanks are analyzed to demonstrate freedom from carry-over (section 3) and contamination.

8.5.1 The level at which the purge and trap system will carry greater than 5 ug/L of a pollutant of interest (tables 1 and 2) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the 5 ug/L level.

8.5.2 With each sample lot (samples analyzed on the same 8 hr shift), a blank shall be

Table 6

ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

	Acceptance criteria at 20 ug/L or as noted			
	Initial precision and accuracy Section 8.2.3		Labeled compound recovery Sec 8.3 and 14.2	On-going accuracy Sec 11.5
Compound	s (ug/L)	X (ug/L)	P (%)	R (ug/L)
acetone*	51.0	77 - 153	35 - 165	55 - 145
acrolein*	72.0	32 - 168	37 - 163	7 - 190
acrylonitrile*	16.0	70 - 132	ns - 204	58 - 144
benzene	9.0	13 - 28	ns - 196	4 - 33
bromodichloromethane	8.2	7 - 32	ns - 99	4 - 34
bromoform	7.0	7 - 35	ns - 214	6 - 36
bromomethane	25.0	d - 54	ns - 414	d - 61
carbon tetrachloride	6.9	16 - 25	42 - 165	12 - 30
chlorobenzene	8.2	14 - 30	ns - 205	4 - 35
chloroethane	15.0	d - 47	ns - 308	d - 51
2-chloroethylvinyl ether	36.0	d - 70	ns - 554	d - 79
chloroform	7.9	12 - 26	18 - 172	8 - 30
chloromethane	26.0	d - 56	ns - 410	d - 64
dibromochloromethane	7.9	11 - 29	16 - 185	8 - 32
1,1-dichloroethane	6.7	11 - 31	23 - 191	9 - 33
1,2-dichloroethane	7.7	12 - 30	12 - 192	8 - 33
1,1-dichloroethene	12.0	d - 50	ns - 315	d - 52
trans-1,2-dichlorethene	7.4	11 - 32	15 - 195	8 - 34
1,2-dichloropropane	19.0	d - 47	ns - 343	d - 51
cis-1,3-dichloropropene	22.0	d - 51	ns - 381	d - 56
trans-1,3-dichloropropene	15.0	d - 40	ns - 284	d - 44
diethyl ether*	44.0	75 - 146	44 - 156	55 - 14
p-dioxane	7.2	13 - 27	ns - 239	11 - 29
ethylbenzene	9.6	16 - 29	ns - 203	5 - 35
methylene chloride	9.7	d - 50	ns - 316	d - 50
methyl ethyl ketone*	57.0	66 - 159	36 - 164	42 - 158
1,1,2,2-tetrachloroethane	9.6	11 - 30	5 - 199	7 - 34
tetrachlorethene	6.6	15 - 29	31 - 181	11 - 32
toluene	6.3	15 - 29	4 - 193	6 - 33
1,1,1-trichloroethane	5.9	11 - 33	12 - 200	8 - 35
1,1,2-trichloroethane	7.1	12 - 30	21 - 184	9 - 32
trichloroethene	8.9	17 - 30	35 - 196	12 - 34
vinyl chloride	228.0	d - 59	ns - 452	d - 65

* Acceptance criteria at 100 ug/L

d = detected; result must be greater than zero.

ns = no specification; limit would be below detection limit.

analyzed immediately after analysis of the aqueous performance standard (section 11.1) to demonstrate freedom from contamination. If any of the compounds of interest (tables 1 and 2) or any potentially interfering compound is found in a blank at greater than 10 ug/L (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in tables 1 and 2), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration *verification (section 11.5) and for* initial (section 8.2) and on-going (section 11.5) precision and accuracy should be identical, so that the most precise results will be obtained. The GCMS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal method is used.

9 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Grab samples are collected in glass containers having a total volume greater than 20 mL. For aqueous samples which pour freely, fill sample bottles so that no air bubbles pass through the sample as the bottle is filled and seal each bottle so that no air bubbles are entrapped. Maintain the hermetic seal on the sample bottle until time of analysis.

9.2 Samples are maintained at 0 - 4 °C from the time of collection until analysis. If an aqueous sample contains residual *chlorine, add sodium* thiosulfate preservative (10 mg/40 mL) to the empty sample bottles just prior to shipment to the sample site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (reference 9). If preservative has been added, shake the bottle vigorously for one minute immediately after filling.

9.3 For aqueous samples, experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve *these compounds in wastewaters for more* than seven days.

For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in section 9.1. If residual chlorine is present, add sodium thiosulfate to a separate sample container and fill as in section 9.1.

9.4 All samples shall be analyzed within 14 days of collection.

10 PURGE, TRAP, AND GCMS ANALYSIS

Samples containing less than one percent solids are analyzed directly as aqueous samples (section 10.4). Samples containing one percent solids or greater are analyzed as solid samples (section 10.5).

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker.

10.1.2 Dry overnight (12 hours minimum) at 110 ± 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of sample dry}}{\text{weight of sample wet}} \times 100$$

10.2 Remove standards and samples from cold storage and bring to 20 - 25 °C.

10.3 Adjust the purge gas flow rate to 40 ± 4 mL/min.

10.4 Samples containing less than one percent solids

10.4.1 Mix the sample by shaking vigorously. Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample bottle and carefully pour the sample into the syringe barrel until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ± 0.1 mL. Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data.

10.4.2 Add an appropriate amount of the labeled compound spiking solution (section 6.6) through the valve bore, then close the valve.

10.4.3 Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber. Purge the sample per section 10.6.

10.5 Weighing of samples containing one percent solids or greater.

10.5.1 Mix the sample thoroughly using a clean spatula.

10.5.2 Weigh 5 ± 1 grams of sample into a purging vessel (figure 2). Record the weight to three significant figures.

10.5.3 Add 5.0 ± 0.1 mL of reagent water to the vessel.

10.5.4 Using a metal spatula, break up any lumps of sample to disperse the sample in the water.

10.5.5 Add an appropriate amount of the labeled compound spiking solution (section 6.6) to the sample in the purge vessel. Place a cap on the purging vessel and and shake vigorously to further disperse the sample. Attach the purge vessel to the purging device.

10.6 Purge the sample for 11.0 ± 0.1 minutes at 20 - 25 °C for samples containing less than one percent solids. Purge samples containing one percent solids or greater at 40 ± 2 °C. If the compounds in table 2 that do not purge at 20 - 40 °C are to be determined, a purge temperature of 80 ± 5 °C is used.

10.7 After the 11 minute purge time, attach the trap to the chromatograph and set the purge and trap apparatus to the desorb mode (figure 5). Desorb the trapped compounds into the GC column by heating the trap to 170 - 180 °C while backflushing with carrier gas at 20 - 60 mL/min for four minutes. Start MS data acquisition upon start of the desorb cycle, and start the GC column temperature program 3 minutes later. Table 3 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and minimum levels that can be achieved under these conditions. An example of the separations achieved by the column listed is shown in figure 9. Other columns may be used provided the requirements in section 8 are met. If the priority pollutant gases produce GC peaks so broad that the precision and recovery specifications (section 8.2) cannot be met, the column may be cooled to ambient

or subambient temperatures to sharpen these peaks.

10.8 After desorbing the sample for four minutes, recondition the trap by purging with purge gas while maintaining the trap temperature at 170 - 180 °C. After approximately seven minutes, turn off the trap heater to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

10.9 While analysis of the desorbed compounds proceeds, remove and clean the purge device. Rinse with tap water, clean with detergent and water, rinse with tap and distilled water, and dry for one hour minimum in an oven at a temperature greater than 150 °C.

11 SYSTEM PERFORMANCE

11.1 At the beginning of each 8 hr shift during which analyses are performed, system calibration and performance shall be verified for the pollutants and labeled compounds (table 1). For these tests, analysis of the aqueous performance standard (section 6.7.2) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may blanks and samples be analyzed.

11.2 BFB spectrum validity--the criteria in table 4 shall be met.

11.3 Retention times--the absolute retention times of the internal standards shall be as follows: bromochloromethane: 653 - 782 seconds; 2-bromo-1-chloropropane: 1270 - 1369 seconds; 1,4-dichlorobutane: 1510 - 1605 seconds. The relative retention times of all pollutants and labeled compounds shall fall within the limits given in table 3.

11.4 GC resolution--the valley height between toluene and toluene-d_8 (at m/z 91 and 99 plotted on the same graph) shall be less than 10 percent of the taller of the two peaks.

11.5 Calibration verification and on-going precision and accuracy -- compute the concentration of each pollutant (table 1) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant (table 1) which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

11.5.1 For each pollutant and labeled compound, compare the concentration with the corresponding limit for on-going accuracy in table 6.

If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 6 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure may be attributed to probability, proceed as follows:

11.5.1.1 Analyze a second aliquot of the aqueous performance standard (section 6.7.2).

11.5.1.2 Compute the concentration for only those compounds which failed the first test (section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds and analyses of blanks and samples may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the

system (section 7), and repeat the entire test (section 11.1) for all compounds.

11.5.2 Add results which pass the specification in 11.5.1.2 to initial (section 8.2) and previous on-going data. Update QC charts to form a graphic representation of laboratory performance (figure 8).

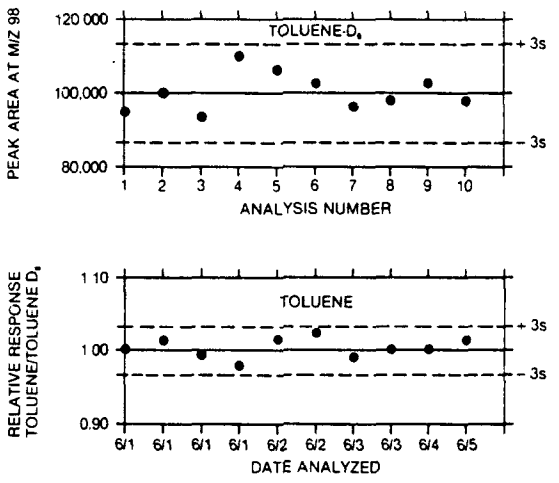

FIGURE 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d8 (lower graph) Plotted as Function of Time or Analysis Number

Develop a statement of accuracy for each pollutant and labeled compound by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85 - 105 percent.

12 QUALITATIVE DETERMINATION

Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the mass spectral libraries. For compounds for which the relative retention times and mass spectra are known, identification is confirmed per sections 12.1 and 12.2. For unidentified GC peaks, the spectrum is compared to spectra in the EPA/NIH mass spectral file per section 12.3.

12.1 Labeled compounds and pollutants having no labeled analog (tables 1 and 2):

12.1.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

12.1.3 For the compounds for which the system has been calibrated (table 1), the relative retention time shall be within the windows specified in table 3.

12.1.4 For the compounds for which the system has not been calibrated but the relative retention times and mass spectra are known (table 2), the retention time relative to the internal standard specified in table 3 shall be within ± 20 scans or ± 60 seconds, whichever is greater, based on the nominal relative retention time specified in table 3.

12.2 Pollutants having a labeled analog (table 1):

12.2.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

13.2.3 The relative retention time between the pollutant and its labeled analog shall be within the windows specified in table 3.

12.3 Unidentified GC peaks

12.3.1 The signals for m/z's specific to a GC peak shall all maximize within the same two consecutive scans.

12.3.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two with the masses stored in the EPA/NIH Mass Spectral File.

12.4 M/z's present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

13 QUANTITATIVE DETERMINATION

13.1 Isotope dilution -- by adding a known amount of a labeled compound to every sample prior to purging, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the toluene example given in figure 7 (section 7.4.3), RR would be equal to 1.174. For this RR value, the toluene calibration curve given in figure 6 indicates a concentration of 31.8 ug/L.

13.2 Internal standard--calculate the concentration of each pollutant using the response factor determined from calibration data (section 7.5) for the compounds which were calibrated (table 1), or from table 5 for compounds which were not calibrated (table 2), using the following equation:

$$\text{Concentration} = \frac{(A_s \times C_{is})}{(A_{is} \times RF)}$$

where the terms are as defined in section 7.5.1.

13.3 The concentration of the pollutant in the solid phase of the sample is computed using the concentration of the pollutant detected in the aqueous solution, as follows:

Concentration in solid (ug/kg) =

$$\frac{0.005\ L \times \text{aqueous conc (ug/L)}}{\text{weight of solids (g)}}$$

where "% solids" is from section 10.1.3.

13.4 If the EICP area at the quantitation m/z exceeds the calibration range of the system, samples are diluted by successive factors of 10 until the area is within the calibration range.

13.4.1 For aqueous samples, bring 0.50 mL, 0.050 mL, 0.0050 mL etc. to 5 mL volume with reagent water and analyze per section 10.4.

13.4.2 For samples containing high solids, substitute 0.50 or 0.050 gram in section 10.5.2 to achieve a factor of 10 or 100 dilution, respectively.

13.4.3 For dilution of high solids samples greater than a factor of 100, add 5 grams of sample to 10 mL methanol in a calibrated 15 - 25 mL centrifuge tube. Cap and shake vigorously for 15 - 20 seconds to disperse the sample in the methanol. Centrifuge to settle suspended particles, if necessary.

13.4.3.1 Remove 0.1 percent of the volume of the supernate with a 15 - 25 uL syringe. This volume will be in the range of 10 - 15 uL.

Add this volume to 5 mL reagent water in a 5 mL syringe and analyze per section 10.4.1.

13.4.3.2 For further dilutions, remove 1 mL of the supernate (14.4.3) and dilute to 10 mL, 100 mL, 1000 mL etc. in reagent water. Remove a volume of this sample/reagent water mixture equivalent to the volume determined in step 13.4.3.1, add to 5 mL reagent water in a 5 mL syringe, and analyze per section 10.4.1.

13.5 For GC peaks which are to be identified (per section 12.3), the sample is diluted by successive factors of 10 when any peak in the uncorrected mass spectrum at the GC peak maximum is saturated.

13.6 Report results for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples, in ug/L for samples containing less than one percent solids and in ug/kg for samples in which the undiluted sample contains one percent solids or greater, to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 13.4) or at which no m/z in the spectrum is saturated (section 13.5). For compounds having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 13.4) and the labeled compound recovery is within the normal range for the method (section 14.2).

14 ANALYSIS OF COMPLEX SAMPLES

14.1 Some samples may contain high levels (>1000 ug/kg) of the compounds of interest and of interfering compounds. Some samples will foam excessively when purged; others will overload the trap/or GC column.

14.2 Dilute 0.5 mL of samples containing less than one percent solids or 0.5 gram of samples containing one percent solids or greater with 4.5 mL of reagent water and analyze this diluted sample when the recovery of any labeled compound is outside the range given in table 6. If the recovery remains outside of the range for this diluted sample, the aqueous performance standard shall be analyzed (section 11) and calibration verified (section 11.5). If the recovery for the labeled compound in the aqueous performance standard is outside the range given in table 6, the analytical system is out of control. In this case, the instrument shall be repaired, the performance specifications in section 11 shall be met, and the analysis of the undiluted sample shall be repeated.

If the recovery for the aqueous performance standard is within the range given in table 6, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

14.3 Reverse search computer programs can misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra when a high level of the pollutant is present. Examine each chromatogram for peaks greater than the height of the internal standard peaks. These peaks can obscure the compounds of interest.

15 METHOD PERFORMANCE

15.1 The specifications for this method were taken from the interlaboratory validation of EPA Method 624 (reference 10). Method 1624 has been shown to yield slightly better performance on treated effluents than method 624. Results of initial tests of this method at a purge temperature of 80 °C can be found in reference 11 and results of initial tests of this method on municipal sludge can be found in reference 12.

15.2 A chromatogram of the 20 ug/L aqueous performance standards (sections 6.7.2 and 11.1) is shown in figure 9.

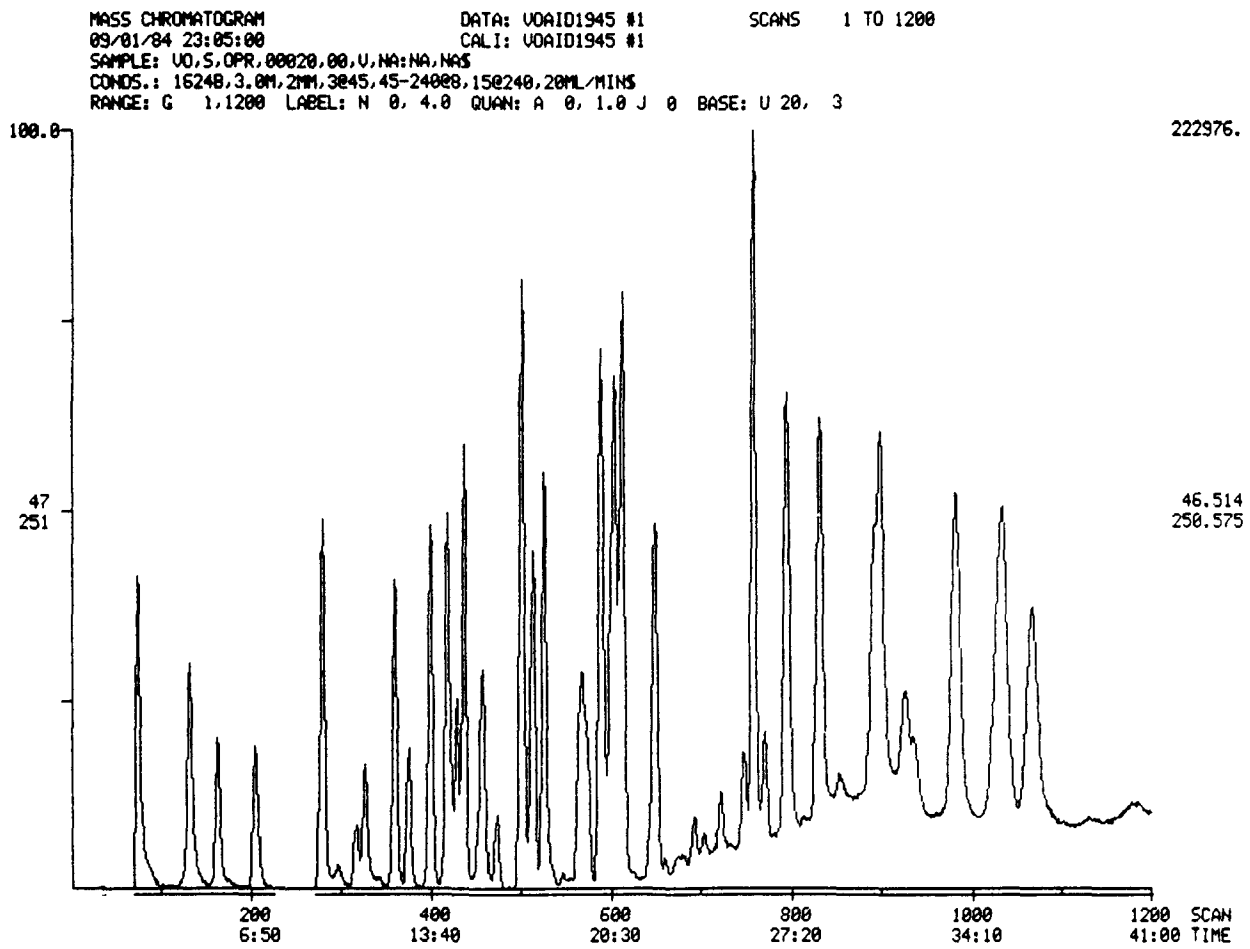

FIGURE 9 Chromatogram of Aqueous Performance Standard

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Appendix A: Mass Spectra in the Form of Mass/intensity Lists

532 allyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	30	43	39	44	232	45	12	53	13	55	59
56	58	57	1000	58	300	61	15				

533 carbon disulfide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	282	46	10	64	14	76	1000	77	27	78	82

534 2-chloro-1,3-butadiene (chloroprene)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
48	21	49	91	50	223	51	246	52	241	53	1000
54	41	61	30	62	54	63	11	64	16	73	21
87	12	88	452	89	22	90	137				

535 chloroacetonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	135	48	1000	49	88	50	294	51	12	73	22
74	43	75	884	76	39	77	278				

536 3-chloropropene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
35	39	36	40	40	44	42	206	47	40	58	35
49	176	51	64	52	31	61	29	73	22	75	138
76	1000	77	74	78	324						

537 crotonaldehyde

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
35	26	40	28	42	339	43	48	44	335	49	27
50	40	51	20	52	21	53	31	55	55	68	24
69	511	70	1000	71	43						

538 1,2-dibromoethane (EDB)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
79	50	80	13	31	51	82	15	93	54	95	42
105	32	106	29	107	1000	108	38	109	922	110	19
186	13	188	27	190	13						

539 dibromomethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
43	99	44	101	45	30	79	184	80	35	81	175
91	142	92	61	93	1000	94	64	95	875	160	18
172	375	173	14	174	719	175	12	176	342		

540 trans-1,4-dichloro-2-butene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	166	50	171	51	289	52	85	53	878	54	273
62	286	64	91	75	1000	77	323	88	246	89	415
90	93	91	129	124	138	126	86	128	12		

541 1,3-dichloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	15	42	44	47	19	48	20	49	193	51	55
61	18	62	22	63	131	65	38	75	47	76	1000
77	46	78	310	79	12						

542 cis-1,3-dichloropropene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
37	262	38	269	39	998	49	596	51	189	75	1000
77	328	110	254	112	161						

543 ethyl cyanide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	115	50	34	51	166	52	190	53	127	54	1000
55	193										

544 ethyl methacrylate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	127	43	48	45	155	55	32	58	39	68	60
69	1000	70	83	71	25	85	14	86	169	87	21
96	17	99	93	113	11	114	119				

545 2-hexanone (methyl butyl ketone)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	61	43	1000	44	24	55	12	57	130	58	382
59	21	71	36	85	37	100	56				

546 iodomethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	57	127	328	128	17	139	39	140	34	141	120
142	1000	143	12								

547 isobutyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
34	21	35	13	36	13	37	11	39	10	42	575
43	1000	44	42	45	21	55	40	56	37	57	21
59	25	73	12	74	63						

548 methacrylonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
38	24	39	21	41	26	42	100	49	19	50	60
51	214	52	446	53	19	62	24	63	59	64	136
65	55	66	400	67	1000	68	51				

549 methyl methacrylate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	127	43	52	45	48	53	30	55	100	56	49
59	124	68	28	69	1000	70	51	82	26	85	45
98	20	99	89	100	442	101	22				

550 4-methyl-2-pentanone (methyl isobutyl ketone; MIBK)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	69	43	1000	44	54	53	11	55	15	56	17
57	205	58	346	59	20	67	12	69	10	85	9
100	94										

551 1,1,1,2-tetrachloroethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	144	49	163	60	303	61	330	62	98	82	45
84	31	95	416	96	152	97	270	98	84	117	804
121	236	131	1000	133	955	135	301				

552 trichlorofluoromethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	95	47	153	49	43	51	21	52	14	66	162
68	53	82	40	84	28	101	1000	102	10	103	671
105	102	117	16	119	14						

553 1,2,3-trichloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	285	51	87	61	300	62	107	63	98	75	1000
76	38	77	302	83	23	96	29	97	166	98	20
99	103	110	265	111	28	112	164	114	25		

554 vinyl acetate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
36	5	42	103	43	1000	44	70	45	8	86	57

951 m-xylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
65	62	77	124	91	1000	105	245	106	580		

951 o- + p-xylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	88	77	131	91	1000	105	229	106	515		

Method 1625, Revision C 15 February 1988 Draft

Semivolatile Organic Compounds by Isotope Dilution GCMS

1 SCOPE AND APPLICATION

1.1 This method is designed to determine the semivolatile toxic organic pollutants associated with the 1976 Consent Decree; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liabilities Act; and other compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GCMS).

1.2 The chemical compounds listed in tables 1 through 4 may be determined in waters, soils, and municipal sludges by this method. The method is designed to meet the survey requirements of the Environmental Protection Agency (EPA).

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in tables 5 and 6 typify the minimum quantity that can be detected with no interferences present.

1.4 The GCMS portions of this method are for use only by analysts experienced with GCMS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GCMS should run the performance tests in reference 1 before beginning.

Table 1

BASE/NEUTRAL EXTRACTABLE COMPOUNDS
DETERMINED BY CALIBRATED GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

	Pollutant				Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
acenaphthene	34205	83-32-9	001 B	001 B	d_{10}	15067-20-2	201 B
acenaphthylene	34200	208-96-8	077 B	002 B	d_{8}	93951-97-4	277 B
anthracene	34220	120-12-7	078 B	003 B	d_{10}	1719-06-8	278 B
benzidine	39120	92-87-5	005 B	004 B	d_{8}	92890-63-6	205 B
benzo(a)anthracene	34526	56-55-3	072 B	005 B	d_{12}	1718-53-2	272 B
benzo(b)fluoranthene	34230	205-99-2	074 B	007 B	d_{12}	93951-98-5	274 B
benzo(k)fluoranthene	34242	207-08-9	075 B	009 B	d_{12}	93952-01-3	275 B
benzo(a)pyrene	34247	50-32-8	073 B	006 B	d_{12}	63466-71-7	273 B
benzo(ghi)perylene	34521	191-24-2	079 B	008 B	d_{12}	93951-66-7	279 B
biphenyl (Appendix C)	81513	92-52-4	512 B		d_{10}	1486-01-7	612 B
bis(2-chloroethyl) ether	34273	111-44-4	018 B	011 B	d_{8}	93952-02-4	218 B
bis(2-chloroethoxy)methane	34278	111-91-1	043 B	010 B	d_{8}	93966-78-0	243 B
bis(2-chloroisopropyl) ether	34283	108-60-1	042 B	012 B	d_{12}	93951-67-8	242 B
bis(2-ethylhexyl) phthalate	39100	117-81-7	066 B	013 B	d_{4}	93951-87-2	266 B
4-bromophenyl phenyl ether	34636	101-55-3	041 B	014 B	d_{5}	93951-83-8	241 B
butyl benzyl phthalate	34292	85-68-7	067 B	015 B	d_{4}	93951-88-3	267 B
n-C10 (Appendix C)	77427	124-18-5	517 B		d_{22}	16416-29-8	617 B

Compound	Pollutant Storet	CAS Registry	EPA-EGD	NPDES	Labeled Compound Analog	CAS Registry	EPA-EGD
n-C12 (Appendix C)	77588	112-40-3	506 B		d_{26}	16416-30-1	606 B
n-C14 (Appendix C)	77691	629-59-4	518 B				618 B
n-C16 (Appendix C)	77757	544-76-3	519 B		d_{34}	15716-08-2	619 B
n-C18 (Appendix C)	77804	593-45-3	520 B				620 B
n-C20 (Appendix C)	77830	112-95-8	521 B		d_{42}	62369-67-9	621 B
n-C22 (Appendix C)	77859	629-97-0	522 B				622 B
n-C24 (Appendix C)	77886	646-31-1	523 B		d_{50}	16416-32-3	623 B
n-C26 (Appendix C)	77901	630-01-3	524 B				624 B
n-C28 (Appendix C)	78116	630-02-4	525 B				625 B
n-C30 (Appendix C)	78117	638-68-6	526 B		d_{62}	93952-07-9	626 B
carbazole (4c)	77571	86-74-8	528 B		d_8	38537-24-5	628 B
2-chloronaphthalene	34581	91-58-7	020 B	016 B	d_7	93951-84-9	220 B
4-chlorophenyl phenyl ether	34641	7005-72-3	040 B	017 B	d_5	93951-85-0	240 B
chrysene	34320	218-01-9	076 B	018 B	d_{12}	1719-03-5	276 B
p-cymene (Appendix C)	77356	99-87-6	513 B		d_{14}	93952-03-5	613 B
dibenzo(a,h)anthracene	34556	53-70-3	082 B	019 B	d_{14}	13250-98-1	282 B
dibenzofuran (Appendix C & 4c)	81302	132-64-9	505 B		d_8	93952-04-6	605 B
dibenzothiophene (Synfuel)	77639	132-65-0	504 B		d_8	33262-29-2	604 B
di-n-butyl phthalate	39110	84-74-2	068 B	026 B	d_4	93952-11-5	268 B
1,2-dichlorobenzene	34536	95-50-1	025 B	020 B	d_4	2199-69-1	225 B
1,3-dichlorobenzene	34566	541-73-1	026 B	021 B	d_4	2199-70-4	226 B
1,4-dichlorobenzene	34571	106-46-7	027 B	022 B	d_4	3855-82-1	227 B
3,3'-dichlorobenzidine	34631	91-94-1	028 B	023 B	d_6	93951-91-8	228 B
diethyl phthalate	34336	84-66-2	070 B	024 B	d_4	93952-12-6	270 B
2,4-dimethylphenol	34606	105-67-9	034 A	003 A	d_3	93951-75-8	234 A
dimethyl phthalate	34341	131-11-3	071 B	025 B	d_4	93951-89-4	271 B
2,4-dinitrotoluene	34611	121-14-2	035 B	027 B	d_3	93951-68-9	235 B
2,6-dinitrotoluene	34626	606-20-2	036 B	028 B	d_3	93951-90-7	236 B
di-n-octyl phthalate	34596	117-84-0	069 B	029 B	d_4	93952-13-7	269 B
diphenylamine (Appendix C)	77579	122-39-4	507 B		d_{10}	37055-51-9	607 B
diphenyl ether (Appendix C)	77587	101-84-8	508 B		d_{10}	93952-05-7	608 B
1,2-diphenylhydrazine	34346	122-66-7	037 B	030 B	d_{10}	93951-92-9	237 B
fluoranthene	34376	206-44-0	039 B	031 B	d_{10}	93951-69-0	231 B
fluorene	34381	86-73-7	080 B	032 B	d_{10}	81103-79-9	280 B
hexachlorobenzene	39700	118-74-1	009 B	033 B	$^{13}C_6$	93952-14-8	209 B
hexachlorobutadiene	34391	87-68-3	052 B	034 B	$^{13}C_4$	93951-70-3	252 B
hexachloroethane	34396	67-72-1	012 B	036 B	^{13}C	93952-15-9	212 B
hexachlorocyclopentadiene	34386	77-47-4	053 B	035 B	$^{13}C_4$	93951-71-4	253 B
ideno(1,2,3-cd)pyrene	34403	193-39-5	083 B	037 B			
isophorone	34408	78-59-1	054 B	038 B	d_8	93952-16-0	254 B
naphthalene	34696	91-20-3	055 B	039 B	d_8	1146-65-2	255 B
beta-naphthylamine (Appendix C)	82553	91-59-8	502 B		d_7	93951-94-1	602 B
nitrobenzene	34447	98-95-3	056 B	040 B	d_5	4165-60-0	256 B
N-nitrosodimethylamine	34438	62-75-9	061 B	041 B	d_6	17829-05-9	261 B
N-nitrosodi-n-proplyamine	34428	621-64-7	063 B	042 B	d_{14}	93951-96-3	263 B
N-nitrosodiphenylamine	34433	86-30-6	062 B	043 B	d_6	93951-95-2	262 B
phenanthrene	34461	85-01-8	081 B	044 B	d_{10}	1517-22-2	281 B
phenol	34694	108-95-2	065 A	010 A	d_5	4165-62-2	265 A
alpha-picoline (Synfuel)	77088	109-06-8	503 B		d_7	93951-93-0	603 B
pyrene	34469	129-00-0	084 B	045 B	d_{10}	1718-52-1	284 B
styrene (Appendix C)	77128	100-42-5	510 B		d_5	5161-29-5	610 B
alpha-terpineol (Appendix C)	77493	98-55-5	509 B		d_3	93952-06-8	609 B
1,2,3-trichlorobenzene (4c)	77613	87-61-6	529 B		d_3	3907-98-0	629 B
1,2,4-trichlorobenzene	34551	120-82-1	008 B	046 B	d_3	2199-72-6	208 B

Table 2

ACID EXTRACTABLE COMPOUNDS
DETERMINED BY CALIBRATED GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

Compound	Pollutant Storet	CAS Registry	EPA-EGD	NPDES	Labeled Compound Analog	CAS Registry	EPA-EGD
4-chloro-3-methylphenol	34452	59-50-7	022 A	008 A	d_2	93951-72-5	222 A
2-chlorophenol	34586	95-57-8	024 A	001 A	d_4	93951-73-6	224 A
2,4-dichlorophenol	34601	120-83-2	031 A	002 A	d_3	93951-74-7	231 A
2,4-dinitrophenol	34616	51-28-5	059 A	005 A	d_3	93951-77-0	259 A
2-methyl-4,6-dinitrophenol	34657	534-52-1	060 A	004 A	d_2	93951-76-9	260 A
2-nitrophenol	34591	88-75-5	057 A	006 A	d_4	93951-75-1	257 A
4-nitrophenol	34646	100-02-7	058 A	007 A	d_4	93951-79-2	258 A
pentachlorophenol	39032	87-86-5	064 A	009 A	$^{13}C_6$	85380-74-1	264 A
2,3,6-trichlorophenol (4c)	77688	933-75-5	530 A		d_2	93951-81-6	630 A
2,4,5-trichlorophenol (4c)		95-95-4	531 A		d_2	93951-82-7	631 A
2,4,6-trichlorophenol	34621	88-06-2	021 A	011 A	d_2	93951-80-5	221 A

Table 3

BASE/NEUTRAL EXTRACTABLE COMPOUNDS TO BE DETERMINED BY REVERSE SEARCH AND QUANTITATION
USING KNOWN RETENTION TIMES, RESPONSE FACTORS, REFERENCE COMPOUND, AND MASS SPECTRA

EGD No.	Compound	CAS Registry
555	acetophenone	98-86-2
556	4-aminobiphenyl	92-67-1
557	aniline	62-53-3
558	o-anisidine	90-04-0
559	aramite	140-57-8
560	benzanthrone	82-05-3
561	1,3-benzenediol (resorcinol)	108-46-3
562	benzenethiol	108-98-5
563	2,3-benzofluorene	243-17-4
564	benzyl alcohol	100-51-6
565	2-bromochlorobenzene	694-80-4
566	3-bromochlorobenzene	108-37-2
567	4-chloro-2-nitroaniline	89-63-4
568	5-chloro-o-toluidine	95-79-4
569	4-chloroaniline	106-47-8
570	3-chloronitrobenzene	121-73-3
571	o-cresol	95-48-7
572	crotoxyphos	7700-17-6
573	2,6-di-tert-butyl-p-benzoquinone	719-22-2
574	2,4-diaminotoluene	95-80-7
575	1,2-dibromo-3-chloropropane	96-12-8
576	2,6-dichloro-4-nitroaniline	99-30-9
577	1,3-dichloro-2-propanol	96-23-1
578	2,3-dichloroaniline	608-27-5
579	2,3-dichloronitro-benzene3209-22-1	
580	1,2:3,4-diepoxybutane	1464-53-5
581	3,3'-dimethoxybenzidine	119-90-4
582	dimethyl sulfone	67-71-0
583	p-dimethylamino-azobenzene	60-11-7
584	7,12-dimethylbenz-(a)anthracene	57-97-6
585	N,N-dimethylformamide	68-12-2
586	3,6-dimethylphenanthrene	1576-67-6
587	1,4-dinitrobenzene	100-25-4
588	diphenyldisulfide	882-33-7
589	ethyl methanesulfonate	62-50-0
590	ethylenethiourea	96-45-7
591	ethynylestradiol 3-methyl ether	72-33-3
592	hexachloropropene	1888-71-7
593	2-isopropylnaphthalene	2027-17-0

EGD No.	Compound	CAS Registry
594	isosafrole	120-58-1
595	longifolene	475-20-7
596	malachite green	569-64-2
597	methapyrilene	91-80-5
598	methyl methanesulfonate	66-27-3
599	2-methylbenzothioazole	120-75-2
900	3-methylcholanthrene	56-49-5
901	4,4'-methylene-bis(2-chloroaniline)	101-14-4
902	4,5-methylene-phenanthrene	203-64-5
903	1-methylfluorene	1730-37-6
904	2-methylnaphthalene	91-57-6
905	1-methylphenanthrene	832-69-9
906	2-(methylthio)-benzothiazole	615-22-5
907	1,5-naphthalenediamine	2243-62-1
908	1,4-naphthoquinone	130-15-4
909	alpha-naphthylamine	134-32-7
910	5-nitro-o-toluidine	99-55-8
911	2-nitroaniline	88-74-4
912	3-nitroaniline	99-09-2
913	4-nitroaniline	100-01-6
914	4-nitrobiphenyl	92-93-3
915	N-nitrosodi-n-butylamine	924-16-3
916	N-nitrosodiethylamine	55-18-5
917	N-nitrosomethyl-ethylamine	10595-95-6
918	N-nitrosomethyl-phenylamine	614-00-6
919	N-nitrosomorpholine	59-89-2
920	N-nitrosopiperidine	100-75-4
921	pentachlorobenzene	608-93-5
922	pentachloroethane	76-01-7
923	pentamethylbenzene	700-12-9
924	perylene	198-55-0
925	phenacetin	62-44-2
926	phenothiazine	92-84-2
927	1-phenylnaphthalene	605-02-7
928	2-phenylnaphthalene	612-94-2
929	pronamide	23950-58-5
930	pyridine	110-86-1
931	safrole	94-59-7
932	squalene	7683-64-9
933	1,2,4,5-tetra-chlorobenzene	95-94-3
934	thianaphthene (2,3-benzothiophene)	95-15-8
935	thioacetamide	62-55-5
936	thioxanthone	492-22-8
937	o-toluidine	95-53-4
938	1,2,3-trimethoxybenzene	634-36-6
939	2,4,5-trimethylaniline	137-17-7
940	triphenylene	217-59-4
941	tripropyleneglycol methyl ether	20324-33-8
942	1,3,5-trithiane	291-21-4

Table 4

ACID EXTRACTABLE COMPOUNDS
TO BE DETERMINED BY REVERSE SEARCH
AND QUANTITATION USING
KNOWN RETENTION TIMES,
RESPONSE FACTORS,
REFERENCE COMPOUND,
AND MASS SPECTRA

EGD No.	Compound	CAS Registry
943	benzoic acid	65-85-0
944	p-cresol	106-44-5
945	3,5-dibromo-4-hydroxybenzonitrile	1689-84-5
946	2,6-dichlorophenol	87-65-0
947	hexanoic acid	142-62-1
948	2,3,4,6-tetrachlorophenol	58-90-2

2 SUMMARY OF METHOD

2.1 The percent solids content of a sample is determined. Stable isotopically labeled analogs of the compounds of interest are added to the sample. If the solids content is less than one percent, a one liter sample is extracted at pH 12 - 13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is 30 percent percent or less, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted at pH 12-13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is greater than 30 percent, the sample is extracted using ultrasonic techniques.

Table 5

GAS CHROMATOGRAPHY OF BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time Mean (sec)	EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	high solids (ug/kg)
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000 - 1.000	10		
930	pyridine	378	164	0.325			
261	N-nitrosodimethylamine-d_6 (5)	378	164	0.286 - 0.364	50		
361	N-nitrosodimethylamine (5)	385	261	1.006 - 1.028	50	16	27
585	N,N-dimethylformamide	407	164	0.350			
580	1,2:3,4-diepoxybutane	409	164	0.352			
603	alpha picoline-d_7	417	164	0.326 - 0.393	50		
703	alpha picoline	426	603	1.006 - 1.028	50	25	87
917	N-nitrosomethylethylamine	451	164	0.338			
598	methyl methanesulfonate	511	164	0.439			
610	styrene-d_5	546	164	0.450 - 0.488	10		
710	styrene	549	610	1.002 - 1.009	10	149*	17
916	N-nitrosodiethylamine	570	164	0.490			
577	1,3-dichloro-2-propanol	589	164	0.506			
589	ethyl methanesulfonate	637	164	0.548			
582	dimethyl sulfone	649	164	0.558			
562	benzenethiol	667	164	0.574			
922	pentachloroethane	680	164	0.585			
557	aniline	694	164	0.597			
613	p-cymene-d_{14}	742	164	0.624 - 0.652	10		
713	p-cymene	755	613	1.008 - 1.023	10	426*	912*
265	phenol-d_5	696	164	0.584 - 0.613	10		
365	phenol	700	265	0.995 - 1.010	10	2501*	757*
218	bis(2-chloroethyl) ether-d_8	696	164	0.584 - 0.607	10		
318	bis(2-chloroethyl) ether	704	218	1.007 - 1.016	10	32	22
617	n-decane-d_{22}	698	164	0.585 - 0.615	10		
717	n-decane	720	617	1.022 - 1.038	10	299*	1188*
226	1,3-dichlorobenzene-d_4	722	164	0.605 - 0.636	10		
326	1,3-dichlorobenzene	724	226	0.998 - 1.008	10	46	26
227	1,4-dichlorobenzene-d_4	737	164	0.601 - 0.666	10		
327	1,4-dichlorobenzene	740	227	0.997 - 1.009	10	35	20
225	1,2-dichlorobenzene-d_4	758	164	0.632 - 0.667	10		
325	1,2-dichlorobenzene	760	225	0.995 - 1.008	10	63	16
935	thioacetamide	768	164	0.660			
564	benzyl alcohol	785	164	0.675			
242	bis(2-chloroisopropyl) ether-d_{12}	788	164	0.664 - 0.691	10		
342	bis(2-chloroisopropyl) ether	799	242	1.010 - 1.016	10	24	39
571	o-cresol	814	164	0.700			
263	N-nitrosodi-n-propylamine-d_{14} (5)	817	164	0.689 - 0.716	20		
363	N-nitrosodi-n-propylamine (5)	830	263	1.008 - 1.023	20	46	47
555	acetophenone	818	164	0.703			
212	hexachloroethane-^{13}C	819	164	0.690 - 0.717	10		
312	hexachloroethane	823	212	0.999 - 1.001	10	58	55
937	o-toluidine	830	164	0.714			
919	N-nitrosomorpholine	834	164	0.717			
575	1,2-dibromo-3-chloropropane	839	164	0.721			
256	nitrobenzene-d_5	845	164	0.706 - 0.727	10		

EGD No. (1)	Compound	Retention time Mean (sec)	EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	high solids (ug/kg)
356	nitrobenzene	849	256	1.002 - 1.007	10	39	28
566	3-bromochlorobenzene	854	164	0.734			
565	2-bromochlorobenzene	880	164	0.757			
941	tripropylene glycol methyl ether	881	164	0.758			
254	isophorone-d_8	881	164	0.747 - 0.767	10		
354	isophorone	889	254	0.999 - 1.017	10	8	5
942	1,3,5-trithiane	889	164	0.764			
920	N-nitrosopiperidine	895	164	0.770			
234	2,4-dimethylphenol-d_3	921	164	0.781 - 0.803	10		
334	2,4-dimethylphenol	924	234	0.999 - 1.003	10	26	13
243	bis(2-chloroethoxy) methane-d_6 (5)	933	164	0.792 - 0.807	10		
343	bis(2-chloroethoxy) methane (5)	939	243	1.000 - 1.013	10	26	23
208	1,2,4-trichlorobenzene-d_3	955	164	0.813 - 0.830	10		
308	1,2,4-trichlorobenzene	958	208	1.000 - 1.005	10	49	24
558	o-anisidine	962	164	0.827			
255	naphthalene-d_8	963	164	0.819 - 0.836	10		
355	naphthalene	967	255	1.001 - 1.006	10	62	42
934	thianapthene	971	164	0.835			
609	alpha-terpineol-d_3	973	164	0.829 - 0.844	10		
709	alpha-terpineol	975	609	0.998 - 1.008	10	nd	nd
606	n-dodecane-d_{26}	953	164	0.730 - 0.908	10		
706	n-dodecane	981	606	0.986 - 1.051	10	860*	3885*
629	1,2,3-trichlorobenzene-d_3 (5)	1000	164	0.852 - 0.868	10		
729	1,2,3-trichlorobenzene (5)	1003	629	1.000 - 1.005	10	260*	164*
252	hexachlorobutadiene-$^{13}C_4$	1005	164	0.856 - 0.871	10		
352	hexachlorobutadiene	1006	252	0.999 - 1.002	10	46	22
918	N-nitrosomethylphenylamine	1006	164	0.865			
592	hexachloropropene	1013	164	0.871			
569	4-chloroaniline	1016	164	0.874			
570	3-chloronitrobenzene	1018	164	0.875			
915	N-nitrosodi-n-butylamine	1063	164	0.914			
923	pentamethylbenzene	1083	164	0.931			
561	1,3-benzenediol	1088	164	0.936			
931	safrole	1090	164	0.937			
939	2,4,5-trimethylaniline	1091	164	0.938			
904	2-methylnaphthalene	1098	164	0.944			
599	2-methylbenzothiazole	1099	164	0.945			
568	5-chloro-o-toluidine	1101	164	0.947			
938	1,2,3-trimethoxybenzene	1128	164	0.970			
933	1,2,4,5-tetrachlorobenzene	1141	164	0.981			
253	hexachlorocyclopentadiene-$^{13}C_4$	1147	164	0.976 - 0.986	10		
353	hexachlorocyclopentadiene	1142	253	0.999 - 1.001	10	nd	nd
594	isosafrole (cis or trans)	1147	164	0.986			
594	isosafrole (cis or trans)	1190	164	1.023			
578	2,3-dichloroaniline	1160	164	0.997			
574	2,4-diaminotoluene	1187	164	1.021			
220	2-chloronaphthalene-d_7	1185	164	1.014 - 1.024	10		
320	2-chloronaphthalene	1200	220	0.997 - 1.007	10	80	59
518	n-tetradecane	1203	164	1.034	10	256	3533
612	biphenyl-d_{10}	1195	164	1.016 - 1.027	10		
712	biphenyl	1205	612	1.001 - 1.006	10	67	55
608	diphenyl ether-d_{10}	1211	164	1.036 - 1.047	10		
708	diphenyl ether	1216	608	0.997 - 1.009	10	44	12

EGD No. (1)	Compound	Retention time Mean (sec)	EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	high solids (ug/kg)
579	2,3-dichloronitrobenzene	1214	164	1.044			
911	2-nitroaniline	1218	164	1.047			
908	1,4-naphthoquinone	1224	164	1.052			
595	longifolene	1225	164	1.053			
277	acenaphthylene-d_8	1265	164	1.080 - 1.095	10		
377	acenaphthylene	1247	277	1.000 - 1.004	10	57	18
593	2-isopropylnaphthalene	1254	164	1.078			
587	1,4-dinitrobenzene	1255	164	1.079			
576	2,6-dichloro-4-nitroaniline	1259	164	1.083			
271	dimethyl phthalate-d_4	1269	164	1.083 - 1.102	10		
371	dimethyl phthalate	1273	271	0.998 - 1.005	10	62	21
573	2,6-di-t-butyl-p-benzoquinone	1273	164	1.095			
236	2,6-dinitrotoluene-d_3	1283	164	1.090 - 1.112	10		
336	2,6-dinitrotoluene	1300	236	1.001 - 1.005	10	55	47
912	3-nitroaniline	1297	164	1.115			
201	acenaphthene-d_{10}	1298	164	1.107 - 1.125	10		
301	acenaphthene	1304	201	0.999 - 1.009	10	64	55
605	dibenzofuran-d_8	1331	164	1.134 - 1.155	10		
705	dibenzofuran	1335	605	0.998 - 1.007	10	77	210*
921	pentachlorobenzene	1340	164	1.152			
909	alpha-naphthylamine	1358	164	1.168			
235	2,4-dinitrotoluene-d_3	1359	164	1.152 - 1.181	10		
335	2,4-dinitrotoluene	1364	235	1.000 - 1.002	10	65	209*
602	beta-naphthylamine-d_7	1368	164	1.163 - 1.189	50		
702	beta-naphthylamine	1371	602	0.996 - 1.007	50	49	37
590	ethylenethiourea	1381	164	1.187			
280	fluorene-d_{10}	1395	164	1.185 - 1.214	10		
380	fluorene	1401	281	0.999 - 1.008	10	69	61
240	4-chlorophenyl phenyl ether-d_5	1406	164	1.194 - 1.223	10		
340	4-chlorophenyl phenyl ether	1409	240	0.990 - 1.015	10	73	59
270	diethyl phthalate-d_4	1409	164	1.197 - 1.229	10		
370	diethyl phthalate	1414	270	0.996 - 1.006	10	52	16
906	2-(methylthio)benzothiazole	1415	164	1.217			
567	4-chloro-2-nitroaniline	1421	164	1.222			
910	5-nitro-o-toluidine	1422	164	1.223			
913	4-nitroaniline	1430	164	1.230			
619	n-hexadecane-d_{34}	1447	164	1.010 - 1.478	10		
719	n-hexadecane	1469	619	1.013 - 1.020	10	116*	644*
237	1,2-diphenylhydrazine-d_8	1433	164	1.216 - 1.248	20		
337	1,2-diphenylhydrazine (6)	1439	237	0.999 - 1.009	20	48	27
607	diphenylamine-d_{10}	1437	164	1.213 - 1.249	20		
707	diphenylamine	1439	607	1.000 - 1.007	20	58	54
262	N-nitrosodiphenylamine-d_6	1447	164	1.225 - 1.252	20		
362	N-nitrosodiphenylamine (7)	1464	262	1.000 - 1.002	20	55	36
241	4-bromophenyl phenyl ether-d_5 (5)	1495	164	1.271 - 1.307	10		
341	4-bromophenyl phenyl ether (5)	1498	241	0.990 - 1.015	10	55	17
925	phenacetin	1512	164	1.300			
903	1-methylfluorene	1514	164	1.302			
209	hexachlorobenzene-$^{13}C_6$	1521	164	1.288 - 1.327	10		
309	hexachlorobenzene	1522	209	0.999 - 1.001	10	51	48
556	4-aminobiphenyl	1551	164	1.334			
929	pronamide	1578	164	1.357			
281	phenanthrene-d_{10}	1578	164	1.334 - 1.380	10		

EGD No. (1)	Compound	Retention time Mean (sec)	EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	high solids (ug/kg)
520	n-octadecane	1580	164	1.359	10	134*	844*
381	phenanthrene	1583	281	1.000 - 1.005	10	42	22
278	anthracene-d_{10}	1588	164	1.342 - 1.388	10		
378	anthracene	1592	278	0.998 - 1.006	10	52	21
604	dibenzothiophene-d_8	1559	164	1.314 - 1.361	10		
704	dibenzothiophene	1564	604	1.000 - 1.006	10	72	71
588	diphenyldisulfide	1623	164	1.396			
914	4-nitrobiphenyl	1639	164	1.409			
927	1-phenylnaphthalene	1643	164	1.413			
628	carbazole-d_8 (5)	1645	164	1.388 - 1.439	20		
728	carbazole (5)	1650	628	1.000 - 1.006	20	47	24
621	n-eicosane-d_{42}	1655	164	1.184 - 1.662	10		
721	n-eicosane	1677	621	1.010 - 1.021	10	83	229*
907	1,5-naphthalenediamine	1676	164	1.441			
902	4,5-methylenephenanthrene	1690	164	1.453			
905	1-methylphenanthrene	1697	164	1.459			
268	di-n-butyl phthalate-d_4	1719	164	1.446 - 1.510	10		
368	di-n-butyl phthalate	1723	268	1.000 - 1.003	10	64	80
928	2-phenylnaphthalene	1733	164	1.490			
586	3,6-dimethylphenanthrene	1763	164	1.516			
597	methapyrilene	1781	164	1.531			
926	phenothiazine	1796	164	1.544			
239	fluoranthene-d_{10}	1813	164	1.522 - 1.596	10		
339	fluoranthene	1817	239	1.000 - 1.004	10	54	22
572	crotoxyphos	1822	164	1.567			
936	thioxanthone	1836	164	1.579			
284	pyrene-d_{10}	1844	164	1.523 - 1.644	10		
384	pyrene	1852	284	1.001 - 1.003	10	40	48
205	benzidine-d_8	1854	164	1.549 - 1.632	50		
305	benzidine	1853	205	1.000 - 1.002	50	nd	nd
522	n-docosane	1889	164	1.624	10	432*	447*
559	aramite	1901	164	1.635			
559	aramite	1916	164	1.647			
583	p-dimethylaminoazobenzene	1922	164	1.653			
563	2,3-benzofluorene	1932	164	1.661			
623	n-tetracosane-d_{50}	1997	164	1.671 - 1.764	10		
723	n-tetracosane	2025	612	1.012 - 1.015	10	--	--
932	squalene	2039	164	1.753			
267	butylbenzyl phthalate-d_4 (5)	2058	164	1.715 - 1.824	10		
367	butylbenzyl phthalate (5)	2060	267	1.000 - 1.002	10	60	65
276	chrysene-d_{12}	2081	164	1.743 - 1.837	10		
376	chrysene	2083	276	1.000 - 1.004	10	51	48
901	4,4'methylenebis(2-chloroaniline)	2083	164	1.791			
272	benzo(a)anthracene-d_{12}	2082	164	1.735 - 1.846	10		
372	benzo(a)anthracene	2090	272	0.999 - 1.007	10	61	47
581	3,3'-dimethoxybenzidine	2090	164	1.797			
228	3,3'-dichlorobenzidine-d_6	2088	164	1.744 - 1.848	50		
328	3,3'-dichlorobenzidine	2086	228	1.000 - 1.001	50	62	111
940	triphenylene	2088	164	1.795			
560	benzanthrone	2106	164	1.811			
266	bis(2-ethylhexyl) phthalate-d_4	2123	164	1.771 - 1.880	10		
366	bis(2-ethylhexyl) phthalate	2124	266	1.000 - 1.002	10	553*	1310*
524	n-hexacosane	2147	164	1.846	10	609*	886*

EGD No. (1)	Compound	Retention time Mean (sec)	EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	high solids (ug/kg)
591	ethynylestradiol 3-methyl ether	2209	164	1.899			
269	di-n-octyl phthalate-d_4	2239	164	1.867 - 1.982	10		
369	di-n-octyl phthalate	2240	269	1.000 - 1.002	10	72	62
525	n-octacosane	2272	164	1.954	10	492*	1810*
584	7,12-dimethylbenz(a)anthracene	2284	164	1.964			
274	benzo(b)fluoranthene-d_{12}	2281	164	1.902 - 2.025	10		
374	benzo(b)fluoranthene	2293	274	1.000 - 1.005	10	54	30
275	benzo(k)fluoranthene-d_{12}	2287	164	1.906 - 2.033	10		
375	benzo(k)fluoranthene	2293	275	1.000 - 1.005	10	95	20
924	perylene	2349	164	2.020			
273	benzo(a)pyrene-d_{12}	2351	164	1.954 - 2.088	10		
373	benzo(a)pyrene	2350	273	1.000 - 1.004	10	52	15
626	n-triacontane-d_{62}	2384	164	1.972 - 2.127	10		
726	n-triacontane	2429	626	1.011 - 1.028	10	252*	658*
596	malachite green	2382	164	2.048			
900	3-methylcholanthrene	2439	164	2.097			
083	indeno(1,2,3-cd)pyrene	2650	164	2.279	20	67	263*
282	dibenzo(a,h)anthracene-d_{14} (5)	2649	164	2.107 - 2.445	20		
382	dibenzo(a,h)anthracene (5)	2660	282	1.000 - 1.007	20	49	125
279	benzo(ghi)perylene-d_{12}	2741	164	2.187 - 2.524	20		
379	benzo(ghi)perylene	2750	279	1.001 - 1.006	20	44	nd

(1) Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) Single values in this column are based on single laboratory data.

(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. The concentration in the aqueous or solid phase is determined using the equations in section 14.

(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).

(5) Specification derived from related compound.

(6) Detected as azobenzene

(7) Detected as diphenylamine

nd = not detected when spiked into the sludge tested

*Background levels of these compounds were present in the sludge tested, resulting in higher than expected MDL's. The MDL for these compounds is expected to be approximately 50 ug/kg with no interferences present.

Column: 30 +/- 2 m x 0.25 +/- 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary

Temperature program: 5 min at 30°C; 30 - 280°C at 8°C per min; isothermal at 280°C until benzo(ghi)perylene elutes

Gas velocity: 30 +/- 5 cm/sec at 30°C

Table 6

GAS CHROMATOGRAPHY OF ACID EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	Method Detection Limit (4) high solids (ug/kg)
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000 - 1.000	10		
224	2-chlorophenol-d_4	701	164	0.587 - 0.618	10		
324	2-chlorophenol	705	224	0.997 - 1.010	10	18	10
947	hexanoic acid	746	164	0.641			
944	p-cresol	834	164	0.717			
257	2-nitrophenol-d_4	898	164	0.761 - 0.783	20		
357	2-nitrophenol	900	257	0.994 - 1.009	20	39	44
231	2,4-dichlorophenol-d_3	944	164	0.802 - 0.822	10		
331	2,4-dichlorophenol	947	231	0.997 - 1.006	10	24	116
943	benzoic acid	971	164	0.835			
946	2,6-dichlorophenol	981	164	0.844			
222	4-chloro-3-methylphenol-d_2	1086	164	0.930 - 0.943	10		
322	4-chloro-3-methylphenol	1091	222	0.998 - 1.003	10	41	62
221	2,4,6-trichlorophenol-d_2	1162	164	0.994 - 1.005	10	46	111
321	2,4,6-trichlorophenol	1165	221	0.998 - 1.004	10		
631	2,4,5-trichlorophenol-d_2 (5)	1167	164	0.998 - 1.009	10		
731	2,4,5-trichlorophenol	1170	631	0.998 - 1.004	10	32	55
530	2,3,6-trichlorophenol	1195	164	1.028	10	58	37
259	2,4-dinitrophenol-d_3	1323	164	1.127 - 1.149	50		
359	2,4-dinitrophenol	1325	259	1.000 - 1.005	50	565	642
258	4-nitrophenol-d_4	1349	164	1.147 - 1.175	50		
358	4-nitrophenol	1354	258	0.997 - 1.006	50	287	11
948	2,3,4,6-tetrachlorophenol	1371	164	1.179			
260	2-methyl-4,6-dinitrophenol-d_2	1433	164	1.216 - 1.249	20		
360	2-methyl-4,6-dinitrophenol	1435	260	1.000 - 1.002	20	385	83
945	3,5-dibromo-4-hydroxybenzonitrile	1481	164	1.273			
264	pentachlorophenol-$^{13}C_6$	1559	164	1.320 - 1.363	50		
364	pentachlorophenol	1561	264	0.998 - 1.002	50	51	207

(1) Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) Single values in this column are based on single laboratory data.

(3) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. The concentration in the aqueous or solid phase is determined using the equations in section 14.

(4) Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).

*Background levels of these compounds were present in the sludge resulting in higher than expected MDL's. The MDL for these compounds is expected to be approximately 50 ug/kg with no interferences present.

(5) Specification derived from related compound.

Column: 30 +/- 2 m x 0.25 +/- 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary

Temperature program: 5 min at 30°C; 30 - 250°C or until pentachlorophenol elutes

Gas velocity: 30 +/- 5 cm/sec at 30°C

Each extract is dried over sodium sulfate, concentrated to a volume of five mL, cleaned up using gel permeation chromatography (GPC), if necessary, and concentrated to one mL. An internal standard is added to the extract, and a one uL aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated by GC and detected by a mass spectrometer (MS). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a pollutant (qualitative analysis) is performed in one of three ways: (1) For compounds listed in tables 1 and 2, and for other compounds for which authentic standards are available, the GCMS system is calibrated and the mass spectrum and retention time for each standard are stored in a user created library. A compound is identified when its retention time and mass spectrum agree with the library retention time and spectrum. (2) For compounds listed in tables 3 and 4, and for other compounds for which standards are not available, a compound is identified when the retention time and mass spectrum agree with those specified in this method. (3) For chromatographic peaks which are not identified by (1) and (2) above, the background corrected spectrum at the peak maximum is compared with spectra in the EPA/NIH Mass Spectral File (reference 2). Tentative identification is established when the spectrum agrees.

2.3 Quantitative analysis is performed in one of four ways by GCMS using extracted ion current profile (EICP) areas: (1) For compounds listed in tables 1 and 2, and for other compounds for which standards and labeled analogs are available, the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique. (2) For compounds listed in tables 1 and 2, and for other compounds for which authentic standards but no labeled compounds are available, the GCMS system is calibrated and the compound concentration is determined using an internal standard technique. (3) For compounds listed in tables 3 and 4, and for other compounds for which standards are not available, compound concentrations are determined using known response factors. (4) For compounds for which neither standards nor known response factors are available, compound concentration is determined using the sum of the EICP areas relative to the sum of the EICP areas of the internal standard.

2.4 Quality is assured through reproducible calibration and testing of the extraction and GCMS systems.

3 CONTAMINATION AND INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms and spectra. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks initially and with each sample lot (samples started through the extraction process on a given 8 hr shift, to a maximum of 20). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Glassware and, where possible, reagents are cleaned by solvent rinse and baking at 450°C for one hour minimum.

3.2 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

4 SAFETY

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining

a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 3 - 5.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and beta-naphthylamine. Primary standards of these compounds shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 APPARATUS AND MATERIALS

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Sample Bottles and Caps

5.1.1.1 Liquid Samples (waters, sludges and similar materials that contain less than five percent solids)--Sample bottle, amber glass, 1.1 liters minimum, with screw cap.

5.1.1.2 Solid samples (soils, sediments, sludges, filter cake, compost, and similar materials that contain more than five percent solids)--Sample bottle, wide mouth, amber glass, 500 mL minimum.

5.1.1.3 If amber bottles are not available, samples shall be protected from light.

5.1.1.4 Bottle caps--threaded to fit sample bottles. Caps shall be lined with Teflon.

5.1.1.5 Cleaning

5.1.1.5.1 Bottles are detergent water washed, then solvent rinsed or baked at 450 °C for one hour minimum before use.

5.1.1.5.2 Liners are detergent water washed, then reagent water (section 6.5.1) and solvent rinsed, and baked at approx 200 °C for one hour minimum prior to use.

5.1.2 Compositing equipment--automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Sample containers are kept at 0 - 4 °C during sampling. Glass or Teflon tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water (section 6.5.1) to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

5.2 Equipment for determining percent moisture

5.2.1 Oven, capable of being temperature controlled at 110 +/- 5 °C.

5.2.2 Dessicator

5.3 Sonic disruptor--375 watt with pulsing capability and 3/4 in. disruptor horn (Ultrasonics, Inc, Model 375C, or equivalent).

5.4 Extraction apparatus

5.4.1 Continuous liquid-liquid extractor--Teflon or glass connecting joints and stopcocks without lubrication, 1.5 - 2 liter capacity (Hershberg-Wolf Extractor, Ace Glass 6841-10, or equivalent).

5.4.2 Beakers

5.4.2.1 1.5 - 2 liter, calibrated to one liter

5.4.2.2 400 - 500 mL

5.4.2.3 Spatulas--stainless steel

5.4.3 Filtration apparatus

5.4.3.1 Glass funnel--125 - 250 mL

5.4.3.2 Filter paper for above (Whatman 41, or equivalent)

5.5 Drying column--15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

5.6 Kuderna-Danish (K-D) apparatus

5.6.1 Concentrator tube--10mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

5.6.2 Evaporation flask--500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

5.6.3 Snyder column--three ball macro (Kontes K-503000-0232, or equivalent).

5.6.4 Snyder column--two ball micro (Kontes K-469002-0219, or equivalent).

5.6.5 Boiling chips--approx 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hr minimum.

5.7 Water bath--heated, with concentric ring cover, capable of temperature control (+/- 2 °C), installed in a fume hood.

5.8 Sample vials--amber glass, 2 - 5 mL with Teflon-lined screw cap.

5.9 Balances

5.9.1 Analytical--capable of weighing 0.1 mg.

5.9.2 Top loading--capable of weighing 10 mg.

5.10 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc., Columbia, MO, Model GPC Autoprep 1002, or equivalent)

5.10.1 Column--600 - 700 mm x 25 mm i.d., packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA)

5.10.2 UV detectors -- 254-mu, preparative or semi-prep flow cell:

5.10.2.1 Schmadzu, 5 mm path length

5.10.2.2 Beckman-Altex 152W, 8 uL micro-prep flow cell, 2 mm path

5.10.2.3 Pharmacia UV-1, 3 mm flow cell

5.10.2.4 LDC Milton-Roy UV-3, monitor #1203

5.11 Gas chromatograph--shall have splitless or on-column injection port for capillary column, temperature program with 30 °C hold, and shall meet all of the performance specifications in section 12.

5.11.1 Column--30 ±5 m x 0.25 ± 0.02 mm i.d. 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase fused silica capillary column (J & W DB-5, or equivalent).

5.12 Mass spectrometer--70 eV electron impact ionization, shall repetitively scan from 35 to 450 amu in 0.95 - 1.00 second, and shall produce a unit resolution (valleys between m/z 441-442 less than 10 percent of the height of the 441 peak), background corrected mass spectrum from 50 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum shall meet the mass-intensity criteria in table 7 (reference 6). The mass spectrometer shall be interfaced to the GC such that the end of the capillary column terminates within one centimeter of the ion source but does not intercept the electron or ion beams. All portions of the column which connect the GC to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

Table 7

DFTPP MASS-INTENSITY SPECIFICATIONS*

Mass	Intensity required
51	8 - 82 percent of m/z 198
68	less than 2 percent of m/z 69
69	11 - 91 percent of m/z 198
70	less than 2 percent of m/z 69
127	32 - 59 percent of m/z 198
197	less than 1 percent of m/z 198
198	base peak, 100 percent abundance
199	4 - 9 percent of m/z 198
275	11 - 30 percent of m/z 198
441	44 - 110 percent of m/z 443
442	30 - 86 percent of m/z 198
443	14 - 24 percent of m/z 442

*Reference 6

5.13 Data system--shall collect and record MS data, store mass- intensity data in spectral libraries, process GCMS data, generate reports, and shall compute and record response factors.

5.13.1 Data acquisition--mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.13.2 Mass spectral libraries--user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GCMS runs for the compounds of interest (section 7.2).

5.13.3 Data processing--the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GCMS analysis. Software routines shall be employed to compute retention times and peak areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.13.4 Response factors and multipoint calibrations--the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are used for testing calibration linearity. Statistics on initial (section 8.2) and on-going (section 12.7) performance shall be computed and maintained.

6 REAGENTS AND STANDARDS

6.1 Reagents for adjusting sample pH

6.1.1 Sodium hydroxide--reagent grade, 6N in reagent water.

6.1.2 Sulfuric acid--reagent grade, 6N in reagent water.

6.2 Sodium sulfate--reagent grade, granular anhydrous, rinsed with methylene chloride (20 mL/g), baked at 450 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering.

6.3 Methylene chloride--distilled in glass (Burdick and Jackson, or equivalent).

6.4 GPC calibration solution -- containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl) phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur

6.5 Reference matrices

6.5.1 Reagent water--water in which the compounds of interest and interfering compounds are not detected by this method.

6.5.2 High solids reference matrix--playground sand or similar material in which the compounds of interest and interfering compounds are not detected by this method.

6.6 Standard solutions--purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used

without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10 °C in screw-capped vials with Teflon-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

6.7 Preparation of stock solutions--prepare in methylene chloride, benzene, p-dioxane, or a mixture of these solvents per the steps below. Observe the safety precautions in section 4. The large number of labeled and unlabeled acid and base/neutral compounds used for combined calibration (section 7) and calibration verification (12.5) require high concentrations (approx 40 mg/mL) when individual stock solutions are prepared, so that dilutions of mixtures will permit calibration with all compounds in a single set of solutions. The working range for most compounds is 10-200 ug/mL. Compounds with a reduced MS response may be prepared at higher concentrations.

6.7.1 Dissolve an appropriate amount of assayed reference material in a suitable solvent. For example, weigh 400 mg naphthalene in a 10 mL ground glass stoppered volumetric flask and fill to the mark with benzene. After the naphthalene is completely dissolved, transfer the solution to a 15 mL vial with Teflon-lined cap.

6.7.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Quality control check samples that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7.3 Stock standard solutions shall be replaced after six months, or sooner if comparison with quality control check standards indicates a change in concentration.

6.8 Labeled compound spiking solution--from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution at a concentration of 200 ug/mL, or at a concentration appropriate to the MS response of each compound.

6.9 Secondary standard--using stock solutions (section 6.7), prepare a secondary standard containing all of the compounds in tables 1 and 2 at a concentration of 400 ug/mL, or higher concentration appropriate to the MS response of the compound.

6.10 Internal standard solution--prepare 2,2'-difluorobiphenyl (DFB) at a concentration of 10 mg/mL in benzene.

6.11 DFTPP solution--prepare at 50 ug/mL in acetone.

6.12 Solutions for obtaining authentic mass spectra (section 7.2)--prepare mixtures of compounds at concentrations which will assure authentic spectra are obtained for storage in libraries.

6.13 Calibration solutions--combine 0.5 mL of the solution in section 6.8 with 25, 50, 125, 250, and 500 uL of the solution in section 6.9 and bring to 1.00 mL total volume each. This will produce calibration solutions of nominal 10, 20, 50, 100 and 200 ug/mL of the pollutants and a constant nominal 100 ug/mL of the labeled compounds. Spike each solution with 10 uL of the internal standard solution (section 6.10). These solutions permit the relative response (labeled to unlabeled) to be measured as a function of concentration (section 7.4).

6.14 Precision and recovery standard--used for determination of initial (section 8.2) and on-going (section 12.7) precision and recovery. This solution shall contain the pollutants and labeled compounds at a nominal concentration of 100 ug/mL.

6.15 Stability of solutions--all standard solutions (sections 6.8 - 6.14) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area at the quantitation mass relative to the DFB internal standard remains within ± 15 percent of the area obtained in the initial analysis of the standard.

7 CALIBRATION

7.1 Assemble the GCMS and establish the operating conditions in table 5. Analyze standards per the procedure in section 11 to demonstrate that the analytical system meets the minimum levels in tables 5 and 6, and the mass-intensity criteria in table 7 for 50 ng DFTPP.

7.2 Mass spectral libraries--detection and identification of compounds of interest are dependent upon spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each pollutant, labeled compound, and the internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound.

7.2.2 Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic masses or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under DFTPP tuning conditions (section 7.1 and table 7) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. The spectrum may be further edited to remove common

Table 8

BASE/NEUTRAL EXTRACTABLE COMPOUND CHARACTERISTIC M/Z'S AND RESPONSE FACTORS

Compound	Labeled analog	Primary m/z	Response Factor (1)
acenaphthene	d_{10}	154/164	
acenaphthylene	d_8	152/160	
acetophenone		105	0.79
4-aminobiphenyl		169	0.81
aniline		93	1.04
o-anisidine		108	0.43
anthracene	d_{10}	178/188	
aramite		185	0.19
benzanthrone		230	0.15
1,3-benzenediol		110	0.78
benzenethiol		110	0.18
benzidine	d_8	184/192	
benzo(a)anthracene	d_{12}	228/240	
benzo(b)fluoranthene	d_{12}	252/264	
benzo(k)fluoranthene	d_{12}	252/264	

Compound	Labeled analog	Primary m/z	Response Factor (1)
benzo(a)pyrene	d_{12}	252/264	
benzo(ghi)perylene	d_{12}	276/288	
2,3-benzofluorene		216	0.35
benzoic acid		105	0.16
benzyl alcohol		79	0.47
biphenyl	d_{10}	154/164	
bis(2-chloroethyl) ether	d_8	93/101	
bis(2-chloroethoxy)methane	d_6	93/99	
bis(2-chloroisopropyl) ether	d_{12}	121/131	
bis(2-ethylhexyl) phthalate	d_4	149/153	
2-bromochlorobenzene		111	0.33
3-bromochlorobenzene		192	0.40
4-bromophenyl phenyl ether	d_5	248/253	
butyl benzyl phthalate	d_4	149/153	
n-C10	d_{22}	55/66	
n-C12	d_{26}	55/66	
n-C14		55	
n-C16	d_{34}	55/66	
n-C18		55	
n-C20	d_{42}	55/66	
n-C22		55	
n-C24	d_{50}	55/66	
n-C26		55	
n-C28		55	
n-C30	d_{62}	55/66	
carbazole	d_8	167/175	
4-chloro-2-nitroaniline		172	0.20
5-chloro-o-toluidine		106	0.50
4-chloroaniline		127	0.73
2-chloronaphthalene	d_7	162/169	
3-chloronitrobenzene		157	0.18
4-chlorophenyl phenyl ether	d_5	204/209	
3-chloropropionitrile		54	0.42
chrysene	d_{12}	228/240	
o-cresol		108	0.59
crotoxyphos		127	0.017
p-cymene	d_{14}	119/130	
2,6-di-tert-butyl-p-benzoquinone		220	0.078
di-n-butyl phthalate	d_4	149/153	
2,4-diaminotoluene		122	0.059
dibenzo(a,h)anthracene	d_{14}	278/292	
dibenzofuran	d_8	168/176	
dibenzothiophene	d_8	184/192	
1,2-dibromo-3-chloropropane		157	0.22
2,6-dichloro-4-nitroaniline		124	0.019
1,3-dichloro-2-propanol		79	0.68
2,3-dichloroaniline		161	0.47
1,2-dichlorobenzene	d_4	146/152	
1,3-dichlorobenzene	d_4	146/152	
1,4-dichlorobenzene	d_4	146/152	
3,3'-dichlorobenzidine	d_6	252/258	
2,2'-difluorobiphenyl (int std)		190	
2,3-dichloronitrobenzene		191	0.11
1,2:3,4-diepoxybutane		55	0.27

Compound	Labeled analog	Primary m/z	Response Factor (1)
diethyl phthalate	d_4	149/153	
3,3'-dimethoxybenzidine		244	0.19
dimethyl phthalate	d_4	163/167.	
dimethyl sulfone		79	0.40
p-dimethylaminoazobenzene		120	0.23
7,12-dimethylbenz(a)anthracene		256	0.58
N,N-dimethylformamide		73	0.51
3,6-dimethylphenanthrene		206	0.72
2,4-dimethylphenol	d_3	122/125	
1,4-dinitrobenzene		168	0.24
2,4-dinitrotoluene	d_3	165/168	
2,6-dinitrotoluene	d_3	165/167	
di-n-octyl phthalate	d_4	149/153	
diphenylamine	d_{10}	169/179	
diphenyl ether	d_{10}	170/180	
diphenyldisulfide		218	0.25
1,2-diphenylhydrazine (2)	d_{10}	77/82	
ethyl methanesulfonate		109	0.28
ethylenethiourea		102	0.22
ethynylestradiol 3-methyl ether		227	0.28
fluoranthene	d_{10}	202/212	
fluorene	d_{10}	166/176	
hexachlorobenzene	$^{13}C_6$	284/292	
hexachlorobutadiene	$^{13}C_4$	225/231	
hexachloroethane	^{13}C	201/204	
hexachlorocyclopentadiene	$^{13}C_4$	237/241	
hexachloropropene		213	0.23
indeno(1,2,3-cd)pyrene		276	
isophorone	d_8	82/88	
2-isopropylnaphthalene		170	0.32
isosafrole		162	0.33
longifolene		161	0.14
malachite green		330	
methapyrilene		97	0.43
methyl methanesulfonate		80	0.20
2-methylbenzothiazole		149	0.59
3-methylcholanthrene		268	0.59
4,4'-methylenebis(2-chloroaniline)		231	0.21
4,5-methylenephenanthrene		190	0.44
1-methylfluorene		180	0.37
2-methylnaphthalene		142	0.99
1-methylphenanthrene		192	0.65
2-(methylthio)benzothiazole		181	0.42
naphthalene	d_8	128/136	
1,5-naphthalenediamine		158	0.085
1,4-naphthoquinone		158	0.021
alpha-naphthylamine		143	0.89
beta-naphthylamine	d_7	143/150	
5-nitro-o-toluidine		152	0.31
2-nitroaniline		138	0.39
3-nitroaniline		138	0.27
4-nitroaniline		138	0.11
nitrobenzene	d_5	128/128	
4-nitrobiphenyl		199	0.35
N-nitrosodi-n-butylamine		84	0.47
N-nitrosodi-n-propylamine	d_{14}	70/84	

Compound	Labeled analog	Primary m/z	Response Factor (1)
N-nitrosodiethylamine		102	0.45
N-nitrosodimethylamine	d_6	74/80	
N-nitrosodiphenylamine (3)	d_6	169/175	
N-nitrosomethylethylamine		88	0.33
N-nitrosomethylphenylamine		106	0.024
N-nitrosomorpholine		56	0.49
N-nitrosopiperidine		114	0.41
pentachlorobenzene		248	0.25
pentachloroethane		117	0.20
pentamethylbenzene		148	0.42
perylene		252	0.30
phenacetin		108	0.38
phenanthrene	d_{10}	178/188	
phenol	d_5	94/71	
phenothiazine		199	0.15
1-phenylnaphthalene		204	0.48
2-phenylnaphthalene		204	0.73
alpha-picoline	d_7	93/100	
pronamide		173	0.31
pyrene	d_{10}	202/212	
pyridine		79	0.68
safrole		162	0.45
squalene		69	0.042
styrene	d_5	104/109	
alpha-terpineol	d_3	59/62	
1,2,4,5-tetrachlorobenzene		216	0.43
thianaphthene		134	1.52
thioacetamide		75	0.28
thioxanthone		212	0.23
o-toluidine		106	1.04
1,2,3-trichlorobenzene	d_3	180/183	
1,2,4-trichlorobenzene	d_3	180/183	
1,2,3-trimethoxybenzene		168	0.48
2,4,5-trimethylaniline		120	0.28
triphenylene		228	1.32
tripropylene glycol methyl ether		59	0.092
1,3,5-trithiane		138	0.15

(1) referenced to 2,2'-difluorobiphenyl

(2) detected as azobenzene

(3) detected as diphenylamine

interfering masses. If 5 mass spectral peaks cannot be obtained under the scan conditions given in section 5.12, the mass spectrometer may be scanned to an m/z lower than 35 to gain additional spectral information. The spectrum obtained is stored for reverse search and for compound confirmation.

7.2.5 For the compounds in tables 3 and 4 and for other compounds for which the mass spectra, quantitation m/z's, and retention times are known but the instrument is not to be calibrated, add the retention time and reference compound (tables 5 and 6); the response factor and the quantitation m/z (tables 8 and 9); and spectrum (Appendix A) to the reverse search library. Edit the spectrum per section 7.2.4, if necessary.

Table 9

ACID EXTRACTABLE COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled analog	Primary m/z	Response Factor (1)
benzoic acid		105	0.16
4-chloro-3-methylphenol	d_2	107/109	
2-chlorophenol	d_4	128/132	
p-cresol		108	0.61
3,5-dibromo-4-hydroxybenzonitrile		277	0.12
2,4-dichlorophenol	d_3	162/167	
2,6-dichlorophenol		162	0.42
2,4-dinitrophenol	d_3	184/187	
hexanoic acid		60	0.62
2-methyl-4,6-dinitrophenol	d_2	198/200	
2-nitrophenol	d_4	139/143	
4-nitrophenol	d_4	139/143	
pentachlorophenol	$^{13}C_6$	266/272	
2,3,4,6-tetrachlorophenol		232	0.17
2,3,6-trichlorophenol	d_2	196/200	
2,4,5-trichlorophenol	d_2	196/200	
2,4,6-trichlorophenol	d_2	196/200	

(1) referenced to 2,2'-difluorobiphenyl

7.3 Analytical range--demonstrate that 20 ng anthracene or phenanthrene produces an area at m/z 178 approx one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required, and to diagnose instrument sensitivity problems (section 15.3). The 20 ug/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.3.1 Polar compound detection--demonstrate that unlabeled pentachlorophenol and benzidine are detectable at the 50 ug/mL level (per all criteria in section 13). The 50 ug/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.4 Calibration with isotope dilution--isotope dilution is used when 1) labeled compounds are available, 2) interferences do not preclude its use, and 3) the quantitation m/z (tables 8 and 9) extracted ion current profile (EICP) area for the compound is in the calibration range. Alternate labeled compounds and quantitation m/z's may be used based on availability. If any of the above conditions preclude isotope dilution, the internal standard method (section 7.5) is used.

7.4.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (pollutant to labeled) vs concentration in standard solutions is plotted or computed using a linear regression. The example in Figure 1 shows a calibration curve for phenol using phenol-d_5 as the isotopic diluent. Also shown are the ± 10 percent error limits (dotted lines). Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

7.4.2 The relative response of a pollutant to its labeled analog is determined from isotope ratio values computed from

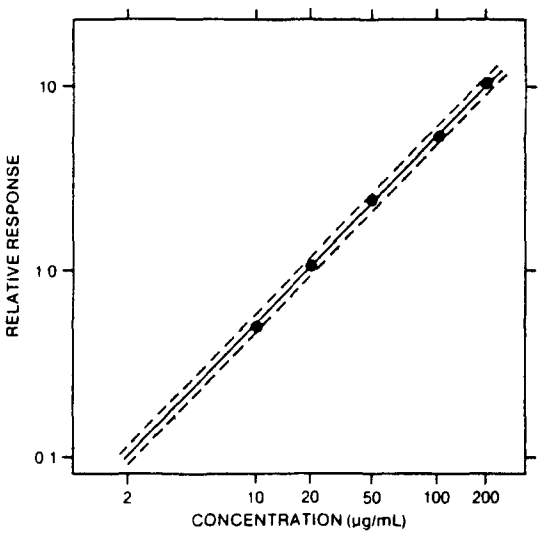

FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a ± 10 Percent Error Window.

acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured for the pure pollutant.

R_y = the isotope ratio measured for the labeled compound.

R_m = the isotope ratio of an analytical mixture of pollutant and labeled compounds.

The m/z's are selected such that $R_x > R_y$. If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method.

7.4.3 Capillary columns usually separate the pollutant-labeled pair, with the labeled compound eluted first (figure 2). For this case,

$$R_x = \frac{[\text{area } m_1/z \text{ (at } RT_2)]}{1}$$

$$R_y = \frac{1}{[\text{area } m_2/z \text{ (at } RT_1)]}$$

$$R_m = \frac{[\text{area } m_1/z \text{ (at } RT_2)]}{[\text{area } m_2/z \text{ (at } RT_1)]}$$

as measured in the mixture of the pollutant and labeled compounds (figure 2), and RR = R_m.

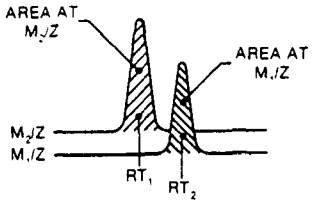

FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled (m_2/z) and Unlabeled (m_1/z) Pairs.

7.4.4 Special precautions are taken when the pollutant-labeled pair is not separated, or when another labeled compound with interfering spectral masses overlaps the pollutant (a case which can occur with isomeric compounds). In this case, it is necessary to determine the respective contributions of the pollutant and labeled compounds to the respective EICP areas. If the peaks are separated well enough to permit the data system or operator to remove the contributions of the compounds to each other, the equations in section 7.4.3 apply. This usually occurs when the height of the valley between the two GC peaks at the same m/z is less than 10 percent of the height of the shorter of the two peaks. If significant GC and spectral overlap occur, RR is computed using the following equation:

$$RR = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

where R_x is measured as shown in figure 3A, R_y is measured as shown in figure 3B, and R_m is measured as shown in figure 3C. For the example,

$$R_x = \frac{46100}{4780} = 9.644$$

$R_y = \frac{2650}{43600} = 0.0608$

$R_m = \frac{49200}{48300} = 1.019$

RR = 1.114.

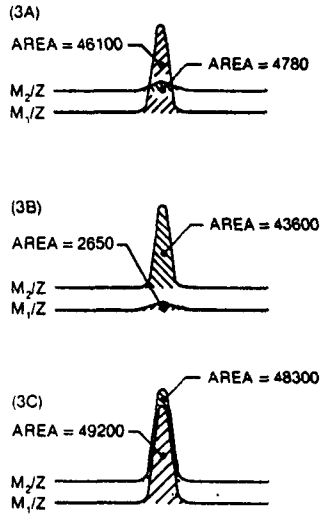

FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

7.4.5 To calibrate the analytical system by isotope dilution, analyze a 1.0 uL aliquot of each of the calibration standards (section 6.13) using the procedure in section 11. Compute the RR at each concentration.

7.4.6 Linearity--if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard--used when criteria for isotope dilution (section 7.4) cannot be met. The internal standard to be used for both acid and base/neutral analyses is 2,2'-difluorobiphenyl. The internal standard method is also applied to determination of compounds having no labeled analog, and to measurement of labeled compounds for intra-laboratory statistics (sections 8.4 and 12.7.4).

7.5.1 Response factors--calibration requires the determination of response factors (RF) which are defined by the following equation:

$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)}$, where

A_s is the area of the characteristic mass for the compound in the daily standard

A_{is} is the area of the characteristic mass for the internal standard

C_{is} is the concentration of the internal standard (ug/mL)

C_s is the concentration of the compound in the daily standard (ug/mL)

7.5.1.1 The response factor is determined for at least five concentrations appropriate to the response of each compound (section 6.13); nominally, 10, 20, 50, 100, and 200 ug/mL. The amount of internal standard added to each extract is the same (100 ug/mL) so that C_{is} remains constant. The RF is plotted vs concentration for each compound in the standard (C_s) to produce a calibration curve.

7.5.1.2 Linearity--if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration--by using calibration solutions (section 6.13) containing the

pollutants, labeled compounds, and the internal standard, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 12.5) by analyzing the 100 ug/mL calibration standard (section 6.13). Recalibration is required only if calibration verification (section 12.5) criteria cannot be met.

8 QUALITY ASSURANCE/QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (reference 7). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method. If the method is to be applied routinely to samples containing high solids with very little moisture (e.g., soils, filter cake, compost), the high solids reference matrix (section 6.5.2) is substituted for the reagent water (6.5.1) in all performance tests, and the high solids method (section 10) is used for these tests.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in section 8.5.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 15).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (section 6.14) that the analysis system is in control. These procedures are described in sections 12.1, 12.5, and 12.7.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in section 8.4.

8.2 Initial precision and accuracy--to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 For low solids (aqueous samples), extract, concentrate, and analyze two sets of four one-liter aliquots (8 aliquots total) of the precision and recovery standard (section 6.14) according to the procedure in section 10. For high solids samples, two sets of four 30 gram aliquots of the high solids reference matrix are used.

8.2.2 Using results of the first set of four analyses, compute the average recovery (X) in ug/mL and the standard deviation of the recovery (s) in ug/mL for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy in table 10. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. NOTE: The large number of compounds in table 10 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for these compounds. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the labeled compound recovery for each compound with the corresponding limits in table 10. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample is complex. Water samples are diluted, and smaller amounts of soils, sludges, and sediments are reanalyzed per section 15.

Table 10

ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. (1)	Compound	Acceptance criteria Initial precision and accuracy Section 8.2.3 (ug/L) s	X	Labeled compound recovery Sec 8.3 and 14.2 P (%)	Calibration verification Sec 12.5 (ug/mL)	On-going accuracy Sec 12.7 R (ug/L)
301	acenaphthene	21	79 - 134		80 - 125	72 - 144
201	acenaphthene-d_{10}	38	38 - 147	20 - 270	71 - 141	30 - 180
377	acenaphthylene	38	69 - 186		60 - 166	61 - 207
277	acenaphthylene-d_8	31	39 - 146	23 - 239	66 - 152	33 - 168
378	anthracene	41	58 - 174		60 - 168	50 - 199
278	anthracene-d_{10}	49	31 - 194	14 - 419	58 - 171	23 - 242
305	benzidine	119	16 - 518		34 - 296	11 - 672
205	benzidine-d_8	269	ns(2) ns	ns - ns	ns - ns	ns - ns
372	benzo(a)anthracene	20	65 - 168		70 - 142	62 - 176
272	benzo(a)anthracene-d_{12}	41	25 - 298	12 - 605	28 - 357	22 - 329
374	benzo(b)fluoranthene	183	32 - 545		61 - 164	20 - ns
274	benzo(b)fluoranthene-d_{12}	168	11 - 577	ns - ns	14 - ns	ns - ns
375	benzo(k)fluoranthene	26	59 - 143		13 - ns	53 - 155
275	benzo(k)fluoranthene-d_{12}	114	15 - 514	ns - ns	13 - ns	ns - 685
373	benzo(a)pyrene	26	62 - 195		78 - 129	59 - 206

EGD No. (1)	Compound	Acceptance criteria Initial precision and accuracy Section 8.2.3 (ug/L) s	X	Labeled compound recovery Sec 8.3 and 14.2 P (%)	Calibration verification Sec 12.5 (ug/mL)	On-going accuracy Sec 12.7 R (ug/L)
273	benzo(a)pyrene-d_{12}	24	35 - 181	21 - 290	12 - ns	32 - 194
379	benzo(ghi)perylene	21	72 - 160		69 - 145	58 - 168
279	benzo(ghi)perylene-d_{12}	45	29 - 268	14 - 529	13 - ns	25 - 303
712	biphenyl (Appendix C)	41	75 - 148		58 - 171	62 - 176
612	biphenyl-d_{10}	43	28 - 165	ns - ns	52 - 192	17 - 267
318	bis(2-chloroethyl) ether	34	55 - 196		61 - 164	50 - 213
218	bis(2-chloroethyl) ether-d_8	33	29 - 196	15 - 372	52 - 194	25 - 222
343	bis(2-chloroethoxy)methane	27	43 - 153		44 - 228	39 - 166
243	bis(2-chloroethoxy)methane (3)	33	29 - 196	15 - 372	52 - 194	25 - 222
342	bis(2-chloroisopropyl) ether	17	81 - 138		67 - 148	77 - 145
242	bis(2-chloroisopropyl)ether-d_{12}	27	35 - 149	20 - 260	44 - 229	30 - 169
366	bis(2-ethylhexyl) phthalate	31	69 - 220		76 - 131	64 - 232
266	bis(2-ethylhexyl) phthalate-d_4	29	32 - 205	18 - 364	43 - 232	28 - 224
341	4-bromophenyl phenyl ether	44	44 - 140		52 - 193	35 - 172
241	4-bromophenylphenyl ether-d_5(3)	52	40 - 161	19 - 325	57 - 175	29 - 212
367	butyl benzyl phthalate	31	19 - 233		22 - 450	35 - 170
267	butyl benzyl phthalate-d_4 (3)	29	32 - 205	18 - 364	43 - 232	28 - 224
717	n-C10 (Appendix C)	51	24 - 195		42 - 235	19 - 237
617	n-C10-d_{22}	70	ns - 298	ns - ns	44 - 227	ns - 504
706	n-C12 (Appendix C)	74	35 - 369		60 - 166	29 - 424
606	n-C12-d_{26}	53	ns - 331	ns - ns	41 - 242	ns - 408
518	n-C14 (Appendix C) (3)	109	ns - ns		37 - 268	ns - ns
719	n-C16 (Appendix C)	33	80 - 162		72 - 138	71 - 181
619	n-C16-d_{34}	46	37 - 162	18 - 308	54 - 186	28 - 202
520	n-C18 (Appendix C) (3)	39	42 - 131		40 - 249	35 - 167
721	n-C20 (Appendix C)	59	53 - 263		54 - 184	46 - 301
621	n-C20-d_{42}	34	34 - 172	19 - 306	62 - 162	29 - 198
522	n-C22 (Appendix C) (3)	31	45 - 152		40 - 249	39 - 195
723	n-C24 (Appendix C)	11	80 - 139		65 - 154	78 - 142
623	n-C24-d_{50}	28	27 - 211	15 - 376	50 - 199	25 - 229
524	n-C26 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212
525	n-C28 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212
726	n-C30 (Appendix C)	32	61 - 200		66 - 152	56 - 215
626	n-C30-d_{62}	41	27 - 242	13 - 479	24 - 423	23 - 274
728	carbazole (4c)	38	36 - 165		44 - 227	31 - 188
628	carbazole-d_8 (3)	31	48 - 130	29 - 215	69 - 145	40 - 156
320	2-chloronaphthalene	100	46 - 357		58 - 171	35 - 442
220	2-chloronaphthalene-d_7	41	30 - 168	15 - 324	72 - 139	24 - 204
322	4-chloro-3-methylphenol	37	76 - 131		85 - 115	62 - 159
222	4-chloro-3-methylphenol-d_2	111	30 - 174	ns - 613	68 - 147	14 - 314
324	2-chlorophenol	13	79 - 135		78 - 129	76 - 138
224	2-chlorophenol-d_4	24	36 - 162	23 - 255	55 - 180	33 - 176
340	4-chlorophenyl phenyl ether	42	75 - 166		71 - 142	63 - 194
240	4-chlorophenyl phenyl ether-d_5	52	40 - 161	19 - 325	57 - 175	29 - 212
376	chrysene	51	59 - 186		70 - 142	48 - 221
276	chrysene-d_{12}	69	33 - 219	13 - 512	24 - 411	23 - 290
713	p-cymene (Appendix C)	18	76 - 140		79 - 127	72 - 147
613	p-cymene-d_{14}	67	ns - 359	ns - ns	66 - 152	ns - 468
382	dibenzo(a,h)anthracene	55	23 - 299		13 - 761	19 - 340
282	dibenzo(a,h)anthracene-d_{14} (3)	45	29 - 268	14 - 529	13 - ns	25 - 303

EGD No. (1)	Compound	Acceptance criteria Initial precision and accuracy Section 8.2.3 (ug/L) s	X	Labeled compound recovery Sec 8.3 and 14.2 P (%)	Calibration verification Sec 12.5 (ug/mL)	On-going accuracy Sec 12.7 R (ug/L)
705	dibenzofuran (Appendix C)	20	85 - 136		73 - 136	79 - 146
605	dibenzofuran-d_8	31	47 - 136	28 - 220	66 - 150	39 - 160
704	dibenzothiophene (Synfuel)	31	79 - 150		72 - 140	70 - 168
604	dibenzothiophene-d_8	31	48 - 130	29 - 215	69 - 145	40 - 156
368	di-n-butyl phthalate	15	76 - 165		71 - 142	74 - 169
268	di-n-butyl phthalate-d_4	23	23 - 195	13 - 346	52 - 192	22 - 209
325	1,2-dichlorobenzene	17	73 - 146		74 - 135	70 - 152
225	1,2-dichlorobenzene-d_4	35	14 - 212	ns - 494	61 - 164	11 - 247
326	1,3-dichlorobenzene	43	63 - 201		65 - 154	55 - 225
226	1,3-dichlorobenzene-d_4	48	13 - 203	ns - 550	52 - 192	ns - 260
327	1,4-dichlorobenzene	42	61 - 194		62 - 161	53 - 219
227	1,4-dichlorobenzene-d_4	48	15 - 193	ns - 474	65 - 153	11 - 245
328	3,3'-dichlorobenzidine	26	68 - 174		77 - 130	64 - 185
228	3,3'-dichlorobenzidine-d_6	80	ns - 562	ns - ns	18 - 558	ns - ns
331	2,4-dichlorophenol	12	85 - 131		67 - 149	83 - 135
231	2,4-dichlorophenol-d_3	28	38 - 164	24 - 260	64 - 157	34 - 182
370	diethyl phthalate	44	75 - 196		74 - 135	65 - 222
270	diethyl phthalate-d_4	78	ns - 260	ns - ns	47 - 211	ns - ns
334	2,4-dimethylphenol	13	62 - 153		67 - 150	60 - 156
234	2,4-dimethylphenol-d_3	22	15 - 228	ns - 449	58 - 172	14 - 242
371	dimethyl phthalate	36	74 - 188		73 - 137	67 - 207
271	dimethyl phthalate-d_4	108	ns - 640	ns - ns	50 - 201	ns - ns
359	2,4-dinitrophenol	18	72 - 134		75 - 133	68 - 141
259	2,4-dinitrophenol-d_3	66	22 - 308	ns - ns	39 - 256	17 - 378
335	2,4-dinitrotoluene	18	75 - 158		79 - 127	72 - 164
235	2,4-dinitrotoluene-d_3	37	22 - 245	10 - 514	53 - 187	19 - 275
336	2,6-dinitrotoluene	30	80 - 141		55 - 183	70 - 159
236	2,6-dinitrotoluene-d_3	59	44 - 184	17 - 442	36 - 278	31 - 250
369	di-n-octyl phthalate	16	77 - 161		71 - 140	74 - 166
269	di-n-octyl phthalate-d_4	46	12 - 383	ns - ns	21 - 467	10 - 433
707	diphenylamine (Appendix C)	45	58 - 205		57 - 176	51 - 231
607	diphenylamine-d_{10}	42	27 - 206	11 - 488	59 - 169	21 - 249
708	diphenyl ether (Appendix C)	19	82 - 136		83 - 120	77 - 144
608	diphenyl ether-d_{10}	37	36 - 155	19 - 281	77 - 129	29 - 186
337	1,2-diphenylhydrazine	73	49 - 308		75 - 134	40 - 360
237	1,2-diphenylhydrazine-d_{10}	35	31 - 173	17 - 316	58 - 174	26 - 200
339	fluoranthene	33	71 - 177		67 - 149	64 - 194
239	fluoranthene-d_{10}	35	36 - 161	20 - 278	47 - 215	30 - 187
380	fluorene	29	81 - 132		74 - 135	70 - 151
280	fluorene-d_{10}	43	51 - 131	27 - 238	61 - 164	38 - 172
309	hexachlorobenzene	16	90 - 124		78 - 128	85 - 132
209	hexachlorobenzene-$^{13}C_6$	81	36 - 228	13 - 595	38 - 265	23 - 321
352	hexachlorobutadiene	56	51 - 251		74 - 135	43 - 287
252	hexachlorobutadiene-$^{13}C_4$	63	ns - 316	ns - ns	68 - 148	ns - 413
312	hexachloroethane	227	21 - ns		71 - 141	13 - ns
212	hexachloroethane-^{13}C	77	ns - 400	ns - ns	47 - 212	ns - 563
353	hexachlorocyclopentadiene	15	69 - 144		77 - 129	67 - 148
253	hexachlorocyclopentadiene-$^{13}C_4$	60	ns - ns	ns - ns	47 - 211	ns - ns
083	ideno(1,2,3-cd)pyrene (3)	55	23 - 299		13 - 761	19 - 340
354	isophorone	25	76 - 156		70 - 142	70 - 168
254	isophorone-d_8	23	49 - 133	33 - 193	52 - 194	44 - 147

EGD No. (1)	Compound	Acceptance criteria Initial precision and accuracy Section 8.2.3 (ug/L) s	X	Labeled compound recovery Sec 8.3 and 14.2 P (%)	Calibration verification Sec 12.5 (ug/mL)	On-going accuracy Sec 12.7 R (ug/L)
360	2-methyl-4,6-dinitrophenol	19	77 - 133		69 - 145	72 - 142
260	2-methyl-4,6-dinitrophenol-d_2	64	36 - 247	16 - 527	56 - 177	28 - 307
355	naphthalene	20	80 - 139		73 - 137	75 - 149
255	naphthalene-d_8	39	28 - 157	14 - 305	71 - 141	22 - 192
702	beta-naphthylamine (Appendix C)	49	10 - ns		39 - 256	ns - ns
602	beta-naphthylamine-d_7	33	ns - ns	ns - ns	44 - 230	ns - ns
356	nitrobenzene	25	69 - 161		85 - 115	65 - 169
256	nitrobenzene-d_5	28	18 - 265	ns - ns	46 - 219	15 - 314
357	2-nitrophenol	15	78 - 140		77 - 129	75 - 145
257	2-nitrophenol-d_4	23	41 - 145	27 - 217	61 - 163	37 - 158
358	4-nitrophenol	42	62 - 146		55 - 183	51 - 175
258	4-nitrophenol-d_4	188	14 - 398	ns - ns	35 - 287	ns - ns
361	N-nitrosodimethylamine	49	10 - ns		39 - 256	ns - ns
261	N-nitrosodimethylamine-d_6 (3)	33	ns - ns	ns - ns	44 - 230	ns - ns
363	N-nitrosodi-n-propylamine	45	65 - 142		68 - 148	53 - 173
263	N-nitrosodi-n-propylamine (3)	37	54 - 126	26 - 256	59 - 170	40 - 166
362	N-nitrosodiphenylamine	45	65 - 142		68 - 148	53 - 173
262	N-nitrosodiphenylamine-d_6	37	54 - 126	26 - 256	59 - 170	40 - 166
364	pentachlorophenol	21	76 - 140		77 - 130	71 - 150
264	pentachlorophenol-$^{13}C_6$	49	37 - 212	18 - 412	42 - 237	29 - 254
381	phenanthrene	13	93 - 119		75 - 133	87 - 126
281	phenanthrene-d_{10}	40	45 - 130	24 - 241	67 - 149	34 - 168
365	phenol	36	77 - 127		65 - 155	62 - 154
265	phenol-d_5	161	21 - 210	ns - ns	48 - 208	ns - ns
703	alpha-picoline (Synfuel)	38	59 - 149		60 - 165	50 - 174
603	alpha-picoline-d_7	138	11 - 380	ns - ns	31 - 324	ns - 608
384	pyrene	19	76 - 152		76 - 132	72 - 159
284	pyrene-d_{10}	29	32 - 176	18 - 303	48 - 210	28 - 196
710	styrene (Appendix C)	42	53 - 221		65 - 153	48 - 244
610	styrene-d_5	49	ns - 281	ns - ns	44 - 228	ns - 348
709	alpha-terpineol (Appendix C)	44	42 - 234		54 - 186	38 - 258
609	alpha-terpineol-d_3	48	22 - 292	ns - 672	20 - 502	18 - 339
729	1,2,3-trichlorobenzene (4c)	69	15 - 229		60 - 167	11 - 297
629	1,2,3-trichlorobenzene-d_3 (3)	57	15 - 212	ns - 592	61 - 163	10 - 282
308	1,2,4-trichlorobenzene	19	82 - 136		78 - 128	77 - 144
208	1,2,4-trichlorobenzene-d_3	57	15 - 212	ns - 592	61 - 163	10 - 282
530	2,3,6-trichlorophenol (4c) (3)	30	58 - 137		56 - 180	51 - 153
731	2,4,5-trichlorophenol (4c)	30	58 - 137		56 - 180	51 - 153
631	2,4,5-trichlorophenol-d_2 (3)	47	43 - 183	21 - 363	69 - 144	34 - 226
321	2,4,6-trichlorophenol	57	59 - 205		81 - 123	48 - 244
221	2,4,6-trichlorophenol-d_2	47	43 - 183	21 - 363	69 - 144	34 - 226

(1) Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) ns = no specification: limit is outside the range that can be measured reliably.

(3) This compound is to be determined by internal standard; specification is derived from related compound.

8.4 As part of the QA program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five samples or a given matrix type (water, soil, sludge, sediment) for which the labeled compounds pass the tests in section 8.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from P -$2s_p$ to P + $2s_p$ for each matrix. For example, if P = 90% and s_p = 10% for five analyses of compost, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound in each matrix on a regular basis (e.g. after each 5 - 10 new accuracy measurements).

8.5 Blanks--reagent water and high solids reference matrix blanks are analyzed to demonstrate freedom from contamination.

8.5.1 Extract and concentrate a one liter reagent water blank or a high solids reference matrix blank with each sample lot (samples started through the extraction process on the same 8 hr shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the precision and recovery standard (section 6.14) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (tables 1 thru 4) or any potentially interfering compound is found in an aqueous blank at greater than 10 ug/L, or in a high solids reference matrix blank at greater than 100 ug/kg (assuming a response factor of 1 relative to the internal standard for compounds not listed in tables 1 thru 4), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration verification (section 12.5), and for initial (section 8.2) and on-going (section 12.7) precision and recovery should be identical, so that the most precise results will be obtained. The GCMS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of semi-volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

9 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Collect samples in glass containers following conventional sampling practices (reference 8). Aqueous samples which flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide mouth jars.

9.2 Maintain samples at 0 - 4 °C from the time of collection until extraction. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA methods 330.4 and 330.5 may be used to measure residual chlorine (reference 9).

9.3 Begin sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction.

10 SAMPLE EXTRACTION, CONCENTRATION, AND CLEANUP

Samples containing one percent solids or less are extracted directly using continuous liquid/liquid extraction techniques (section 10.2.1 and figure 4).

Samples containing one to 30 percent solids are diluted to the one percent level with reagent water (section 10.2.2) and extracted using continuous liquid/liquid extraction techniques. Samples containing greater than 30 percent solids are extracted using ultrasonic techniques (section 10.2.5)

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker.

10.1.2 Dry overnight (12 hours minimum) at 110 ± 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of dry sample}}{\text{weight of wet sample}} \times 100$$

10.2 Preparation of samples for extraction

10.2.1 Samples containing one percent solids or less--extract sample directly using continuous liquid/liquid extraction techniques.

10.2.1.1 Measure 1.00 ± 0.01 liter of sample into a clean 1.5 - 2.0 liter beaker.

10.2.1.2 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, measure an additional 100.0 ± 1.0 mL into a clean 1.5 - 2.0 liter beaker and dilute to a final volume of 1.00 ± 0.1 liter with reagent water.

10.2.1.3 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into the sample aliquots. Proceed to preparation of the QC aliquots for low solids samples (section 10.2.3).

10.2.2 Samples containing one to 30 percent solids

10.2.2.1 Mix sample thoroughly.

10.2.2.2 Using the percent solids found in 10.1.3, determine the weight of sample required to produce one liter of solution containing one percent solids as follows:

$$\text{sample weight} = \frac{1000}{\% \text{ solids}} \text{ grams}$$

10.2.2.3 Place the weight determined in 10.2.2.2 in a clean 1.5 - 2.0 liter beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.2.4 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, weigh an amount of sample equal to one-tenth the amount determined in 10.2.2.2 into a second clean 1.5 - 2.0 liter beaker. When diluted to 1.0 liter, this dilute aliquot will contain 0.1 percent solids.

10.2.2.5 Bring the sample aliquot(s) above to 100 - 200 mL volume with reagent water.

10.2.2.6 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into each sample aliquot.

10.2.2.7 Using a clean metal spatula, break any solid portions of the sample into small pieces.

10.2.2.8 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of each sample aliquot and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication.

Clean the probe with methylene chloride:acetone (1:1) between samples to preclude cross-contamination.

10.2.2.9 Bring the sample volume to 1.0 ± 0.1 liter with reagent water.

10.2.3 Preparation of QC aliquots for samples containing low solids (<30 percent).

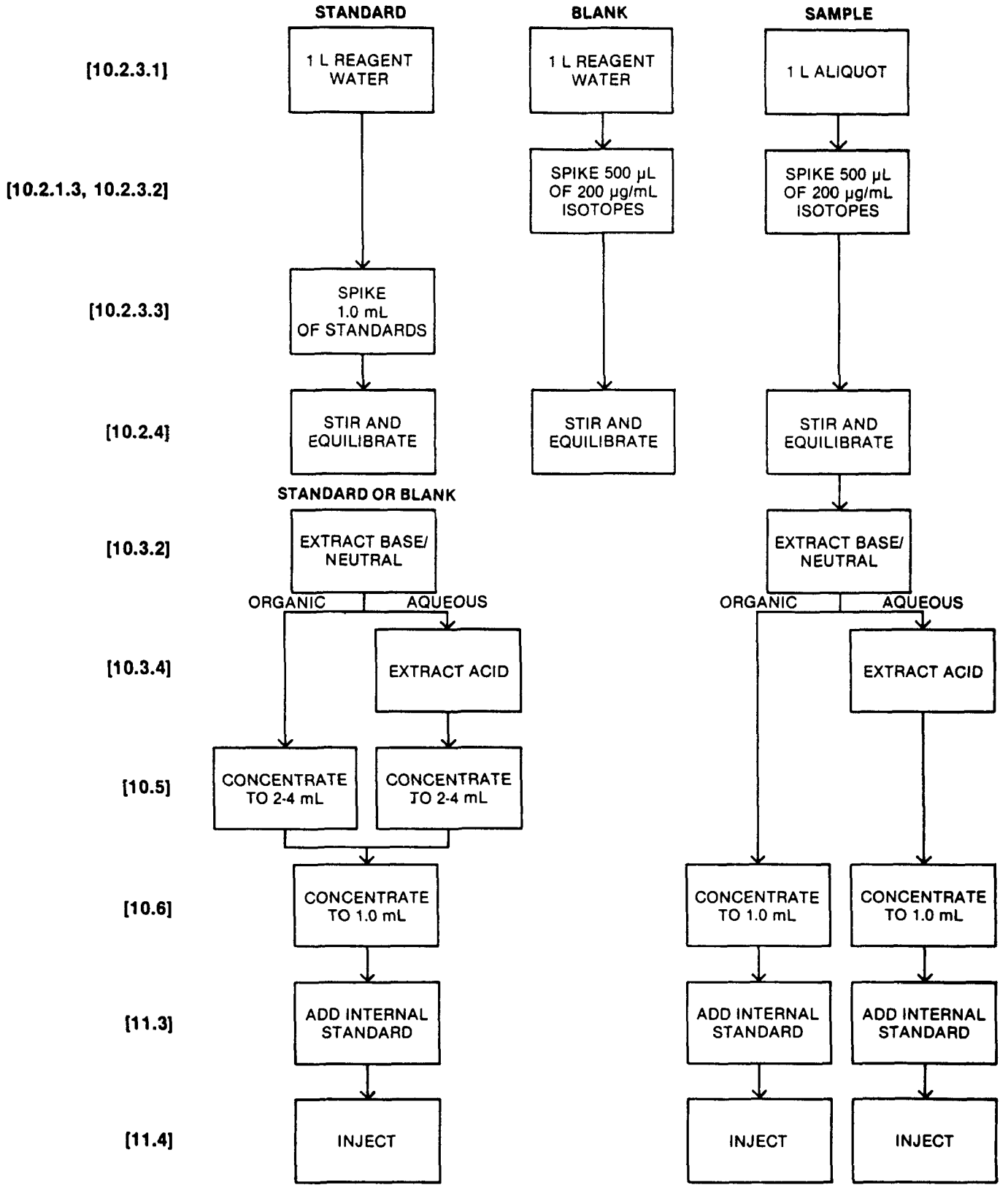

FIGURE 4 Flow Chart for Extraction/Concentration of Low Solids Precision and Recovery Standard, Blank, and Sample by Method 1635. Numbers in Brackets [ ] Refer to Section Numbers in the Method.

10.2.3.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 1.0 ± 0.01 liter aliquots of reagent water in clean 1.5 - 2.0 liter beakers.

10.2.3.2 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into one reagent water aliquot. This aliquot will serve as the blank.

10.2.3.3 Spike 1.0 mL of the precision and recovery standard (section 6.14) into the two remaining reagent water aliquots.

10.2.4 Stir and equilibrate all sample and QC solutions for 1 - 2 hours. Extract the samples and QC aliquots per section 10.3.

10.2.5 Samples containing 30 percent solids or greater

10.2.5.1 Mix the sample thoroughly

10.2.5.2 Weigh 30 ± 0.3 grams into a clean 400 - 500 mL beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.5.3 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, weigh 3 ± 0.03 grams into a clean 400 - 500 mL beaker.

10.2.5.4 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into each sample aliquot.

10.2.5.5 QC aliquots--for each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 30 ± 0.3 gram aliquots of the high solids reference matrix in clean 400 - 500 mL beakers.

10.2.5.6 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into one high solids reference matrix aliquot. This aliquot will serve as the blank.

10.2.5.7 Spike 1.0 mL of the precision and recovery standard (section 6.14) into the two remaining high solids reference matrix aliquots. Extract, concentrate, and clean up the high solids samples per sections 10.4 through 10.8.

10.3 Continuous extraction of low solids (aqueous) samples--place 100 - 150 mL methylene chloride in each continuous extractor and 200 - 300 mL in each distilling flask.

10.3.1 Pour the sample(s), blank, and standard aliquots into the extractors. Rinse the glass containers with 50 - 100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

10.3.2 Base/neutral extraction--adjust the pH of the waters in the extractors to 12 - 13 with 6N NaOH while monitoring with a pH meter. Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1 - 2 drops of methylene chloride per second will fall from the condensor tip into the water. Test and adjust the pH of the waters during the first to second hour and during the fifth to tenth hour of extraction. Extract for 24 - 48 hours.

10.3.3 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm anhydrous sodium sulfate. Rinse the distilling flask with 30 - 50 mL of methylene chloride and pour through the drying column. Collect the solution in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal, label as the base/neutral fraction, and concentrate per sections 10.5 to 10.6.

10.3.4 Acid extraction--adjust the pH of the waters in the extractors to 2 or less using 6N sulfuric acid. Charge clean distilling flasks with 300 - 400 mL of methylene chloride. Test and adjust the pH of the waters during the first 1 - 2 hr and during the fifth to tenth hr of extraction. Extract for 24 - 48 hours.

Repeat section 10.3.3, except label as the acid fraction.

10.4 Ultrasonic extraction of high solids samples

10.4.1 Add 60 grams of anhydrous sodium sulfate the sample and QC aliquot(s) (section 10.2.5) and mix thoroughly.

10.4.2 Add 100 ± 10 mL of acetone:methylene chloride (1:1) to the sample and mix thoroughly.

10.4.3 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of the solvent but above the solids layer and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication.

10.4.4 Decant the extracts through Whatman 41 filter paper using glass funnels and collect in 500 - 1000 mL graduated cylinders.

10.4.5 Repeat the extraction steps (10.4.2 - 10.4.4) twice more for each sample and QC aliquot. On the final extraction, swirl the sample or QC aliquot, pour into its respective glass funnel, and rinse with acetone:methylene chloride. Record the total extract volume.

10.4.6 Pour each extract through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the graduated cylinder with 30 - 50 mL of methylene chloride and pour through the drying column. Collect each extract in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal and label as the high solids semi-volatile fraction. Concentrate and clean up the samples and QC aliquots per sections 10.5 through 10.8.

10.5 Macro concentration--concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes.

10.5.1 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approx one mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lowers joint into the concentrator tube with 1 - 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.5.2 For performance standards (sections 8.2 and 12.7) and for blanks (section 8.5), combine the acid and base/neutral extracts for each at this point. Do not combine the acid and base/neutral extracts for aqueous samples.

10.6 Micro-concentration--Add a clean boiling chip and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approx 0.5 mL methylene chloride through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature as required to complete the concentration in 5 - 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid reaches an apparent volume of approx 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint into the concentrator tube with approx 0.2 mL of methylene chloride. Adjust the final volume to 5.0 mL if the extract is to be cleaned up by GPC, or to 1.0 mL if it has

been cleaned up or does not require clean-up.

10.7 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid, and mark the level on the vial. Label with the sample number and fraction, and store in the dark at -20 to -10 °C until ready for analysis.

10.8 GPC setup and calibration

10.8.1 Column packing

10.8.1.1 Place 75 ± 5 g of SX-3 Bio-beads in a 400 - 500 mL beaker.

10.8.1.2 Cover the beads and allow to swell overnight (12 hours minimum).

10.8.1.3 Transfer the swelled beads to the column and pump solvent through the column, from bottom to top, at 4.5 - 5.5 mL/min prior to connecting the column to the detector.

10.8.1.4 After purging the column with solvent for 1 - 2 hours, adjust the column head pressure to 7 - 10 psig, and purge for 4 - 5 hours to remove air from the column. Maintain a head pressure of 7 - 10 psig. Connect the column to the detector.

10.8.2 Column calibration

10.8.2.1 Load 5 mL of the calibration solution (section 6.4) into the sample loop.

10.8.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethylhexyl) phthalate, pentachlorophenol, perylene, and sulfur.

10.8.2.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of the phthalate.

10.8.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.

10.8.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

10.9 Extract cleanup

10.9.1 Filter the extract or load through the filter holder to remove particulates. Load the 5.0 mL extract onto the column. The maximum capacity of the column is 0.5 - 1.0 gram. If necessary, split the extract into multiple aliquots to prevent column overload.

10.9.2 Elute the extract using the calibration data determined in 10.8.2. Collect the eluate in a clean 400 - 500 mL beaker.

10.9.3 Concentrate the cleaned up extract per section 10.5.

10.9.4 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

10.9.5 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry-over.

10.9.6 Reconcentrate the extract to one mL and transfer to a screw-cap vial per sections 10.6 and 10.7.

11 GCMS ANALYSIS

11.1 Establish the operating conditions given in tables 5 or 6 for analysis of the base/neutral or acid extracts, respectively. For analysis of combined extracts (section 10.5.2 and 10.9.6), use the operating conditions in table 5.

11.2 Bring the concentrated extract (section 10.7) or standard (sections 6.13 - 6.14) to room temperature and verify that any precipitate has redissolved. Verify the

level on the extract (sections 6.6 and 10.7) and bring to the mark with solvent if required.

11.3 Add the internal standard solution (section 6.10) to the extract (use 1.0 uL of solution per 0.1 mL of extract) immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

11.4 Inject a volume of the standard solution or extract such that 100 ng of the internal standard will be injected, using on-column or splitless injection. For 1 mL extracts, this volume will be 1.0 uL. Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the benzo(ghi)perylene or pentachlorophenol peak elutes for the base/neutral (or semi-volatile) or acid fraction, respectively. Return the column to the initial temperature for analysis of the next sample.

12 SYSTEM AND LABORATORY PERFORMANCE

12.1 At the beginning of each 8 hr shift during which analyses are performed, GCMS system performance and calibration are verified for all pollutants and labeled compounds. For these tests, analysis of the 100 ug/mL calibration standard (section 6.13) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and precision and recovery standards be analyzed.

12.2 DFTPP spectrum validity--inject 1 uL of the DFTPP solution (section 6.11) either separately or within a few seconds of injection of the standard (section 12.1) analyzed at the beginning of each shift. The criteria in table 7 shall be met.

12.3 Retention times--the absolute retention time of 2,2'-difluorobiphenyl shall be within the range of 1078 to 1248 seconds and the relative retention times of all pollutants and labeled compounds shall fall within the limits given in tables 5 and 6.

12.4 GC resolution--the valley height between anthracene and phenanthrene at m/z 178 (or the analogs at m/z 188) shall not exceed 10 percent of the taller of the two peaks.

12.5 Calibration verification--compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

12.5.1 For each pollutant and labeled compound being tested, compare the concentration with the calibration verification limit in table 10. If all compounds meet the acceptance criteria, calibration has been verified and analysis of blanks, samples, and precision and recovery standards may proceed. If, however, any compound fails, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the test (section 12.1), or recalibrate (section 7).

12.6 Multiple peaks--each compound injected shall give a single, distinct GC peak.

12.7 On-going precision and accuracy.

12.7.1 Analyze the extract of one of the pair of precision and recovery standards (section 10) prior to analysis of samples from the same lot.

12.7.2 Compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds

which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method.

12.7.3 For each pollutant and labeled compound, compare the concentration with the limits for on-going accuracy in table 10. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, system performance is unacceptable for that compound.

NOTE: The large number of compounds in table 10 present a substantial probability that one or more will fail when all compounds are analyzed. To determine if the extraction/concentration system is out of control or if the failure is caused by probability, proceed as follows:

12.7.3.1 Analyze the second aliquot of the pair of precision and recovery standards (section 10).

12.7.3.2 Compute the concentration of only those pollutants or labeled compounds that failed the previous test (section 12.7.3). If these compounds now pass, the extraction/concentration processes are in control and analysis of blanks and samples may proceed. If, however, any of the same compounds fail again, the extraction/concentration processes are not being performed properly for these compounds. In this event, correct the problem, re-extract the sample lot (section 10) and repeat the on-going precision and recovery test (section 12.7).

12.7.4 Add results which pass the specifications in section 12.7.3 to initial and previous on-going data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance (Figure 5). Develop a statement of laboratory accuracy for each pollutant and labeled compound in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85 - 105%.

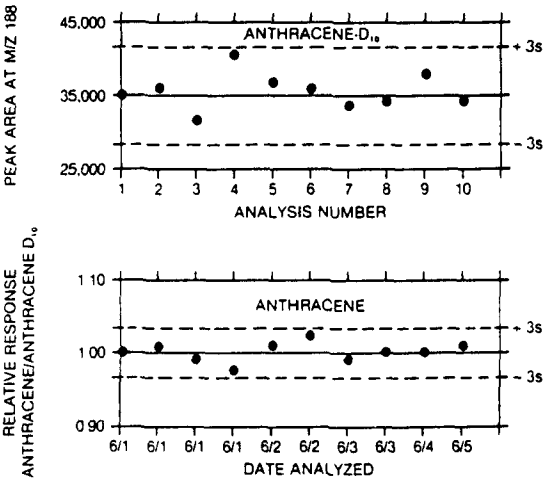

FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d_{10} (lower graph) Plotted as a Function of Time or Analysis Number.

13 QUALITATIVE DETERMINATION

Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the mass spectral libraries. For compounds for which the relative retention times and mass spectra are known, identification is confirmed per sections 13.1 and 13.2. For unidentified GC peaks, the spectrum is compared to spectra in the EPA/NIH mass spectral file per section 13.3.

13.1 Labeled compounds and pollutants having no labeled analog (tables 1 thru 4):

13.1.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

13.1.3 For the compounds for which the system has been calibrated (tables 1 and 2), the retention time shall be within the windows specified in tables 5 and 6, or within ± 15 scans or ± 15 seconds (whichever is greater) for compounds for which no window is specified.

13.1.4 For the compounds for which the system has not been calibrated but the relative retention times and mass spectra are known (tables 3 and 4), the retention time relative to the 2,2'-difluorobiphenyl internal standard shall be within ± 30 scans or ± 30 seconds (whichever is greater) based on the nominal retention time specified in tables 5 and 6.

13.2 Pollutants having a labeled analog (tables 1 and 2):

13.2.1 The signals for all characteristic m/z's stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

13.2.3 The relative retention time between the pollutant and its labeled analog shall be within the windows specified in tables 5 and 6.

13.3 Unidentified GC peaks

13.3.1 The signals for masses specific to a GC peak shall all maximize within ± 1 scan.

13.3.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two with the masses stored in the EPA/NIH Mass Spectral File.

13.4 M/z's present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

14 QUANTITATIVE DETERMINATION

14.1 Isotope dilution--by adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon extraction, concentration, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the phenol example given in figure 1 (section 7.4.1), RR would be equal to 1.114. For this RR value, the phenol calibration curve given in figure 1 indicates a concentration of 27 ug/mL in the sample extract (C_{ex}).

14.2 Internal standard--compute the concentration in the extract using the response factor determined from calibration data (section 7.5) and the following equation:

$$C_{ex}\ (ug/mL) = \frac{(A_s \times C_{is})}{(A_{is} \times RF)}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in section 7.5.1.

14.3 The concentration of the pollutant in the solid phase of the sample is computed using the concentration of the pollutant

in the extract and the weight of the solids (section 10), as follows:

Concentration in solid (ug/kg) = $\frac{(C_{ex} \times V_{ex})}{W_s}$

where V_{ex} is the extract volume in mL, and W_s is the sample weight in kg.

14.4 If the EICP area at the quantitation m/z for any compound exceeds the calibration range of the system, the extract of the dilute aliquot (section 10) is analyzed by isotope dilution. If further dilution is required and the sample holding time has not been exceeded, a smaller sample aliquot is extracted per section 14.4.1 - 14.4.3. If the sample holding time has been exceeded, the sample extract is diluted by successive factors of 10, internal standard is added to give a concentration of 100 ug/mL in the diluted extract, and the diluted extract is analyzed by the internal standard method.

14.4.1 For samples containing one percent solids or less for which the holding time has not been exceeded, dilute 10 mL, 1.0 mL, 0.1 mL etc. of sample to one liter with reagent water and extract per section 10.2.1.

14.4.2 For samples containing 1 - 30 percent solids for which the holding time has not been exceeded, extract an amount of sample equal to 1/100 the amount determined in 10.2.2.2. Extract per section 10.2.2.

14.4.3 For samples containing 30 percent solids or greater for which the holding time has not been exceeded, extract 0.30 ± 0.003 g of sample per section 10.2.5.

14.5 For GC peaks which are to be identified (per section 13.3), the sample is diluted by successive factors of 10 when any peak in the uncorrected mass spectrum at the GC peak maximum is saturated.

14.6 Results are reported for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples, in units of ug/L for aqueous samples or in ug/kg dry weight of solids for samples containing one percent solids or greater (soils, sediments, filter cake, compost), to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 14.4) or at which no m/z in the spectrum is saturated (section 14.5). For compounds having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (section 14.4) and the labeled compound recovery is within the normal range for the method (section 15.4).

15 ANALYSIS OF COMPLEX SAMPLES

15.1 Some samples may contain high levels (>1000 ug/L) of the compounds of interest, interfering compounds, and/or polymeric materials. Some samples will not concentrate to one mL (section 10.6); others will overload the GC column and/or mass spectrometer.

15.2 Analyze the dilute aliquot (section 10) when the sample will not concentrate to 1.0 mL. If a dilute aliquot was not extracted, and the sample holding time (section 9.3) has not been exceeded, dilute an aliquot of an aqueous sample with reagent water, or weigh a dilute aliquot of a high solids sample and re-extract (section 10); otherwise, dilute the extract (section 14.4) and analyze by the internal standard method (section 14.2).

15.3 Recovery of internal standard--the EICP area of the internal standard should be within a factor of two of the area in the shift standard (section 12.1). If the absolute areas of the labeled compounds are within a factor of two of the respective areas in the shift standard, and the internal standard area is less

than one-half of its respective area, then internal standard loss in the extract has occurred. In this case, use one of the labeled compounds (preferably a polynuclear aromatic hydrocarbon) to compute the concentration of a pollutant with no labeled analog.

15.4 Recovery of labeled compounds--in most samples, labeled compound recoveries will be similar to those from reagent water or from the high solids reference matrix (section 12.7). If the labeled compound recovery is outside the limits given in table 10, the extract from the dilute aliquot (section 10) is analyzed as in section 14.4. If the recoveries of all labeled compounds and the internal standard are low (per the criteria above), then a loss in instrument sensitivity is the most likely cause. In this case, the 100 ug/mL calibration standard (section 12.1) shall be analyzed and calibration verified (section 12.5). If a loss in sensitivity has occurred, the instrument shall be repaired, the performance specifications in section 12 shall be met, and the extract reanalyzed. If a loss in instrument sensitivity has not occurred, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

16 METHOD PERFORMANCE

16.1 Interlaboratory performance for this method is detailed in reference 10. Reference mass spectra, retention times, and response factors are from references 11 and 12. Results of initial tests of this method on municipal sludge can be found in reference 13.

16.2 A chromatogram of the 100 ug/mL acid/base/neutral calibration standard (section 6.13) is shown in figure 6.

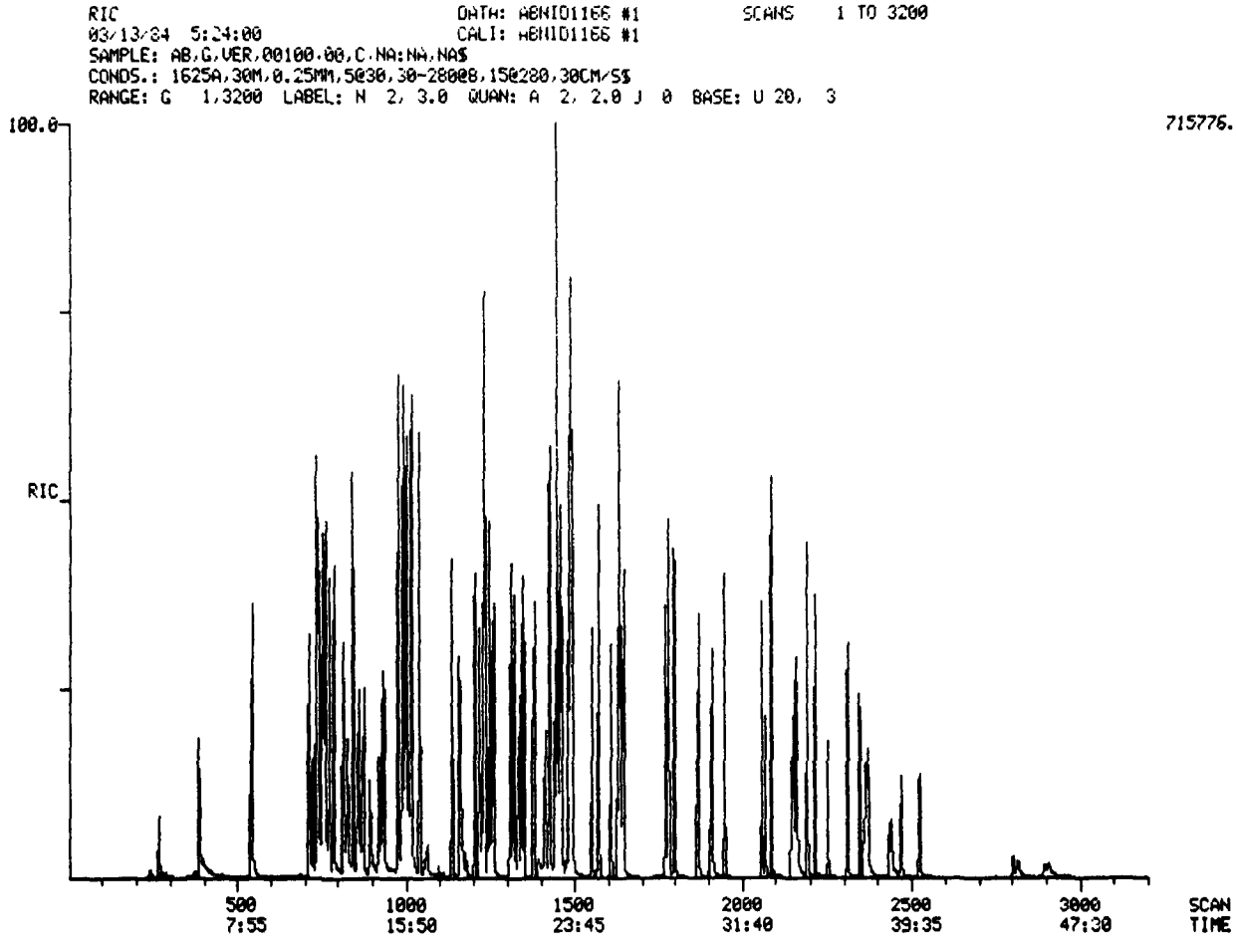

FIGURE 6 Chromatogram of Combined Acid/Base/Neutral Standard.

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Appendix A: Mass Spectra in the Form of Mass/Intensity Lists

555 acetophenone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	21	43	245	49	19	50	221	51	524	52	75
61	13	62	26	63	422	65	31	73	13	74	64
75	36	76	62	77	941	78	11	89	12	91	22
105	1000	106	87	120	479	121	38				

556 4-aminobiphenyl

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	55	63	65	72	82	83	73	85	163	115	142
139	65	141	132	167	163	168	280	169	1000	170	216

557 aniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	65	41	66	42	16	46	11	47	75	50	40
51	47	52	54	53	12	54	40	61	17	62	28
63	59	64	33	65	226	66	461	74	11	78	14
91	10	92	136	93	1000	94	73				

558 o-anisidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	22	41	43	42	10	50	60	51	106	52	202
53	286	54	39	61	12	62	25	63	43	64	24
65	142	66	20	76	13	77	36	68	32	79	25
80	915	81	41	92	47	93	14	94	18	105	18
108	1000	109	55	122	123	844	124	56			

559 aramite

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	606	57	758	59	328	63	782	65	285	74	113
77	155	91	339	105	153	107	239	121	107	123	120
163	143	175	182	185	1000	187	328	191	346	197	191
319	270	334	137								

560 benzanthrone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	69	75	71	87	97	88	160	99	69	100	215
101	278	150	58	174	67	199	63	200	350	201	236
202	762	203	126	230	1000	231	177				

561 1,3-benzenediol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	64	41	19	52	42	43	36	49	11	50	43
51	54	52	29	53	184	54	89	55	97	61	15
62	27	63	74	64	61	65	13	68	56	69	119
71	16	81	201	82	251	95	13	109	11	110	1000
111	51										

562 benzenethiol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	128	50	149	51	205	65	175	66	505	69	114
77	161	84	259	109	316	110	1000	111	102		

563 2,3-benzofluorene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	52	81	69	94	143	95	253	106	60	107	205
108	491	187	75	189	90	213	233	214	60	215	987
216	1000	217	166								

943 benzoic acid

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	29	50	221	51	413	52	45	66	11	74	53
75	25	76	81	77	778	78	76	105	1000	122	868

564 benzyl alcohol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	17	59	16	50	155	51	319	52	78	53	84
61	11	62	31	63	70	64	12	65	75	74	35
75	13	76	18	77	565	78	116	79	1000	80	73
89	65	90	64	91	125	105	38	106	18	107	523
108	737	109	43								

565 2-bromochlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	237	50	890	51	183	73	158	74	506	75	1000
76	202	111	961	113	287	190	638	192	809	194	193

566 3-bromochlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	201	50	834	51	174	73	169	74	509	75	914
76	197	111	1000	113	301	190	625	192	802	194	191

567 4-chloro-2-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	119	50	174	51	260	52	531	61	205	62	394
63	1000	64	315	65	192	73	290	74	105	75	156
76	127	78	152	90	724	91	253	101	232	114	312
126	766	128	234	142	211	172	915	174	289		

568 5-chloro-o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	115	51	261	52	257	53	137	77	420	78	134
79	140	89	152	106	1000	140	599	141	964	142	265
143	313										

569 4-chloroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	60	62	55	63	147	64	135	65	329	73	51
91	63	92	186	99	67	100	115	127	1000	128	81
129	292										

570 3-chloronitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	619	51	189	73	144	74	330	75	1000	76	169
85	101	99	258	111	851	113	266	157	424	159	137

571 o-cresol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	102	51	181	53	144	77	358	79	380	80	159
89	114	90	231	107	783	108	1000				

944 p-cresol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	136	51	224	52	106	53	196	77	420	79	308
80	145	90	122	107	822	108	1000				

572 crotoxyphos

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	633	44	448	67	42	77	70	79	41	104	100
105	484	109	21	127	1000	166	180	193	401	194	20

573 2,6-di-t-butyl-p-benzoquinone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	392	53	586	55	325	57	668	65	416	67	927
77	376	79	308	91	456	95	322	107	248	121	255
135	538	136	240	149	429	163	292	177	1000	205	203
220	410										

574 2,4-diaminotoluene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	70	42	55	51	76	52	70	53	51	61	91
67	50	77	147	78	69	93	63	94	224	104	128
105	134	106	67	121	958	122	1000	123	79		

575 1,2-dibromo-3-chloropropane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	38	59	341	51	104	61	38	75	1000	76	75
77	331	81	43	93	117	95	106	97	12	105	67
106	17	119	74	121	66	155	635	157	784	158	20
159	204	187	10								

945 3,5-dibromo-4-hydroxybenzonitrile

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	148	61	193	62	222	88	632	117	137	168	152
170	141	275	489	277	1000	279	451				

576 2,6-dichloro-4-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	206	52	1000	61	523	62	828	63	588	73	470
65	137	89	218	90	443	97	458	124	954	126	401
133	218	160	401	176	431	178	134	206	378		

577 1,3-dichloro-2-propanol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	14	42	55	43	503	44	22	47	12	58	15
49	113	50	15	51	37	57	10	61	12	75	14
78	11	79	1000	80	25	81	310				

578 2,3-dichloroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
52	138	61	151	62	265	63	455	64	142	65	105
73	130	90	460	99	202	125	108	126	149	161	1000
163	626	165	101								

579 2,3-dichloronitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	220	50	257	61	150	62	120	63	173	73	336
74	976	75	743	84	351	85	166	86	125	109	1000
110	204	111	303	133	701	135	435	145	580	147	368
161	190	163	121	191	411	193	263				

946 2,6-dichlorophenol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
49	111	62	160	63	714	73	132	98	293	99	117
126	260	162	1000	164	613	166	101				

580 1,2:3,4-diepoxybutane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	37	41	29	42	83	43	60	55	1000	56	67
57	155	58	16	85	13						

581 3,3'-dimethoxybenzidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
65	44	79	222	85	69	93	84	107	46	115	110
122	115	158	154	186	144	201	552	229	162	244	1000
245	152										

582 dimethyl sulfone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
44	10	45	94	46	29	47	18	48	69	62	14
63	69	64	22	65	19	79	1000	81	36	94	528
96	23										

583 p-dimethylaminoazobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	483	51	181	77	447	78	120	79	147	91	109
104	142	105	190	120	1000	148	160	225	676		

584 7,12-dimethylbenzo(a)anthracene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
101	24	112	34	113	112	114	38	119	212	120	296
125	46	126	81	127	60	128	76	215	24	226	47
237	23	239	313	240	230	241	433	242	61	250	32
252	68	253	33	255	84	256	1000	257	180		

585 N,N-dimethylformamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	58	41	79	42	497	43	115	44	1000	45	19
57	17	58	83	72	89	73	994	74	35		

586 3,6-dimethylphenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
76	113	89	129	94	179	101	142	102	151	189	388
190	193	191	430	205	246	206	1000	207	159		

587 1,4-dinitrobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	1000	51	131	63	228	64	218	74	311	75	623
76	664	92	240	122	166	168	399				

588 diphenyldisulfide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	153	51	293	65	671	59	282	77	141	109	1000
110	132	154	191	185	117	218	418				

589 ethyl methanesulfonate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	16	43	72	45	208	48	40	59	19	63	23
64	22	65	93	79	1000	80	127	81	42	96	16
97	206	109	579	111	18	123	15	124	33		

590 ethylenethiourea

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	46	42	126	45	97	46	42	59	14	72	89
73	151	102	1000								

591 ethynylestradiol 3-methyl ether

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	155	53	101	91	157	115	143	147	226	159	132
160	115	173	199	174	313	227	1000	228	149	242	153
310	516										

592 hexachloropropene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	131	71	333	106	334	108	200	117	329	119	320
141	206	143	196	211	631	213	1000	215	623	217	186

947 hexanoic acid

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	627	42	535	43	214	45	186	46	19	55	128
56	90	57	102	60	1000	61	66	69	21	70	20
73	412	74	56	87	98						

593 *2-isopropylnaphthalene*

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	100	63	111	76	157	77	129	115	147	127	131
128	216	152	133	153	184	154	114	155	1000	156	139
170	368										

594 isosafrole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	110	51	222	63	127	77	277	78	208	103	355
104	441	131	371	132	107	135	129	161	250	162	1000

595 longifolene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	438	55	719	65	346	67	453	77	566	69	713
91	1000	93	611	94	546	95	404	105	614	107	475
119	394	133	338	161	568	204	172				

596 malachite green

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
118	113	126	313	165	369	208	135	209	233	210	181
237	158	253	1000	254	160	329	189	330	775	331	170

597 methapyriline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
42	72	45	47	53	40	58	1000	71	188	72	225
78	54	79	48	97	516	190	40	191	67		

598 methyl methanesulfonate

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	178	56	15	48	108	50	26	63	35	64	48
65	285	78	27	79	821	80	1000	81	44	82	33
95	137	109	59	110	60						

599 2-methylbenzothiozole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	152	50	133	58	153	62	106	63	309	69	513
82	204	108	392	109	102	148	279	149	1000	150	110

900 3-methylcholanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
113	58	119	55	125	83	126	305	132	99	133	122
134	160	250	56	252	322	253	271	263	59	265	106
266	50	267	192	268	1000	269	185				

901 4,4'-methylenebis(2-chloroaniline)

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
77	190	84	107	98	299	104	133	115	226	140	316
195	352	229	228	231	1000	233	227	265	171	266	631
267	144	268	358								

902 4,5-methylenephenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	50	62	55	63	95	74	69	81	145	86	53
87	60	94	255	95	659	163	80	187	213	188	137
189	900	190	1000								

903 1-methylfluorene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	66	51	87	62	57	63	137	74	64	75	85
76	196	83	135	87	53	88	78	89	203	90	58
139	54	151	73	152	124	163	57	164	58	165	1000
166	136	176	96	177	52	178	202	179	182	180	686
181	99										

904 2-methylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	29	51	39	57	28	58	47	62	26	63	65
65	19	69	56	70	25	71	126	74	25	75	23
76	14	77	15	86	13	87	18	89	42	113	19
114	13	115	303	116	25	126	13	139	98	140	24
141	748	142	1000	143	105						

905 1-methylphenanthrene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	54	63	86	70	62	74	51	81	52	83	164
96	132	163	55	165	217	189	165	191	532	192	1000
193	152										

906 2-(methylthio)benzothiazole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	790	50	212	63	383	69	578	82	233	108	627
136	239	148	938	180	250	181	1000				

907 1,5-naphthalenediamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	48	65	83	77	75	79	111	103	86	118	52
130	262	131	40	141	43	157	89	158	1000	159	117

908 1,4-naphthoquinone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	445	51	62	52	52	66	69	74	189	75	205
76	590	101	51	102	613	103	52	104	550	130	433
158	1000	159	100								

909 alpha-naphthylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	25	51	31	57	36	59	46	62	28	63	59
65	27	71	58	72	104	89	62	113	22	114	34
115	401	116	212	142	53	143	1000	144	101		

910 5-nitro-o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	194	52	159	53	121	77	766	78	176	79	619
94	168	104	120	106	691	152	1000				

911 2-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	64	50	51	51	89	52	207	53	74	62	58
63	181	64	155	65	960	66	96	80	212	91	86
92	566	108	170	138	1000	139	63				

912 3-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	101	52	120	53	59	62	58	63	143	64	121
65	1000	66	114	80	169	91	62	92	764	93	62
108	87	138	717	139	51						

913 4-nitroaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
52	228	53	160	62	110	63	216	64	164	65	1000
66	124	80	266	92	300	108	636	138	520		

914 4-nitrobiphenyl

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	131	63	104	76	179	115	134	141	277	151	259
152	902	153	284	169	374	199	1000	200	125		

915 N-nitroso-di-n-butylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	1000	42	536	43	570	44	313	55	129	56	167
57	994	84	985	86	103	99	197	115	158	116	237
158	161										

916 N-nitrosodiethylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	170	42	079	43	69	44	1000	45	20	54	18
56	525	57	492	70	24	71	28	85	25	87	31
102	807	103	35								

917 N-nitrosomethylethylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	117	42	1000	43	667	44	26	54	17	56	189
57	99	59	13	71	60	73	57	88	772	89	20

918 N-nitrosomethylphenylamine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	181	51	434	52	104	63	110	77	1000	78	194
79	331	104	147	106	673	107	220	212	137		

919 N-nitrosomorpholine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	181	42	192	43	52	44	17	54	85	55	95
56	1000	57	49	85	13	86	333	87	14	116	337

920 N-nitrosopiperidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	320	42	1000	43	43	51	14	52	12	53	32
54	58	55	444	56	224	57	17	67	21	82	26
83	28	84	47	114	491	115	26				

921 pentachlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
73	160	108	239	125	102	178	102	213	179	215	218
217	106	248	648	250	1000	252	642	254	199		

922 pentachloroethane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	203	60	398	62	119	83	378	85	218	94	114
95	165	117	1000	119	979	121	306	130	293	132	272
165	716	167	901	169	422						

923 pentamethylbenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	126	53	84	63	61	65	99	77	145	79	64
91	218	105	128	115	120	117	91	133	1000	134	105
147	60	148	420								

924 perylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	33	111	43	112	70	113	111	124	132	125	251
126	243	224	49	248	75	249	52	250	284	251	86
252	1000	253	219								

925 phenacetin

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
43	443	51	33	52	112	53	164	63	39	64	30
65	47	79	31	80	179	31	154	108	1000	109	196
110	50	137	461	138	40	179	672	180	64		

926 phenothiazine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	145	51	120	63	134	69	190	100	128	154	149
166	240	167	607	198	186	199	1000	200	143		

927 1-phenylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	132	51	156	63	148	74	124	75	142	76	136
87	101	88	183	89	162	100	155	101	527	102	111
200	144	201	136	202	643	203	1000	204	999	205	159

928 2-phenylnaphthalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
51	108	63	101	76	136	88	133	89	158	101	333
102	188	202	398	203	270	204	1000	205	157		

929 pronamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	270	66	109	74	112	75	137	84	194	109	186
145	334	147	198	173	1000	175	615	254	133	255	211
256	102	257	122								

930 pyridine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	45	48	11	49	62	50	324	51	414	52	879
53	112	54	12	55	16	75	21	76	19	77	22
78	151	79	1000	80	101	81	58				

931 safrole

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	132	51	369	63	108	77	391	78	228	103	348
104	477	105	130	131	437	132	166	161	298	162	1000
163	109										

932 squalene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
53	62	55	94	67	105	68	119	69	1000	70	57
79	43	81	465	82	52	93	70	95	104	107	43
109	47	121	46	137	41						

933 1,2,4,5-tetrachlorobenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
47	125	49	176	61	127	72	183	73	332	74	448
84	197	108	284	109	231	143	194	145	117	179	237
181	224	214	791	216	1000	218	482	220	101		

948 2,3,4,6-tetrachlorophenol

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
61	234	65	167	66	105	83	134	84	178	96	202
97	107	131	463	133	270	166	298	168	273	194	168
196	164	230	793	232	1000	234	471				

934 thianaphthene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	80	50	91	51	65	62	82	63	162	67	78
69	139	74	55	89	191	90	136	108	82	134	1000
135	104	136	52								

935 thioacetamide

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	225	42	485	43	44	46	18	57	36	58	93
59	165	60	437	75	1000	76	25	77	43		

936 thioxanthone

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	262	63	180	69	320	74	116	69	176	82	121
92	188	108	129	139	385	152	227	183	112	184	951
185	137	212	1000	213	145						

937 o-toluidine

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
40	51	41	38	42	35	49	10	50	88	51	169
52	164	53	192	53	86	62	26	63	68	64	30
65	59	66	24	74	19	65	14	76	21	77	313
78	113	79	243	80	80	89	107	90	76	91	52
104	45	106	1000	107	90						

938 1,2,3-trimethoxybenzene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
50	257	51	459	52	139	53	276	63	112	65	341
67	114	77	246	79	132	82	117	93	483	95	801
107	190	108	144	110	898	125	578	153	759	168	1000

939 2,4,5-trimethylaniline

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
41	80	52	58	51	63	53	66	65	150	67	74
79	62	91	167	93	51	117	54	118	65	119	93
120	1000	121	87	134	670	135	978	136	99		

940 triphenylene

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
74	52	87	55	100	107	101	108	112	131	113	244
114	181	200	67	202	56	224	84	225	56	226	313
227	132	228	1000	229	184						

941 tripropylene glycol methyl ether

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
45	492	46	15	47	19	55	17	57	68	58	43
59	1000	60	34	71	16	72	44	73	363	74	232
103	57	117	92	161	21						

942 1,3,5-trithiane

m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
46	1000	47	150	48	98	59	93	60	76	64	136
73	102	91	92	92	111	110	58	138	259		

EPA METHOD 1618
THE CONSOLIDATED GC METHOD FOR THE DETERMINATION OF ITD/RCRA PESTICIDES *USING SELECTIVE GC DETECTORS*

Introduction

Method 1618 was developed by EPA's Office of Water Regulations and Standards to provide improved precision and accuracy of analysis of pollutants in aqueous and solid matrices.

Method 1618 is an automated, wide-bore capillary column gas chromatography method for analysis of organo-halide and organo-phosphorus pesticides and phenoxy-acid herbicides and herbicide esters and other compounds amenable to extraction and analysis by wide-bore capillary column gas chromatography with halogen specific and organo-phosphorus detectors.

Questions concerning the Methods or their application should be addressed to:

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USEPA
Office of Water Regulations and Standards
401 M Street SW
Washington, DC 20460
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OR

USEPA OWRS
Sample Control Center
P.O. Box 1407
Alexandria, Virginia 22313
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Publication date: May 1988

Organo-halide and Organo-phosphorus Pesticides and Phenoxy-acid Herbicides by Capillary Column Gas Chromatography

1 SCOPE AND APPLICATION

1.1 This method is designed to meet the survey requirements of the Environmental Protection Agency (EPA). It is used to determine the organo-halide and organo-phosphorus pesticides, and the phenoxy-acid herbicides and herbicide esters associated with the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation and Liability Act; and other compounds amenable to extraction and analysis by automated, wide-bore capillary column gas chromatography (GC) with halogen specific and organo-phosphorus detectors.

1.2 The chemical compounds listed in tables 1 through 3 may be determined in waters, soils, sediments, and sludges by this method. The method is a consolidation of EPA Methods 608, 608.1, 614, 615, 617, 622, and 701. For waters, the sample extraction and concentration steps are essentially the same as in these methods. However, the extraction and concentration steps have been extended to other sample matrices. The method should be applicable to other pesticides and herbicides. The quality assurance/quality control requirements in this method give the steps necessary to determine this applicability.

1.3 When this method is applied to analysis of unfamiliar samples, compound identity shall be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Gas chromatography-mass spectrometry (GCMS) can be used to confirm compounds in extracts produced by this method when analyte levels are sufficient.

Table 1

CHLORINATED PESTICIDES DETERMINED BY LARGE-BORE, FUSED-SILICA, CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH HALIDE SPECIFIC DETECTOR

EPA EGD	Compound	CAS Registry
089	Aldrin	309-00-2
102	alpha-BHC	319-84-6
103	beta-BHC	319-85-7
105	delta-BHC	319-86-8
104	gamma-BHC (Lindane)	58-89-9
434	Captafol	2425-06-1
433	Captan	133-06-2
441	Carbophenothion	786-19-6
091	Chlordane	57-74-9
431	Chlorobenzilate	510-15-6
094	4,4'-DDD	72-54-8
093	4,4'-DDE	72-55-9
092	4,4'-DDT	50-29-3
432	Diallate	2303-16-4
478	Dichlone	117-80-6
090	Dieldrin	60-57-1
095	Endosulfan I	959-98-8
096	Endosulfan II	33213-65-9
097	Endosulfan sulfate	1031-07-8
098	Endrin	72-20-8
099	Endrin aldehyde	7421-93-4
435	Endrin ketone	53494-70-5
100	Heptachlor	76-44-8
101	Heptachlor epoxide	1024-57-3
437	Isodrin	465-73-6
439	Kepone	143-50-0
430	Methoxychlor	72-43-5
438	Mirex	2385-85-5
436	Nitrofen (TOK)	1836-75-5
112	PCB-1016	12674-11-2
108	PCB-1221	11104-28-2
109	PCB-1232	11141-16-5
106	PCB-1242	53469-21-9
110	PCB-1248	12672-29-6
107	PCB-1254	11097-69-1
111	PCB-1260	11096-82-5
440	PCNB (pentachloro-nitrobenzene)	82-68-8
113	Toxaphene	8001-35-2
442	Trifluralin	1582-09-8

Table 1 (continued)

Non-ITD organo-halide compounds

Compound	CAS Registry
Chloroneb	2675-77-6
Chloropropylate	5836-10-2
DBCP	96-12-8
Dicofol	115-32-2
Etridiazole	2593-15-9
Perthane (Ethylan)	72-56-0
Propachlor	1918-16-7
Strobane	8001-50-1

Table 2

PHOSPHORUS PESTICIDES DETERMINED BY LARGE-BORE, FUSED-SILICA, CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH FLAME PHOTOMETRIC DETECTOR

EPA EGD	Compound	CAS Registry
468	Azinphos ethyl	2642-71-9
453	Azinphos methyl	86-50-0
461	Chlorfevinphos	470-90-6
469	Chlorpyrifos	2921-88-2
443	Coumaphos	56-72-4
479	Crotoxyphos	7700-17-6
471	Demeton	8065-48-3
460	Diazinon	333-41-5
450	Dichlorvos	62-73-7
455	Dicrotophos	141-66-2
449	Dimethoate	60-51-5
452	Dioxathion	78-34-2
458	Disulfoton	298-04-4
467	EPN	2104-64-5
463	Ethion	563-12-2
446	Famphur	52-85-7
454	Fensulfothion	115-90-2
447	Fenthion	55-38-9
464	Hexamethylphosphoramide	680-31-9
474	Leptophos	21609-90-5
475	Malathion	121-75-5
456	Methyl parathion	298-00-0
444	Mevinphos	7786-34-7
470	Monocrotophos	6923-22-4
459	Naled	300-76-5
448	Parathion	56-38-2
457	Phorate	298-02-2
465	Phosmet	732-11-6
473	Phosphamidon	13171-21-6
477	Sulfotepp	3689-24-5
476	TEPP	107-40-3
472	Terbufos	13071-79-9
466	Tetrachlorvinphos	961-11-5
445	Trichlorofon	42-68-6
451	Tricresylphosphate	78-30-8
462	Trimethylphosphate	512-56-1

Non-ITD thiophosphate compounds

Compound	CAS Registry
Bolstar	35400-43-2
Dichlorofenthion	97-17-6
Ethoprop	13194-48-4
Merphos	150-50-5
Methyl chlorpyrifos	5598-13-0
Methyl trithion	
Ronnel	299-84-3
Tokuthion	34643-46-4
Trichloronate	327-98-0

Table 3

PHENOXYACID HERBICIDES DETERMINED BY LARGE-BORE, FUSED-SILICA, CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH ELECTRONEGATIVE DETECTOR

EPA EGD	Compound	CAS Registry
481	2,4-D	94-75-7
480	Dinoseb	88-85-7
482	2,4,5-T	93-76-5
483	2,4,5-TP	93-72-1

Non-ITD phenoxyacid herbicides

Compound	CAS Registry
Dalapon	75-99-0
2,4-DB (Butoxon)	94-82-6
Dicamba	1918-00-9
Dichlorprop	120-36-5
MCPA	94-74-6
MCPP	93-65-2

1.4 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in tables 4 - 5 typify the minimum quantity that can be detected with no interferences present.

1.5 This method is for use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatographic data. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 8.2.

2 SUMMARY OF METHOD

2.1 Extraction--the percent solids content of a sample is determined. If the solids content is less than one percent, a one liter sample is extracted with methylene chloride using continuous extraction techniques. If the solids content is 1 - 30 percent, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted with methylene chloride using continuous extraction techniques. If the solids content is greater than 30 percent, the sample is extracted with methylene chloride:acetone using ultrasonic techniques. Samples in which phenoxy-acid herbicides are to be determined are acidified prior to extraction.

2.2 Concentration and cleanup--for samples in which pesticides are to be determined, each extract is dried over sodium sulfate, concentrated using a Kuderna-Danish evaporator, cleaned up (if necessary) using gel permeation chromatography (GPC) and/or adsorption chromatography, and re-concentrated to one mL. Sulfur is removed from the extract, if required. For samples in which the herbicides are to be determined, each extract is processed to remove the acids and esters. The esters are hydrolyzed, combined with the acids, and derivatized to form the methyl esters. The solution containing the methyl esters is cleaned up (if necessary) using adsorption chromatography and concentrated to one mL.

2.3 Gas chromatography--a one uL aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a wide-bore, fused silica capillary column. The organo-halide com pounds, including the derivatized phenoxy-acid herbicides, are detected by an electron capture, microcoulometric, or electrolytic conductivity detector. The phosphorus containing compounds are detected using a flame photometric detector.

2.4 Identification of a pollutant (qualitative analysis) is performed by comparing the GC retention times of the compound on two dissimilar columns with the respective retention times of an authentic standard. Compound identity is confirmed when the retention times agree within their respective windows.

2.5 Quantitative analysis is performed by using an authenic standard to produce a calibration factor or calibration curve, and using the calibration data to determine the concentration of a pollutant in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

2.6 Quality is assured through reproducible calibration and testing of the extraction and GC systems.

3 CONTAMINATION AND INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks as described in section 8.5.

Table 4

GAS CHROMATOGRAPHY OF ORGANO-HALIDE COMPOUNDS

EPA EGD	Compound	DB-5 Column Concentration (Conc) and Retention Time (RT) Conc 1 (ug/mL)	RT 1 (min)	Conc 2 (ug/mL)	RT 2 (min)	Conc 3 (ug/mL)	RT 3 (min)	MDL (1) (ug/L)	(ug/kg)
089	Aldrin				19.77				
102	alpha-BHC				13.77				
103	beta-BHC				14.74				
105	delta-BHC				15.93				
104	gamma-BHC (Lindane)				15.01				
434	Captafol				31.26				
433	Captan				22.03				
441	Carbophenothion				28.44				
091	Chlordane								
431	Chlorobenzilate				26.49				
481	2,4-D				20.84				
094	4,4'-DDD				26.99				
093	4,4'-DDE				24.70				
092	4,4'-DDT				29.01				
432	Diallate				13.57				
478	Dichlone								
090	Dieldrin				24.88				
480	Dinoseb				30.28				
095	Endosulfan I				23.54				
096	Endosulfan II				26.49				
097	Endosulfan sulfate				28.77				
098	Endrin				26.02				
099	Endrin aldehyde				27.48				
435	Endrin ketone				31.25				
100	Heptachlor				18.14				
101	Heptachlor epoxide				21.69				
437	Isodrin				21.19				
439	Kepone				28.04				
430	Methoxychlor				32.17				
438	Mirex				34.49				
436	Nitrofen (TOK)				25.99				
112	PCB-1016								
108	PCB-1221								
109	PCB-1232								
106	PCB-1242								
110	PCB-1248								
107	PCB-1254								
111	PCB-1260								
440	PCNB				15.24				
482	2,4,5-T				26.95				
483	2,4,5-TP				25.78				
113	Toxaphene								
442	Trifluralin				12.95				

Table 4 (continued)

GAS CHROMATOGRAPHY OF ORGANO-HALIDE COMPOUNDS

EPA EGD	Compound	SPB-608 Column Concentration (Conc) and Retention Time (RT) Conc 1 (ug/mL)	RT 1 (min)	Conc 2 (ug/mL)	RT 2 (min)	Conc 3 (ug/mL)	RT 3 (min)	MDL (1) (ug/L)	(ug/kg)
089	Aldrin				18.33				
102	alpha-BHC				13.70				
103	beta-BHC				15.04				
105	delta-BHC				17.15				
104	gamma-BHC (Lindane)				15.22				
434	Captafol				26.83				
433	Captan				24.24				
441	Carbophenothion				28.69				
091	Chlordane								
431	Chlorobenzilate				26.03				
481	2,4-D				22.91				
094	4,4'-DDD				26.79				
093	4,4'-DDE				24.16				
092	4,4'-DDT				28.75				
432	Diallate				12.89				
478	Dichlone								
090	Dieldrin				24.35				
480	Dinoseb				26.25				
095	Endosulfan I				22.81				
096	Endosulfan II				27.15				
097	Endosulfan sulfate				29.41				
098	Endrin				26.11				
099	Endrin aldehyde				28.82				
435	Endrin ketone				33.27				
100	Heptachlor				16.87				
101	Heptachlor epoxide				21.01				
437	Isodrin				20.33				
439	Kepone				26.28				
430	Methoxychlor				33.37				
438	Mirex				33.59				
436	Nitrofen (TOK)				26.35				
112	PCB-1016								
108	PCB-1221								
109	PCB-1232								
106	PCB-1242								
110	PCB-1248								
107	PCB-1254								
111	PCB-1260								
440	PCNB				14.78				
482	2,4,5-T				29.13				
483	2,4,5-TP				29.83				
113	Toxaphene								
442	Trifluralin				11.01				

Table 4 (continued)

GAS CHROMATOGRAPHY OF ORGANO-HALIDE COMPOUNDS

EPA EGD	Compound	DB-608 Column Concentration (Conc) and Retention Time (RT) Conc 1 (ug/mL)	RT 1 (min)	Conc 2 (ug/mL)	RT 2 (min)	Conc 3 (ug/mL)	RT 3 (min)	MDL (1) (ug/L)	(ug/kg)
089	Aldrin				18.33				
102	alpha-BHC				13.70				
103	beta-BHC				15.04				
105	delta-BHC				17.15				
104	gamma-BHC (Lindane)				15.22				
434	Captafol				26.83				
433	Captan				24.24				
441	Carbophenothion				28.69				
091	Chlordane								
431	Chlorobenzilate				26.03				
481	2,4-D				22.91				
094	4,4'-DDD				26.79				
093	4,4'-DDE				24.16				
092	4,4'-DDT				28.75				
432	Diallate				12.89				
478	Dichlone								
090	Dieldrin				24.35				
480	Dinoseb				26.25				
095	Endosulfan I				22.81				
096	Endosulfan II				27.15				
097	Endosulfan sulfate				29.41				
098	Endrin				26.11				
099	Endrin aldehyde				28.82				
435	Endrin ketone				33.27				
100	Heptachlor				16.87				
101	Heptachlor epoxide				21.01				
437	Isodrin				20.33				
439	Kepone				26.28				
430	Methoxychlor				33.37				
438	Mirex				33.59				
436	Nitrofen (TOK)				26.35				
112	PCB-1016								
108	PCB-1221								
109	PCB-1232								
106	PCB-1242								
110	PCB-1248								
107	PCB-1254								
111	PCB-1260								
440	PCNB				14.78				
482	2,4,5-T				29.13				
483	2,4,5-TP				29.83				
113	Toxaphene								
442	Trifluralin				11.01				

Column: 30 +/- 2 m x 0.50 +/- 0.05 mm i.d.
Temperature program: 1 min at 50 oC; 50 - 280 at 5 oC per min; 5 minute hold at 250 oC
Gas velocity: 30 +/- 5 cm/sec at 30 oC

Table 5

CALIBRATION OF THIOPHOSPHATE COMPOUNDS ON DB-5 COLUMN

EPA EGD	Compound	Concentration (Conc) and Retention Time (RT) Conc 1 (ng/mL)	RT 1 (min)	Conc 2 (ng/mL)	RT 2 (min)	Conc 3 (ng/mL)	RT 3 (min)	MDL (1) (ug/L)	(ug/kg)
Calibration Group #1									
450	Dichlorvos	50	9.91	100	9.90	1000	9.91		
470	Monocrotophos	500	21.61	1000	21.66	2000	21.54		
449	Dimethoate	50	23.73	100	23.71	1000	23.69		
458	Disulfoton	50	38.38	100	28.34	1000	28.38		
	Methyl chlorpyrifos	50	33.01	100	32.99	1000	33.01		
447	Fenthion	50	34.98	100	34.97	1000	34.98		
	Merphos	50	36.04	100	36.03	1000	36.03		
	Tokuthion	50	37.52	100	37.51	1000	37.52		
	Bolstar (Sulprofos)	50	39.80	100	39.79	1000	39.80		
453	Azinphos methyl	100	45.67	200	45.64	1000	45.66		
Calibration Group #2									
445	Trichlorofon	100	9.94	200	9.93	1000	9.93		
455	Dicrotophos	200	21.23	400	21.26	1000	21.19		
471	Demeton	100	23.70	400	23.70	1000	23.70		
	Dichlorofenthion	50	32.50	100	32.49	1000	32.51		
	Ronnel	50	33.80	100	33.80	1000	33.81		
469	Chlorpyrifos	50	35.08	100	35.07	1000	35.08		
461	Chlorfevinphos	50	36.20	100	36.20	1000	36.21		
	Methyl trithion (Carbofenthion-methyl)	50	38.77	100	38.77	1000	38.78		
446	Famphur	50	40.15	100	40.14	1000	40.15		
474	Leptophos	50	45.91	100	45.91	1000	45.92		
Calibration Group #3									
444	Mevinphos	50	14.23	100	14.21	1000	14.23		
459	Naled	100	20.71	200	20.67	1000	20.72		
477	Sulfotepp	50	21.78	100	21.74	1000	21.79		
472	Terbufos	50	26.35	100	26.30	1000	26.36		
473	Phosphamidon	200	32.43	600	32.40	1000	32.44		
452	Dioxathion	400	34.03	800	34.00	1000	34.03		
448	Parathion	100	35.05	200	35.03	1000	35.06		
479	Crotoxyphos	100	36.37	200	36.35	1000	36.37		
454	Fensulfothion	100	38.90	200	38.88	1000	38.90		
465	Phosmet	100	43.08	200	43.05	1000	43.08		
468	Azinphos ethyl	100	48.32	200	48.27	1000	48.32		
Calibration Group #4									
	Ethoprop	50	19.85	100	19.84	1000	19.86		
457	Phorate	50	22.24	100	22.22	1000	22.25		
460	Diazinon	50	28.01	100	27.99	1000	28.03		
456	Methyl parathion	50	32.97	100	32.96	1000	32.98		
475	Malathion	50	34.73	100	34.73	1000	34.75		
	Trichloronate	50	35.43	100	35.43	1000	35.45		
466	Tetrachlorvinphos	50	36.93	100	36.93	1000	36.94		
463	Ethion	50	39.32	100	39.31	1000	39.33		
467	EPN	50	43.33	100	43.32	1000	43.35		
443	Coumaphos	100	52.16	200	52.14	1000	52.18		

3.2 Glassware and, where possible, reagents are cleaned by solvent rinse and baking at 450 °C for one hour minimum in a muffle furnace or kiln. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment and thorough rinsing with acetone and pesticide quality hexane may be required.

3.3 Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 Interference by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. Phthalates usually appear in the chromatogram as large, late eluting peaks. Phthalates may be leached from common flexible plastic tubing and other plastic materials during the extraction and clean-up processes. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction, especially when solvent wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory, or by using a microcoulometric or electrolytic conductivity detector.

3.5 The acid forms of the herbicides are strong acids that react readily with alkaline substances and can be lost during analysis. Glassware and glass wool must be acid rinsed with dilute hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use.

3.6 Organic acids and phenols cause the most direct interference with the herbicides. Alkaline hydrolysis and subsequent extraction of the basic solution can remove many hydrocarbons and esters that may interfere with the herbicide analysis.

3.7 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. The cleanup procedures given in this Method can be used to overcome many of these interferences, but unique samples may require additional cleanup to achieve the minimum levels given in tables 4 - 5.

4 SAFETY

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 1 - 3.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDD, 4,4'-DDT, the BHCs and the PCBs. Primary standards of these compounds shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

4.3 Diazomethane is a toxic carcinogen which can decompose or explode under certain conditions. Solutions decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips. The following operations may cause explosion: heating above 90 °C; use of grinding surfaces such as ground glass joints, sleeve bearings, and glass stirrers; and storage near alkali metals. Diazomethane shall be used only behind a safety screen in a well ventilated hood and should be pipetted with mechanical devices only.

4.4 Mercury vapor is highly toxic. If mercury is used for sulfur removal, all operations involving mercury shall be performed in a hood.

4.5 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves that will prevent exposure. The oven used for sample drying to determine percent moisture should be located in a hood so that vapors from samples do not create a health hazard in the laboratory.

5 APPARATUS AND MATERIALS

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Sample bottles and caps

5.1.1.1 Liquid samples (waters, sludges and similar materials that contain less than five percent solids)--sample bottle, amber glass, 1 liter or 1 quart, with screw cap.

5.1.1.2 Solid samples (soils, sediments, sludges, filter cake, com post, and similar materials that contain more than five percent solids)--sample bottle, wide mouth, amber glass, 500 mL minimum.

5.1.1.3 If amber bottles are not available, samples shall be protected from light.

5.1.1.4 Bottle caps--threaded to fit sample bottles. Caps shall be lined with Teflon.

5.1.1.5 Cleaning

5.1.1.5.1 Bottles are detergent water washed, then solvent rinsed or baked at 450 °C for one hour minimum before use.

5.1.1.5.2 Liners are detergent water washed, then reagent water and solvent rinsed, and baked at approx 200 °C for one hour minimum prior to use.

5.1.2 Compositing equipment--automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Sample containers are kept at 0 - 4 °C during sampling. Glass or Teflon tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

5.2 Equipment for determining percent moisture

5.2.1 Oven, capable of being temperature controlled at 110 ± 5 °C.

5.2.2 Dessicator.

5.2.3 Crucibles, porcelain.

5.2.4 Weighing pans, aluminum.

5.3 Extraction equipment.

5.3.1 Equipment for ultrasonic extraction.

5.3.1.1 Sonic disruptor--375 watt with pulsing capability and 1/2 or 3/4 in. disruptor horn (Ultrasonics, Inc, Model 375C, or equivalent).

5.3.1.2 Sonabox (or equivalent), for use with disruptor.

5.3.2 Equipment for liquid-liquid extraction

5.3.2.1 Continuous liquid-liquid extractor--Teflon or glass connecting joints and stopcocks without lubrication, 1.5 - 2 liter capacity (Hershberg-Wolf Extractor, Cal-Glass, Costa Mesa, California, 1000 or 2000 mL continuous extractor, or equivalent).

5.3.2.2 Round-bottom flask, 500 mL, with heating mantle.

5.3.2.3 Condenser, Graham, to fit extractor.

5.3.2.4 pH meter, with combination glass electrode.

5.3.2.5 pH paper, wide range (Hydrion Papers, or equivalent).

5.2.3 Separatory funnels--250, 500, and 1000 mL, with Teflon stop cocks.

5.3.4 Filtration apparatus

5.3.4.1 Glass powder funnels--125 - 250 mL

5.3.4.2 Filter paper for above (Whatman 41, or equivalent)

5.3.5 Beakers

5.3.5.1 1.5 - 2 liter, calibrated to one liter

5.3.5.2 400 - 500 mL

5.3.6 Spatulas--stainless steel or Teflon

5.3.7 Drying column--400 mm x 15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

5.3.7.1 Pyrex glass wool--solvent extracted or baked at 450 °C for one hour minimum.

5.4 Evaporation/concentration apparatus

5.4.1 Kuderna-Danish (K-D) apparatus

5.4.1.1 Evaporation flask--500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

5.4.1.2 Concentrator tube--10 mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

5.4.1.3 Snyder column--three ball macro (Kontes K-503000-0232, or equivalent).

5.4.1.4 Snyder column--two ball micro (Kontes K-469002-0219, or equivalent).

5.4.1.5 Boiling chips

5.4.1.5.1 Glass or silicon carbide--approx 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hr minimum.

5.4.1.5.2 Teflon (optional)--extracted with methylene chloride.

5.4.2 Water bath--heated, with concentric ring cover, capable of temperature control (± 2 °C), installed in a fume hood.

5.4.3 Nitrogen evaporation device--equipped with heated bath that can be maintained at 35 - 40 °C (N-Evap, Organomation Associates, Inc., or equivalent).

5.4.4 Sample vials--amber glass, 1 - 5 mL with Teflon-lined screw or crimp cap, to fit GC autosampler.

5.5 Balances

5.5.1 Analytical--capable of weighing 0.1 mg.

5.5.2 Top loading--capable of weighing 10 mg.

5.6 Apparatus for sample cleanup.

5.6.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).

5.6.1.1 Column--600 - 700 mm x 25 mm i.d., packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).

5.6.1.2 Syringe, 10 mL, with Luer fitting.

5.6.1.3 Syringe filter holder, stainless steel, and glass fiber or Teflon filters (Gelman 4310, or equivalent).

5.6.1.4 UV detectors--254-mu, preparative or semi-prep flow cell: (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman-Altex 152W, 8 uL micro-prep flow cell, 2 mm path; Pharmacia UV-1, 3 mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).

5.6.2 Vacuum system for eluting cleanup cartridges.

5.6.2.1 Vacuum system--capable of achieving 0.1 bar (house vacuum, vacuum pump, or water aspirator), with vacuum gauge.

5.6.2.2 VacElute Manifold (Analytichem International, or equivalent).

5.6.2.3 Vacuum trap--made from 500 mL sidearm flask fitted with single hole rubber stopper and glass tubing.

5.6.2.4 Rack for holding 10 mL volumetric flasks in the manifold.

5.6.3 Chromatographic column--400 mm x 22 mm i.d., with Teflon stop cock and coarse frit (Kontes K-42054, or equivalent).

5.6.4 Sulfur removal tubes--40 - 50 mL bottle or test tube with Teflon lined screw cap.

5.7 Centrifuge apparatus

5.7.1 Centrifuge--capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5,000 rpm minimum.

5.7.2 Centrifuge bottles--500 mL, with screw caps, to fit centrifuge.

5.7.3 Centrifuge tubes--12-15 mL, with screw caps, to fit centrifuge.

5.7.3 Funnel, Buchner, 15 cm.

5.7.3.1 Flask, filter, for use with Buchner funnel.

5.7.3.2 Filter paper, 15 cm (Whatman #41, or equivalent).

5.8 Derivatization apparatus--Diazald kit with clear seal joints for generation of diazomethane (Aldrich Chemical Co. Z10,025-0, or equivalent).

5.9 Miscellaneous glassware

5.9.1 Pipettes, glass, volumetric, 1.00, 5.00, and 10.0 mL

5.9.2 Syringes, glass, with Luerlok tip, 0.1, 1.0 and 5.0 mL. Needles for syringes, two inch, 22 gauge.

5.9.3 Volumetric flasks, 10.0, 25.0, and 50.0 mL

5.9.4 Scintillation vials, glass, 20 - 50 mL, with Teflon-lined screw caps.

5.10 Gas chromatographs--two GCs shall be employed. Both shall have splitless or on-column simultaneous automated injection into separate capillary columns with a halide specific detector or flame photometric detector at the end of each column, temperature program with isothermal holds, data system capable of recording simultaneous signals from the two detectors, and shall meet all of the performance specifications in section 12.

5.10.1 GC columns--bonded phase fused silica capillary

5.10.1.1 Primary--60 ±5 m x 0.5 ± 0.05 mm i.d. 5% phenyl, 94% methyl, 1% vinyl silicone (J & W DB-5 Megabore, Supelco SP-5, or equivalent).

5.10.1.2 Confirmatory--J&W DB-608, Supelco SPB-608, or equivalent, with same dimensions as primary column.

5.10.2 Data system--shall collect and record GC data, store GC runs on magnetic disk or tape, process GC data, compute peak areas, store calibration data including retention times and calibration factors, identify GC peaks through retention times, compute concentrations, and generate reports.

5.10.2.1 Data acquisition--GC data shall be collected continuously throughout the analysis and stored on a mass storage device.

5.10.2.2 Calibration factors and calibration curves--the data system shall be used to record and maintain lists of calibration factors, and multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient

of variation) are used for testing calibration linearity. Statistics on initial (section 8.2) and on-going (section 12.7) performance shall be computed and maintained.

5.10.2.3 *Data processing--the data system shall* be used to search, locate, identify, and quantify the compounds of interest in each GC analysis. Software routines shall be employed to compute and record retention times and peak areas. Displays of chromatograms and library comparisons are required to verify results.

5.10.3 Detectors

5.10.3.1 Halide specific--electron capture or electrolytic conductivity (Micoulometric, Hall, or O.I.), capable of detecting TBD pg of aldrin under the analysis conditions given in table 2.

5.10.3.2 Flame photometric--capable of detecting TBD pg of TBD under the analysis conditions given in table 2.

5.10.4 Chromatographs may be configured in one of two ways: (1) Two halide specific detectors (HSDs) in one GC; two flame photometric detectors (FPDs) in the other. With this configuration, the primary and confirmatory columns and detectors are in the same GC. (2) One HSD and one FPD in each GC. With this configuration, the primary columns and detectors are in one GC, the confirmatory columns and detectors are in the other.

6 REAGENTS AND STANDARDS

6.1 Sample preservation--sodium thiosulfate (ACS), granular.

6.2 pH adjustment

6.2.1 Sodium hydroxide--reagent grade

6.2.1.1 Concentrated solution (10N)--dissolve 40 g NaOH in 100 mL reagent water.

6.2.1.2 Dilute solution (0.1M)--dissolve 4 g NaOH in 1 liter of reagent water.

6.2.2 Sulfuric acid (1 + 1)--reagent grade, 6N in reagent water. Slowly add 50 mL H_2SO_4 (specific gravity 1.84) to 50 mL reagent water.

6.2.3 Potassium hydroxide--37 w/v percent. Dissolve 37 g KOH in 100 mL reagent water.

6.3 Solution drying

6.3.1 Sodium sulfate, reagent grade, granular anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 450 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering.

6.3.2 Acidified sodium sulfate--add 0.5 mL H_2SO_4 and 30 mL ethyl ether to 100 g sodium sulfate. Mix thoroughly. Allow the ether to evaporate completely. Transfer the mixture to a clean container and store at 110 ± 5 °C.

6.4 Solvents--methylene chloride, hexane, ethyl ether, acetone, isooctane, and methanol; pesticide quality; lot certified to be free of interferences.

6.4.1 Ethyl ether must be shown to be free of peroxides before it is used, as indicated by EM Laboratories Quant Test Strips (Scientific Products P1126-8, or equivalent). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol is added to each liter of ether as a preservative.

6.4.2 Acetone:hexane (1:10)--prepare by adding 10 mL acetone to 90 mL hexane

6.5 GPC calibration solution--solution containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl) phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur

6.6 Sample cleanup

6.6.1 Florisil--PR grade, 60/100 mesh, activated at 650 - 700 °C, stored in the dark in glass container with Teflon-lined screw cap. Activate at 130 o for 16 h minimum immediately prior to use. Alternatively, 500 mg cartridges (J.T. Baker, or equivalent) may be used.

6.6.2 Diol cartridges--diol bonded silica, 1 g cartridges with stainless steel frits (Analytichem, Harbor City, CA, or equivalent).

6.6.2.1 Diol cartridge calibration solution--2,4,6-trichlorophenol, 0.1 ug/mL in acetone.

6.6.3 Silicic acid, 100 mesh

6.6.3 Sulfur removal--mercury (triple distilled), copper powder (bright, non-oxidized), or TBA sodium sulfite. If mercury is used, observe the handling precautions in section 4.

6.7 Derivatization--diazald reagent [N-methyl-(N-nitroso-p-toluene sulfanamide)], fresh and high purity (Aldrich Chemical Co.)

6.8 Reference matrices

6.8.1 Reagent water--water in which the compounds of interest and interfering compounds are not detected by this method.

6.8.2 High solids reference matrix--playground sand or similar material in which the compounds of interest and interfering compounds are not detected by this method. May be prepared by extraction with methylene chloride and/or baking at 450 °C for 4 hours minimum.

6.9 Standard solutions--purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10 °C in screw-capped vials with Teflon-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

6.10 Preparation of stock solutions--prepare in isooctane per the steps below. Observe the safety precautions in section 4.

6.10.1 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 mg aldrin in a 10 mL ground glass stoppered volumetric flask and fill to the mark with isooctane. After the aldrin is completely dissolved, transfer the solution to a 15 mL vial with Teflon-lined cap.

6.10.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Quality control check samples that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.10.3 Stock standard solutions shall be replaced after six months, or sooner if comparison with quality control check standards indicates a change in concentration.

6.11 Calibration solutions--using stock solutions (section 6.9), prepare calibration solutions of the mixtures shown in table 5 at the levels specified.

6.12 Surrogate spiking solutions

6.12.1 Chlorinated pesticides--prepare dibutyl chlorendate and TBD at a concentration of 10 ng/mL in acetone.

6.12.2 Phosphorus containing pesticides--prepare TBD and TBD at a concentration of TBD ng/mL in TBD.

6.12.3 Phenoxyacid herbicides--prepare TBD and TBD at a concentration of TBD ng/mL in TBD.

6.13 DDT and endrin decomposition solution--prepare a solution containing endrin and dieldrin each at a concentration of 25 ug/mL and DDT at a concentration of 50 ug/mL.

6.14 Combined QC standards--used for calibration verification (sections 7.5 and 14.5) and for determination of initial (section 8.2) and on-going (section 14.6) precision and recovery. Prepare these solutions at the levels specified in table 5.

6.15 Stability of solutions--all standard solutions (sections 6.9 - 6.13) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area remains within ± 15 percent of the area obtained in the initial analysis of the standard.

7 SETUP AND CALIBRATION

The GC systems can be calibrated using the external standard technique in section 7.3 or the internal standard technique in section 7.4.

7.1 Configure the GC systems in one of the two ways given in section 5.10.4 and establish the operating conditions in table 4.

7.2 Attainment of minimum levels, retention time reproducibility, and DDT/Endrin decomposition--determine that each column/detector system meets minimum level and retention reproducibility requirements, and that the organohalide systems meet the DDT and Endrin decomposition test, as follows:

7.2.1 Analyze 1 uL each of the low level calibration mixtures in tables 4 and 5 per the procedure in section 13 to demonstrate that each column/detector system meets the minimum levels in tables 4 and 5, and that each compound elutes within one minute of its retention time as specified in tables 4 and 5. Note: Failure to meet the minimum levels indicates a problem with the column/detector system under test. Poor GC system sensitivity is usually traceable to a dirty detector, carrier gas leaks, or improper detector and data system sensitivity settings.

7.2.2 On each column/detector system, analyze three replicates of Calibration Group N in table 4 for halogenated pesticides, and of Calibration Group 1 in table 5 for phosphorus containing pesticides. Using the GC data system, measure and record the retention time at the GC peak maximum for each of the compounds in these mixtures. The variation between the minimum and maximum retention time for every compound in the mixtures shall not exceed three seconds. Note: Failure to meet these retention time specifications indicates a problem with the column/detector system under test. Poor retention time reproducibility is usually traceable to poor GC column temperature control (often caused by room temperature or line voltage fluctuations), or carrier gas leaks.

7.2.3 DDT and endrin decomposition--inject one uL of the decomposition test solution (section 6.13), and compute the areas of the dieldrin, DDT, and endrin peaks. The areas of the DDT and endrin peaks shall be greater than nn and mm percent, respectively of the area of the dieldrin peak. Note: The decomposition of DDT and/or endrin are usually accompanied by the appearance of the decomposition products of these compounds. Decomposition of DDT and endrin can be eliminated by a thorough cleaning and deactivation of the GC injection port and/or by removal of a section from the front end of the GC column. GC column replacement may be necessary.

7.3 External standard calibration

7.3.1 Inject 1.0 uL of the mixtures in tables 4 and 5 into the GC column/detector pairs appropriate for the mixture, beginning with the lowest level mixture and proceeding to the highest. For each compound, compute and store, as a function of the concentration injected, the retention time and peak area on both column/detector systems (primary and confirmatory). For the multicomponent analytes (PCBs, chlordane, toxaphene), store the retention time and peak area for the five largest peaks in the chromatogram.

7.3.2 Retention time--the polar nature of some analytes causes the retention time to decrease as the quantity injected increases. To compensate this effect, the retention time for compound identification is correlated with the analyte level.

7.3.2.1 If the difference between the maximum and minimum retention times for any compound is less than five seconds over the calibration range, the retention time for that compound can be considered constant and an average retention time may be used for compound identification.

7.3.2.2 Retention time calibration curve (retention time vs amount)-- If the retention time for a compound in the lowest level standard is more than five seconds greater than the retention time for the compound in the highest level standard, a retention time calibration curve shall be used for identification of that compound.

7.3.3 Calibration factor (ratio of area to amount injected)

7.3.3.1 Compute the coefficient of variation (relative standard deviation) of the calibration factor over the three point range for each compound on each column/detector system.

7.3.3.2 Linearity--if the calibration factor for any compound is constant (less than the limits specified in tables 4 and 5) over the three point calibration range, an average calibration factor may be used for that compound; otherwise, the complete calibration curve (area vs amount) for that compound shall be used.

7.4 Internal standard calibration--The internal standard approach may be used when more precise and accurate results are required than can be obtained with the external standard method. However, this improved precision and accuracy can be attained only if there is no interference with the internal standard by the compounds of interest and compounds found in each sample matrix. Because of this limitation, no internal standard can be suggested that is applicable to all samples. Suggested internal standards are 2,2'-di fluorobiphenyl, TBD, and TBD for halogenated compounds; and deca fluorotriphenylphosphine (DFTPP), TBD and TBD for the phosphorus containing compounds.

7.4.1 Add a constant amount of internal standard to each of the calibration solutions in tables 4 and 5.

7.4.2 Inject 1.0 uL of the solutions in tables 4 and 5 into the GC column/detector system appropriate for the mixture, beginning with the lowest level mixture and proceeding to the highest. For each compound, compute and store, as a function of the concentration injected, the retention time and peak area on both column/detector systems (primary and confirmatory). For the multicomponent analytes (PCBs, chlordane, toxaphene), store the retention time and peak area for the five largest peaks in the chromatogram.

7.4.3 Relative retention time--Using the GC data system, compute the relative retention times for each compound in each of the mixtures:

Relative retention time =

$$\frac{\text{retention time of compound}}{\text{retention time of internal standard}}$$

If multiple internal standards are used, the nearest eluted internal standard shall be used for reference. Note: The polar nature of some compounds causes the retention time to decrease as the quantity injected increases. To compensate this effect, the relative retention time for compound identification shall be correlated with the level of the compound.

7.4.3.1 If the retention time difference between the compound and its internal standard are invariant (less than three seconds) over the three point calibration range, the average relative retention time may be used for identification of that compound.

7.4.3.2 Relative retention time calibration curve (relative retention time vs amount)--if the retention time difference between the compound and its internal standard in the lowest level standard is more than three seconds greater than this difference in the highest level standard, a relative retention time calibration curve shall be used for identification of that compound.

7.4.4 Response factors--calibration requires the determination of response factors (RF) which are defined by the following equation:

$RF = (A_s \times C_{is})/(A_{is} \times C_s)$, where; A_s is the area for the compound, A_{is} is the area for the internal standard, C_{is} is the concentration of the internal standard (ug/mL), and C_s is the concentration of the compound (ug/mL).

7.4.4.1 The response factor is determined for the three concentrations given in tables 4 and 5. The amount of internal standard added to each extract is the same so that C_{is} remains constant. The RF is plotted vs concentration for each compound in the standard (C_s) to produce a calibration curve.

7.4.4.2 Linearity--if the response factor (RF) for any compound is constant (less than 15 percent coefficient of variation) over the three point calibration range, the average response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used.

7.5 Combined QC standards--to preclude periodic analysis of all of the calibration solutions listed in tables 4 and 5, the GC systems are calibrated with the combined QC standards (section 6.14) as a final step. Not all of the compounds in these standards will be separated by the GC columns used in this method. Retention times and calibration or response factors are verified for the compounds that are resolved, and calibration or response factors are obtained for the unresolved peaks.

7.5.1 Analyze the combined QC standards on their respective column/detector pairs.

7.5.2 External standard calibration--for those compounds that exhibit a single, distinct GC peak, the retention time shall be within ± five seconds of the retention time of the peak in the medium level calibration standard (section 7.3.1), and the calibration factor using the primary column shall be within ± 20 percent of the calibration factor in the medium level standard (7.3.1).

7.5.3 Internal standard calibration--for those compounds that exhibit a single, distinct GC peak, the retention time difference between the peak and its internal standard shall be within ± three seconds of this difference in the medium level calibration standard (section 7.4.2), and the response factors on both column/detector systems shall be within ± 10 percent of the response factor in the medium level standard (section 7.4.2).

7.5.4 If all compounds meet the criteria in section 7.5.2 or 7.5.3, analysis of precision and recovery standards (section

8) may begin. If, however, any compound fails, the measurement system is not performing properly for that compound. In this event, correct the problem and repeat the test, or recalibrate the system (section 7.3 or 7.4).

7.5.5 For the peaks containing two or more compounds, compute and store the retention times or relative retention times at the peak maxima on both columns (primary and confirmatory), and also compute and store the calibration factors or response factors on both columns. These results will be used for calibration verification (section 14.2 and 14.5) and for precision and recovery studies (sections 8.2 and 14.6).

7.6 Florisil calibration--the cleanup procedure in section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil that is used, the use of the lauric acid value (reference 4) is suggested. The referenced procedure determines the adsorption of lauric acid (in mg/g of Florisil) from hexane solution. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

8 QUALITY ASSURANCE/QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (reference 5). The minimum requirements of this program consist of an initial demonstration of laboratory capability, an ongoing analysis of standards and blanks as tests of continued performance, and analysis of spiked samples to assess accuracy. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method. If the method is to be applied routinely to samples containing high solids with very little moisture (e.g., soils, compost), the high solids reference matrix (section 6.8.2) is substituted for the reagent water (section 6.8.1) in all performance tests, and the high solids method (section 10) is used for these tests.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve sepa rations or lower the costs of measurements, provided all performance requirements are met. Each time a modification is made to the method or a cleanup procedure is added, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in section 8.5.

8.1.4 The laboratory shall spike all samples with at least one surrogate compound to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 17).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through calibration verification and the analysis of the combined QC standard (section 6.14) that the analysis system is in control. These procedures are described in sections 14.1, 14.5, and 14.6.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in section 8.4.

8.1.7 Other analytes may be determined by this method. The procedure for establishing a

preliminary quality control limit for a new analyte is given in section 8.6.

8.2 Initial precision and accuracy--to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 For low solids (aqueous samples), extract, concentrate, and analyze one set of four one-liter aliquots of the combined QC standards (section 6.14) according to the procedure in section 10. For high solids samples, one set of four 30 gram aliquots of the high solids reference matrix are used.

8.2.2 Using results of the set of four analyses, compute the average recovery (X) in ug/mL in the extract and the standard deviation of the recovery (s) in ug/mL for each compound, by the external standard (section 7.3) or internal standard (section 7.4) method.

8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy in tables 6 - 8. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, how ever, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound.

8.3 The laboratory shall spike all samples with at least one surrogate compound to assess method performance on the sample matrix.

8.3.1 Analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the surrogate compound(s) using the external or internal standard method (section 7.3 or 7.4).

Table 6

PRECISION AND RECOVERY OF ORGANO-HALIDE COMPOUNDS

EPA EGD	Compound	Recovery (percent)	RSD
089	Aldrin	82.2	5.1
102	alpha-BHC	105.9	7.9
103	beta-BHC	94.2	9.1
105	delta-BHC	30.4	48.
104	gamma-BHC (Lindane)	109.9	3.8
434	Captafol	78.	10.
433	Captan	37.	
441	Carbophenothion	185.2	8.
091	Chlordane		
431	Chlorobenzilate	118.2	12.
094	4,4'-DDD	117.2	8.5
093	4,4'-DDE	82.1	32.
092	4,4'-DDT	97.3	18.
432	Diallate	62.	12.
478	Dichlone	42.	10.
090	Dieldrin	93.7	16.
095	Endosulfan I	81.6	16.
096	Endosulfan II	63.7	34.
097	Endosulfan sulfate	38.3	
098	Endrin	97.2	22.
099	Endrin aldehyde	22.2	
435	Endrin ketone	14.1	23.
100	Heptachlor	59.1	28.
101	Heptachlor epoxide	468.3	
437	Isodrin	54.9	21.
439	Kepone	76.	30.
430	Methoxychlor	104.9	12.
438	Mirex	90.5	9.8
436	Nitrofen (TOK)	90.3	11.
112	PCB-1016		
108	PCB-1221		
109	PCB-1232		
106	PCB-1242		
110	PCB-1248		
107	PCB-1254		
111	PCB-1260		
440	PCNB	97.5	14.
113	Toxaphene		
442	Trifluralin	111.3	5.5

Table 7

PRECISION AND RECOVERY OF THIOPHOSPHATE COMPOUNDS

EPA EGD	Compound	Recovery (percent)	RSD
468	Azinphos ethyl	77.0	8.9
461	Chlorfevinphos	98.	17.
469	Chlorpyrifos	84.1	4.8
443	Coumaphos	73.0	9.3
479	Crotoxyphos		
471	Demeton	23.	3.
460	Diazinon	86.9	4.6
450	Dichlorvos	80.6	4.5
455	Dicrotophos	95.8	5.8
449	Dimethoate	42.5	31.4
452	Dioxathion	79.6	7.2
458	Disulfoton	69.	5.
467	EPN	81.8	6.0
463	Ethion	82.0	5.4
446	Famphur	62.8	14.5
454	Fensulfothion	67.	26.
447	Fenthion	32.	2.
453	Guthion	77.0	8.9
464	Hexamethyl-phosphoramide 120.	4.	
474	Leptophos	77.2	8.9
475	Malathion	89.8	5.9
456	Methyl parathion	82.0	5.6
444	Mevinphos	85.	10.
470	Monocrotophos	9.	
459	Naled	74.	
448	Parathion	82.6	7.4
457	Phorate	97.0	5.0
465	Phosmet	79.	6.
473	Phosphamidon	61.	16.
477	Sulfotepp	101.	5.
476	TEPP	82.0	18.2
472	Terbufos	87.3	4.5
466	Tetrachlorvinphos	88.3	11.0
445	Trichlorofon	40.4	27.9
451	Tricresylphosphate	82.	8.
462	Trimethylphosphate	25.6	15.1

Table 8

PRECISION AND RECOVERY OF PHENOXYACID HERBICIDES

EPA EGD	Compound	Recovery (percent)	RSD
481	2,4-D	92.	5.0
480	Dinoseb	58.	9.8
482	2,4,5-T	69.	9.1
483	2,4,5-TP	60.	7.6
	2,4-DB	86.	9.5

8.3.3 The recovery of the surrogate compound shall be within the limits of 20 to 200 percent. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample, and the sample is complex. Water samples are diluted, and smaller amounts of soils, sludges, and sediments are reanalyzed per section 17.

8.4 Method accuracy--the laboratory shall spike at least ten percent of the samples from a given site type (e.g., influent to treatment, treated effluent, produced water, river sediment). If only one sample from a given site type is analyzed, a spiked analysis on that sample shall be performed.

8.4.1 The concentration of the spike in the sample shall be determined as follows:

8.4.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike shall be at that limit or at one to five times higher than the background concentration determined in section 8.4.2, whichever concentration is larger.

8.4.1.2 If the concentration of an analyte in the sample is not being checked against a limit specific to that analyte, the spike shall be at the concentration of the combined QC standard (section 6.14) or at one to five times higher than the

background concentration, whichever concentration is larger.

8.4.1.3 If it is impractical to determine the background concentration before spiking (e.g., maximum holding times will be exceeded), the spike concentration shall be (1) the regulatory concentration limit, if any; otherwise, the larger of either five times the expected background concentration or at the concentration of the combined QC standard (section 6.14).

8.4.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a standard solution appropriate to produce a level in the sample one to five times the background concentration. Spike a second sample aliquot with the standard solution and analyze it to determine the concentration after spiking (A) of each analyte. Calculate the percent recovery (P) of each analyte:

P = 100 (A - B) / T, where

T is the true value of the spike.

8.4.3 Compare the percent recovery for each analyte with the corresponding QC acceptance criteria in tables 6 - 8. If any analyte fails the acceptance criteria for recovery, the sample is complex and must be diluted and reanalyzed per section 17.

8.4.4 As part of the QA program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five spiked samples of a given matrix type (water, soil, sludge, sediment) in which the analytes pass the tests in section 8.4, compute the average percent recovery (P) and the standard deviation of the percent recovery (sp) for each compound (or co-eluting compound group). Express the accuracy assessment as a percent recovery interval from P - 2sp to P + 2sp for each matrix. For example, if P = 90% and sp = 10% for five analyses of compost, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound in each matrix on a regular basis (e.g. after each 5 - 10 new accuracy measurements).

8.5 Blanks--reagent water and high solids reference matrix blanks are analyzed to demonstrate freedom from contamination.

8.5.1 Extract and concentrate a one liter reagent water blank or a high solids reference matrix blank with each sample lot (samples started through the extraction process on the same 8 hr shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the combined QC standard (section 14.6) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (tables 1 thru 3) or any potentially interfering compound is found in an aqueous blank at greater than one ug/L, or in a high solids reference matrix blank at greater than 10 ug/kg (assuming the same calibration factor as aldrin and diazinon or a response factor of 1 relative to the nearest eluted internal standard, for compounds not listed in tables 1 thru 3), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 Other analytes may be determined by this method. To establish a quality control limit for an analyte, determine the precision and accuracy by analyzing four replicates of the analyte along with the combined QC standard per the procedure in section 8.2. Compute the average percent recovery (A) and the standard deviation of percent recovery (s_n) for the analyte, and measure the recovery and standard deviation of recovery for the other analytes. The data for the new analyte is assumed to be valid if the precision and recovery specifications for the other analytes are met. Establish a preliminary quality control limit of A ± $2s_n$ for the

new analyte and add the limit to table 6, 7, or 8.

8.7 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration verification (section 14.5), and for initial (section 8.2) and on-going (section 14.6) precision and recovery should be identical, so that the most precise results will be obtained. The GC instruments will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of the analytes given in this method.

8.8 Depending on specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

9 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Collect samples in glass containers following conventional sampling practices (reference 6), except that the bottle shall not be prerinsed with sample before collection. Aqueous samples which flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide mouth jars.

9.2 Maintain samples at 0 - 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, adjust the sample to a pH of 5.0 to 9.0 using sodium hydroxide or sulfuric acid solution. Record the volume of acid or base used. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA methods 330.4 and 330.5 may be used to measure residual chlorine (reference 7).

9.3 Begin sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction.

10 SAMPLE EXTRACTION AND CONCENTRATION

Samples containing one percent solids or less are extracted directly using continuous liquid/ liquid extraction techniques (section 10.2.1 and figure 3). Samples containing one to 30 percent solids are diluted to the one percent level with reagent water (section 10.2.2) and extracted using continuous liquid/liquid extraction techniques. Samples containing greater than 30 percent solids are extracted using ultrasonic techniques (section 10.2.5) For determination of the phenoxy-acid herbicides, a separate sample aliquot is extracted, derivatized, and cleaned up. The derivatized extract is then combined with the organo-chlorine extract.

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker. Record the weight to three figures.

10.1.2 Dry overnight (12 hours minimum) at 110 +/- 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of dry sample} \times 100}{\text{weight of wet sample}}$$

10.2 Preparation of samples for extraction

10.2.1 Samples containing one percent solids or less--extract the sample directly using continuous liquid/liquid extraction techniques.

10.2.1.1 Measure 1.00 +/- 0.01 liter of sample into a clean 1.5 - 2.0 liter beaker. For the phenoxy-acid herbicides, measure a separate one liter aliquot.

10.2.1.2 Spike 0.5 mL of the surrogate spiking solution (section 6.8) into the sample aliquot. For the phenoxy-acid herbicides, spike 0.5 mL of the herbicide surrogate spiking solution into the herbicide aliquot. Proceed to preparation of the QC aliquots for low solids samples (section 10.2.3).

10.2.2 Samples containing one to 30 percent solids

10.2.2.1 Mix sample thoroughly.

10.2.2.2 Using the percent solids found in 10.1.3, determine the weight of sample required to produce one liter of solution containing one percent solids as follows:

$$\text{sample weight} = \frac{1000 \text{ grams}}{\% \text{ solids}}$$

10.2.2.3 Place the weight determined in 10.2.2.2 in a clean 1.5 - 2.0 liter beaker. For the phenoxy-acid herbicides, place a separate aliquot in a clean beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.2.5 Bring the sample aliquot(s) to 100 - 200 mL volume with reagent water.

10.2.2.6 Spike 0.5 mL of the appropriate surrogate spiking solution (section 6.12) into each sample aliquot.

10.2.2.7 Using a clean metal spatula, break any solid portions of the sample into small pieces.

10.2.2.8 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in below the surface of each sample aliquot and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication. Clean the probe with methylene chloride:acetone (1:1) between samples to preclude cross-contamination.

10.2.2.9 Bring the sample volume to 1.0 +/- 0.1 liter with reagent water.

10.2.3 Preparation of QC aliquots for samples containing low solids (<30 percent).

10.2.3.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place two 1.0 +/- 0.01 liter aliquots of reagent water in clean 1.5 - 2.0 liter beakers. For the phenoxy-acid herbicides, place two additional one liter aliquots in clean beakers.

10.2.3.2 To serve as a blank, spike 0.5 mL of the pesticide surrogate spiking solution (section 6.12.1 and 6.12.2) into one reagent water aliquot, and 0.5 mL of the herbicide surrogate spiking solution (section 6.12.3) into a second reagent water aliquot.

10.2.3.3 Spike the combined QC standard (section 6.14) into a reagent water aliquot. For the herbicides, spike the herbicide standard into the remaining reagent water aliquot.

10.2.4 Stir and equilibrate all sample and QC solutions for 1 - 2 hours. Extract the samples and QC aliquots per section 10.3.

10.2.5 Samples containing 30 percent solids or greater

10.2.5.1 Mix the sample thoroughly

10.2.5.2 Weigh 30 +/- 0.3 grams into a clean 400 - 500 mL beaker. For the herbicides, weigh an additional two 30 gram aliquots into clean beakers. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.5.3 Herbicide acidification--add 50 mL of reagent water to one of the herbicide sample aliquots and stir on a stirring plate for one hour minimum. Using a pH meter, determine and record the sample pH while stirring. Slowly add H_2SO_4 while stirring and determine and record the

amount of acid required to acidify the sample to pH <2 Discard this aliquot.

10.2.5.4 Spike 0.5 mL of the appropriate surrogate spiking solution (section 6.12) into the pesticide and herbicide aliquots.

10.2.5.5 QC aliquots--for each sample or sample lot (to a maximum of 20) to be extracted at the same time, place two 30 +/- 0.3 gram aliquots of the high solids reference matrix in clean 400 - 500 mL beakers. For the herbicides, place three additional aliquots in clean beakers and use one of these to determine the amount of acid required for acidification per step 10.2.5.3. Discard this aliquot.

10.2.5.6 To serve as a blank, spike 0.5 mL of the pesticide surrogate spiking solution (section 6.12.1 and 6.12.2) into one aliquot of the high solids reference matrix, and 0.5 mL of the herbicide surrogate spiking solution (section 6.12.3) into a second aliquot of the high solids reference matrix.

10.2.5.7 Spike 1.0 mL of the combined QC standard (section 6.14) into a high solids reference matrix aliquot. For the herbicides, spike the herbicide standard into the remaining high solids reference matrix aliquot. Extract the high solids samples per section 10.4.

10.3 Continuous extraction of low solids (aqueous) samples--place 100 - 150 mL methylene chloride in each continuous extractor and 200 - 300 mL in each distilling flask.

10.3.1 Pour the sample(s), blank, and standard aliquots into the extractors. Rinse the glass containers with 50 - 100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

10.3.2 Extraction--for the pesticides, adjust the pH of the waters in the extractors to 5 - 9 with NaOH or H_2SO_4 while monitoring with a pH meter. For the herbicides, adjust the pH to two or less Caution: some samples require acidification in a hood because of the potential for generating hydrogen sulfide.

10.3.3 Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1 - 2 drops of methylene chloride per second will fall from the condensor tip into the water. Test and adjust the pH of the waters during the first 1 - 2 hours of extraction. Extract for 18 - 24 hours.

10.3.4 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a prerinsed drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the distilling flask with 30 - 50 mL of methylene chloride and pour through the drying column. For pesticide extracts and for herbicide extracts to be cleaned up using GPC, collect the solution in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal, label the pesticide and herbicide fractions, and concentrate per sections 10.5 to 10.6. For herbicide extracts not to be cleaned up by GPC, collect the solution in a 500 - 1000 mL separatory funnel and proceed to section 12 for hydrolysis and esterification of the herbicides.

10.4 Ultrasonic extraction of high solids samples

10.4.1 For the herbicide aliquots, add the amount of acid determined in section 10.2.5.3 to the sample aliquot and the amount determined in section 10.2.5.5 to the QC aliquots and mix thoroughly.

10.4.2 Add 60 - 70 grams of sodium sulfate to the pesticide aliquots and an equal amount of acidified sodium sulfate to the herbicide aliquots and mix each aliquot thoroughly. Some wet sludge samples may require more than 70 grams for complete removal of water. All water must be removed prior to

addition of organic solvent so that the extraction process is efficient.

10.4.3 Add 100 +/- 10 mL of acetone:methylene chloride (1:1) to each of the aliquots and mix thoroughly.

10.4.4 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in below the surface of the solvent but above the solids layer and pulse at 50 percent for three minutes at full power. If necessary, remove the probe from the solution and break any large pieces using a metal spatula or a stirring rod and repeat the sonication. Clean the horn with five percent aqueous sodium bicarbonate immediately after sonicating any of the herbicide aliquots to prevent acid damage to the horn.

10.4.5 Decant the pesticide extracts through a prerinsed drying column containing 7 to 10 cm anhydrous sodium sulfate into 500 - 1000 mL graduated cylinders. Decant the herbicide extracts similarly using acidified sodium sulfate.

10.4.6 Repeat the extraction steps (10.4.2 - 10.4.4) twice more for each sample and QC aliquot. On the final extraction, swirl the sample or QC aliquot, pour into its respective drying column, and rinse with acetone:methylene chloride. Record the total extract volume. If necessary, transfer the extract to a centrifuge tube and centrifuge for 10 minutes to settle fine particles.

10.4.7 For all pesticide extracts and for herbicide extracts to be cleaned up using GPC, filter these extracts through Whatman #41 paper into a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Rinse the graduated cylinder or centrifuge tube with 30 - 50 mL of methylene chloride and pour through filter to complete the transfer. Seal and label the K-Ds as the pesticide and herbicide fractions. Concentrate these fractions per sections 10.5 through 10.8. For herbicide extracts not to be cleaned up by GPC, filter the solution through Whatman #41 paper into a 500 - 1000 mL separatory funnel and proceed to section 12 for hydrolysis and esterification of the herbicides.

10.5 Macro concentration

10.5.1 Concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes. Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approx one mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

10.5.2 When the liquid has reached an apparent volume of one mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes.

10.5.3 If the extract is to be cleaned up using GPC, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 - 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation. Adjust the final volume to 10 mL and proceed to GPC cleanup in section 11.

10.6 Hexane exchange--extracts to be subjected to diol or Florisil cleanup and extracts that have been cleaned up are exchanged into hexane.

10.6.1 Remove the Snyder column, add approximately 50 mL of hexane and a clean boiling chip, and reattach the Snyder column. Concentrate the extract as in section 10.5 except use hexane to prewet the column. The elapsed time of the concentration should be 5 - 10 minutes.

10.6.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 - 2 mL of hexane. Adjust the final volume of extracts that have not been cleaned up by GPC to 10 mL and those that have been cleaned up by GPC to 5 mL (the difference accounts for the 50 percent loss in the GPC cleanup) Clean up the extracts using the diol, Florisil, and/or sulfur removal procedures in section 11.

11 CLEANUP AND SEPARATION

11.1 Cleanup procedures may not be necessary for relatively clean samples (treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. However, the analyst first shall demonstrate that the requirements of section 8.2 can be met using the cleanup procedure(s) as an integral part of the method.

11.1.1 Gel permeation chromatography (section 11.2) removes many high molecular weight interferents that cause GC column performance to degrade. It is used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

11.1.2 The diol cartridge (section 11.3) removes polar organic compounds such as phenols. It is used for all extracts.

11.1.3 The Florisil column (section 11.4) allows for selected fractionation of the compounds of interest and will also eliminate polar interferences. Its use is optional Note: Some organophosphorus pesticides may be irreversibly absorbed by Florisil.

11.1.4 Alumina column cleanup (section 11.5) is used to remove polar interferences. Its use is optional.

11.1.5 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides and herbicides, is removed using mercury or activated copper. Sulfur removal (section 11.6) is required when sulfur is known or suspected to be present.

11.2 Gel permeation chromatography (GPC)

11.2.1 Column packing

11.2.1.1 Place 70 - 75 g of SX-3 Bio-beads in a 400 - 500 mL beaker.

11.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (12 hours minimum).

11.2.1.3 Transfer the swelled beads to the column and pump solvent through the column, from bottom to top, at 4.5 - 5.5 mL/min prior to connecting the column to the detector.

11.2.1.4 After purging the column with solvent for 1 - 2 hours, adjust the column head pressure to 7 - 10 psig, and purge for 4 - 5 hours to remove air. Maintain a head pressure of 7 - 10 psig. Connect the column to the detector.

11.2.2 Column calibration

11.2.2.1 Load 5 mL of the calibration solution (section 6.5) into the sample loop.

11.2.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethyl hexyl) phthalate, pentachlorophenol, perylene, and sulfur.

11.2.2.3 Set the "dump time" to allow >85 percent removal of the corn oil and >85 percent collection of the phthalate.

11.2.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.

11.2.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the

recovery of the pentachlorophenol is greater than 85 percent. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

11.2.3 Extract cleanup--GPC requires that the column not be over loaded. The column specified in this method is designed to handle a maximum of 0.5 gram of high molecular weight material in a 5 mL extract. If the extract is known or expected to contain more than 0.5 gram, the extract is split into fractions for GPC and the fractions are combined after elution from the column. The solids content of the extract may be obtained gravimetrically by evaporating the solvent from a 50 uL aliquot.

11.2.3.1 Filter the extract or load through the filter holder to remove particulates. Load the 5.0 mL extract onto the column.

11.2.3.2 Elute the extract using the calibration data determined in 11.2.2. Collect the eluate in a clean 400 - 500 mL beaker.

11.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

11.2.3.4 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry-over.

11.2.3.5 Concentrate the pesticide extract and exchange into hexane per sections 10.5 and 10.6. Proceed to section 12 with the herbicide extract.

11.3 Diol cartridge

11.3.1 Setup

11.3.1.1 Attach the Vac-elute manifold to a water aspirator or vacuum pump with the trap and gauge installed between the manifold and vacuum source.

11.3.1.2 Place the diol cartridges in the manifold, turn on the vacuum source, and adjust the vacuum to 5 - 10 psia.

11.3.2 Cartridge washing--pre-elute each cartridge prior to use with 5 mL of hexane:acetone (9:1) to remove potential interferences.

11.3.3 Cartridge certification--each cartridge lot must be certified to ensure recovery of the compounds of interest and removal of 2,4,6-trichlorophenol.

11.3.3.1 To make the diol test mixture, add 1.0 mL of the trichlorophenol solution (section 6.6.2.1) to 1.0 mL of the combined calibration standard (section 6.14). Elute the mixture using the procedure in 11.3.4.

11.3.3.2 Concentrate the eluant to 1.0 mL using the nitrogen blowdown apparatus (section 5.4.3) and inject 1.0 uL of the concentrated eluant into the GC using the procedure in section 13. The recovery of all organo-halide and organo-phosphorus analytes (including the unresolved GC peaks) shall be in the range of 75 - 125 percent, and the peak for trichlorophenol shall not be detectable; otherwise the diol cartridge is not performing properly and the cartridge lot shall to rejected.

11.3.4 Extract cleanup

11.3.4.1 After cartridge washing (section 11.3.2), release the vacuum and place the rack containing the 10 mL volumetric flasks (section 5.6.2.4) in the vacuum manifold. Reestablish the vacuum at 5 - 10 psia.

11.3.4.2 Using a pipet or a one mL syringe, transfer 1.0 mL of extract to a diol cartridge.

11.3.4.3 Elute each cartridge into its volumetric flask with 9 mL of hexane/acetone.

11.3.4.4 Release the vacuum and remove the 10 mL volumetric flasks Quantitatively transfer each eluted extract from its 10 mL flask

into a clean centrifuge tube or sample vial. Rinse the volumetric flask with two 1-mL aliquots of hexane to ensure quantitative transfer.

11.3.4.5 Concentrate the eluted extracts to 1.0 mL using the nitrogen blow-down apparatus. If sulfur crystals are evident in the eluted extract, or if sulfur is suspected to be present, proceed to section 11.5 for sulfur removal. If sulfur is not known or expected to be present, adjust the final volume to 5 or 10 mL (per section 10.6), depending on whether or not the extract was subjected to GPC cleanup, and proceed to section 13 for GC analysis.

11.4 Florisil column

11.4.1 Place a weight of Florisil (nominally 20 g) predetermined by calibration (section 7.6) in a chromatographic column. Tap the column to settle the Florisil and add 1 - 2 cm of anhydrous sodium sulfate to the top.

11.4.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.4.3 Transfer the concentrated extract (section 10.6.2) onto the column. Complete the transfer with two 1-mL hexane rinses.

11.4.4 Place a clean 500 mL K-D flask and concentrator tube under the column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute fraction 1 with 200 mL of six per cent ethyl ether in hexane (v/v) at a rate of approx 5 mL/min Remove the K-D flask. Elute fraction 2 with 200 mL of 15 percent ethyl ether in hexane (v/v) into a second K-D flask. Elute fraction 3 with 200 mL of 50 percent ethyl ether in hexane (v/v). The elution patterns for the organo-halide pesticides and PCBs are shown in table 9.

11.4.5 Concentrate the fractions as in section 10.6, except use hexane to prewet the column. Readjust the final volume to 5 or 10 mL as in section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per the procedure in section 13.

11.5 Alumina column

11.5.1 Reduce the volume of the extract to 0.5 mL and bring to 1.0 mL with acetone.

11.5.2 Add 3 g of activity III neutral alumina to a 10 mL chromatographic column. Tap the column to settle the alumina.

11.5.3 Transfer the extract to the top of the column and collect the eluate in a clean 10 mL concentrator tube. Rinse the extract container with 1 - 2 mL portions of hexane (to a total volume of 9 mL) and add to the alumina column. Do not allow the column to go dry.

11.5.4 Concentrate the extract to 1.0 mL if sulfur is to be removed, or adjust the final volume to 5 or 10 mL as in section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per section 13.

11.6 Sulfur removal--elemental sulfur will usually elute entirely in fraction 1 of the Florisil column cleanup.

11.6.1 Transfer the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1 - 2 drops of mercury or 100 mg of activated copper powder and seal (reference 9). If TBA sulfite is used, add 1 mL of the TBA sulfite reagent and 2 mL of isopropanol.

11.6.2 Agitate the contents of the vial for 1 - 2 hours on a reciprocal shaker. If the mercury or copper appears shiny, or if precipitated sodium sulfite crystals from the TBA sulfite reagent are present, and if the color remains unchanged, all sulfur has been removed; if not, repeat the addition and shaking.

11.6.3.1 If mercury or copper is used, centrifuge and filter the extract to remove all residual mercury or copper. Dispose of the mercury waste properly. Bring the final volume to 1.0 mL and analyze by gas chromatography per the procedure in section 13.

11.6.3.2 If TBA sulfite is used, add 5 mL of reagent water and shake for 1 - 2 minutes. Centrifuge and filter the extract to remove all precipitate. Transfer the hexane (top) layer to a sample vial and adjust the final volume to 5 or 10 mL as in section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per section 13.

12 HYDROLYSIS AND ESTERIFICATION OF PHENOXY-ACID HERBICIDES - Sample extracts that have been cleaned up by GPC are diluted to 100 - 200 mL in a 500 - 1000 mL separatory funnel prior to separation of the acids from the esters.

12.1 Separation of phenoxy-acids and phenoxy-acid esters

12.1.1 Add 100 - 200 mL of 0.1 N aqueous sodium hydroxide solution to the separatory funnel containing the methylene chloride extract (section 10.3.4), the methylene chloride/acetone extract (section 10.4.7), or the GPC cleaned up sample extract (10.6.2).

12.1.2 Insert the stopper into the funnel and shake for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the aqueous layer for a minimum of ten minutes.

12.1.3 Drain the organic and aqueous layers into separate clean beakers. Return the organic phase to the extractor and repeat the extraction twice more. The aqueous layer contains the free acids; the organic layer contains the herbicide esters that must be hydrolyzed.

12.2 Ester hydrolysis

12.2.1 Transfer the organic layer to a K-D flask and concentrate to 20 - 30 mL per section 10.5.1.

12.2.2 After the flask has cooled, remove the Snyder column and add 5 mL of 37 percent aqueous KOH, 30 mL of reagent water, and 40 mL of methanol.

12.2.3 Add one or two boiling chips to the flask, install a condenser, and return the apparatus to the water bath. Reflux the mixture for 2 - 3 hours. Remove the flask from the water bath and allow to drain and cool for at least 10 minutes.

12.2.4 Transfer the hydrolysate to a 100 - 500 mL separatory funnel Add 50 mL of methylene chloride to the funnel and extract the hydrolysate by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the layers to separate for a minimum of ten minutes. Discard the organic phase. Repeat the extraction twice more. The aqueous phase contains the free acids.

12.3 Extraction/concentration of the free acids

12.3.1 Combine the aqueous phases from the separation (12.1.3) and hydrolysis (12.2.4) steps in the separatory funnel.

12.3.2 Adjust the pH of the solution to <2 with H_2SO_4 and extract three times with 100 mL portions of methylene chloride. Combine the organic extracts and pour through a prerinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect in a K-D flask fitted with a 10 mL condenser.

12.3.3 Concentrate the extract to approximately 5 mL per section 10.5 and further concentrate the extract to near dryness using the nitrogen blowdown apparatus. Bring the volume to 5 mL with isooctane. If desired, the extract may be transferred to a 10 mL sample vial and stored at -20 to -10 °C.

12.4 Esterification--observe the safety precautions regarding diazomethane in section 4.

12.4.1 Set up the diazomethane generation apparatus as given in the instructions in the Diazald kit.

12.4.2 Transfer one mL of the isooctane solution (section 12.3.3) to a clean vial and add 0.5 mL of methanol and 3 mL of ether. For extracts that have been cleaned up by GPC, use 2 mL.

12.4.2 Add two mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should persist throughout this period. If the yellow color disappears, add two mL of diazomethane solution and allow to stand, with occasional swirling, for another 10 minutes. Colored or complex samples will require at least 4 mL of diazomethane to ensure complete reaction of the herbicides. Continue adding diazomethane in 2 mL increments until the yellow color persists for the entire 10 minute period or until 10 mL of diazomethane solution has been added.

12.4.3 Rinse the inside wall of the container with 0.2 - 0.5 mL of diethyl ether and add 10 - 20 mg of silicic acid to react excess diazomethane. Filter through Whatman #41 paper into a clean sample vial. If the solution is colored or cloudy, evaporate to near dryness using the nitrogen blowdown apparatus, bring to 10 mL with hexane, and proceed to section 11.1 for diol cleanup. If the solution is clear and colorless, evaporate to near dryness, bring to 1.0 mL with hexane and proceed to section 13 for GC analysis.

13 GAS CHROMATOGRAPHY - tables 4 - 5 summarize the recommended operating conditions for the gas chromatographs. Included in these tables are the retention times and estimated detection limits that can be achieved under these conditions. Examples of the separations achieved by the primary and secondary columns are shown in figures 1 through 10.

13.1 Calibrate the system as described in section 7.

13.2 Combination of pesticide and herbicide extracts

13.2.1 Pesticide extracts cleaned up by diol cartridge--combine the 1.0 mL final pesticide extract (section 11.3.4.5 or 11.5.3) with the 1.0 mL final herbicide extract (section 11.3.4.5 or 11.5.3 if the herbicide extract required cleanup; section 12.4.3 if it did not).

13.2.1 Pesticide extracts cleaned up by Florisil--combine 1.0 mL of the 5.0 mL or 10.0 mL pesticide extract (section 11.4.5) with the 1.0 mL final herbicide extract (section 11.3.4.5 or 11.5.3 if the herbicide extract required cleanup; section 12.4.3 if it did not).

13.3 Addition of internal standard--if the internal standard calibration procedure is being used, add the internal standard solution to the extract immediately prior to loading the extract into the auto sampler to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

13.4 Set the injection volume on the autosampler to inject 1.0 uL of all standards and extracts of blanks and samples.

13.5 Set the data system or GC control to start the temperature program upon sample injection, and begin data collection after the solvent peak elutes. Set the data system to stop data collection at the end of the temperature program and to return the column to the initial temperature.

14 SYSTEM AND LABORATORY PERFORMANCE

14.1 At the beginning of each eight hour shift during which analyses are performed, GC system performance and calibration are

verified for all pollutants and surrogates on all column/detector systems For these tests, analysis of the combined QC standard (tables 4 and 5) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and precision and recovery standards be analyzed.

14.2 Retention times

14.2.1 External standard--the absolute retention times of the peak maxima shall be within +/- 10 seconds of the retention times in the initial calibration (section 7.3.1 and 7.5.5).

14.2.1 Internal standard--the absolute retention times of the peak maxima shall be within +/- 30 seconds of the retention times in the initial calibration (section 7.4.2) and the retention time difference between a compound of interest and its internal standard shall be within +/- 5 seconds of this retention time in the initial calibration (section 7.4.2 and 7.5.5).

14.3 GC resolution--resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 50 percent of the taller of the two peaks.

14.3.1 Organo-halide compounds

14.3.1.1 Primary column (DB-5)--TBD and TBD.

14.3.1.2 Confirmatory column (SPB-608)--TBD and TBD.

14.3.2 Thiophosphorus compounds

14.3.2.1 Primary column (DB-5)--TBD and TBD.

14.3.2.2 Confirmatory column (SPB-608)--TBD and TBD.

14.4 Decomposition of DDT and endrin--TBD

14.5 Calibration verification--calibration is verified for the combined QC standard only. If verification requirements are met, the calibration is assumed to be valid for the multicomponent analytes (PCBs, chlordane, toxaphene).

14.5.1 External standard--compute the area of each peak in the combined calibration standard. This area shall be within +/- 50 percent of the area in the initial analysis of this standard (section 7.5.5).

14.5.1 Internal standard--compute the response factor of each peak in the combined QC standard. The response factor shall be within +/- 25 percent of the response factor in the initial analysis of this standard (section 7.5.5).

14.6 On-going precision and accuracy

14.6.1 Analyze the extract of the precision and recovery standard extracted with each sample lot.

14.6.2 Compute the concentration of each analyte by the internal or external standard method.

14.6.3 For each analyte, compare the concentration with the initial recovery determined in the initial test (section 8.2). The concentration of each analyte shall be within +/- two standard deviations of the average concentration determined in the initial test of the method (section 8.2). If all analytes pass, the extraction, concentration, and cleanup processes are in control and analysis of blanks and samples may proceed. If, however, any of the analytes fail, these processes are not in control. In this event, correct the problem, re-extract the sample lot, and repeat the on-going precision and recovery test.

14.6.4 Add results which pass the specifications in 12.6.3 to initial and previous on-going data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of

laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery sr. Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85 - 105%.

15 QUALITATIVE DETERMINATION

15.1 Qualitative determination is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (section 13.1), and with data stored in the retention time and calibration libraries (section 7.2.3 and 7.4.3) Identification is confirmed when retention time and amounts agree per the criteria below.

15.2 External standard--for each compound on each column/detector system, establish a retention time window +/- 20 seconds on either side of the retention time in the calibration data (section 7.3) For compounds that have a retention time curve (section 7.3.2.2), establish this window as the minimum -20 seconds and maximum +20 seconds. For the multi-component analytes, use the retention times of the five largest peaks in the chromatogram from the calibration data (section 7.3.1).

15.2.1 Compounds not requiring a retention time calibration curve--if a peak from the analysis of a sample or blank is within a window (as defined in section 15.2) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is confirmed when (1) the retention time for the compound on the confirmatory column/detector system is within the retention time window on that system, and (2) the computed amounts (section 16) on each system (primary and confirmatory) agree within a factor of three.

15.2.2 Compounds requiring a retention time calibration curve--if a peak from the analysis of a sample or blank is within a window (as defined in section 15.2) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is confirmed when (1) the retention times on both systems (primary and confirmatory) are within +/- 30 seconds of the retention times for the computed amounts (section 16), as determined by the retention time calibration curve (section 7.3.2.2), and (2) the computed amounts (section 16) on each system (primary and confirmatory) agree within a factor of three.

15.3 Internal standard--for each compound on each column/detector system, establish a relative retention time window equivalent to +/- 10 seconds on either side of the relative retention time in the calibration data (section 7.4). For compounds that have a retention time curve (section 7.4.3.2), establish this window as the minimum -20 seconds and the maximum +20 seconds. For the multi-component analytes, use the relative retention times of the five largest peaks in the chromatogram from the calibration data (section 7.4.3).

15.3.1 Compounds not requiring a relative retention time calibration curve--if a peak from the analysis of a sample or blank is within a window (as defined in section 15.3) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is confirmed when (1) the relative retention time for the compound on the confirmatory column/detector system is within the relative retention time window on that system, and (2) the computed amounts (section 16) on each system (primary and confirmatory) agree within a factor of three.

15.3.2 Compounds requiring a relative retention time calibration curve--if a peak from the analysis of a sample or blank is within a window (as defined in section 15.3) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is

confirmed when (1) the relative retention times on both systems (primary and confirmatory) are within the relative retention time equivalent of +/-20 seconds of the relative retention times for the computed amounts (section 16), as determined by the relative retention time calibration curve (section 7.4.3.2), and (2) the computed amounts (section 16) on each system (primary and confirmatory) agree within a factor of three.

16 QUANTITATIVE DETERMINATION

16.1 External standard

16.1.1 Using the GC data system, compute the concentration of the analyte detected in the extract (in ug/mL) using the calibration factor or calibration curve (section 7.3.3.2).

16.1.2 Liquid samples--compute the concentration in the sample using the following equation:

$$C_s = 10 \frac{(C_{ex})}{(V_s)}$$

where; C_s is the concentration in the sample in ug/L, 10 is the extract total volume in mL, C_{ex} is the concentration in the extract in ug/mL, V_s is the volume of sample extracted in liters

16.1.3 Solid samples--compute the concentration in the solid phase of the sample using the following equation:

$$C_s = 10 \frac{(C_{ex})}{1000\ (W_s)\ (\%\ \text{solids})}$$

where; C_s is the concentration in the sample in ug/kg, 10 is the extract total volume in mL, C_{ex} is the concentration in the extract in ug/mL, 1000 converts grams to kilograms, W_s is the sample weight in grams, % solids in the percent solids determined in section 10.1.3

16.2 Internal standard

16.2.1 Using the GC data system, compute the concentration of the analyte detected in the extract (in ug/mL) using the response fac tor or calibration curve (section 7.4.4.2) using the following equation:

$$C_{ex} = \frac{(A_s \times C_{is})}{(A_{is} \times RF)}$$

where C_{ex} is the concentration of the analyte in the extract, and the other terms are as defined in section 7.4.4

16.2.2 Liquid samples--compute the concentration in the sample using the following equation:

$$C_s = 10 \frac{(C_{ex})}{(V_s)}$$

where the terms are as defined in section 16.1.1.

16.2.3 Solid samples--compute the concentration in the solid phase of the sample using the following equation:

$$C_s = 10 \frac{(C_{ex})}{1000\ (W_s)\ (\%\ \text{solids})}$$

where the terms are as defined in 16.1.2.

16.3 If the concentration of any analyte exceeds the calibration range of the system, the extract is diluted by a factor of 10, and a one mL aliquot of the extract is analyzed. If the internal standard method was used, more internal standard is added to bring the concentration to the same level as in the original extract.

16.4 Two or more PCBs in a given sample are quantitated and reported as total PCB.

16.5 Report results for all pollutants found in all standards, blanks, and samples to three significant figures. Results for samples that have been diluted are reported at the least dilute level at

which the concentration is in the calibration range.

17 ANALYSIS OF COMPLEX SAMPLES

17.1 Some samples may contain high levels (>1000 ug/L) of the com pounds of interest, interfering compounds, and/or polymeric materials. Some samples may not concentrate to 10 mL (section 10.6); others may overload the GC column and/or detector.

17.2 The analyst shall attempt to clean up all samples using GPC (section 10.2), Florisil (section 10.4), diol cartridge (section 10.3), and sulfur removal (section 10.5). If these techniques do not remove the interfering compounds, the extract is diluted by a fac tor of 10 and reanalyzed (section 16.2).

17.3 Recovery of surrogates--in most samples, surrogate recoveries will be similar to those from reagent water or from the high solids reference matrix. If the surrogate recovery is outside the range of 20 - 200 percent, the sample shall be reextracted and reanalyzed. If the surrogate recovery is still outside this range, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

18 METHOD PERFORMANCE

18.1 Development of this method is detailed in reference 10.

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9. Goerlitz, D.F., and Law, L.M. "Bulletin for Environmental Contamination and Toxicology," 6, 9 (1971).

10. "Consolidated GC Method for the Determination of ITD/RCRA Pesticides using Selective GC Detectors," Report Reference 32145-01, Document R70, S-CUBED, A Division of Maxwell Laboratories, Inc, PO Box 1620, La Jolla, CA, 92038-1620 (September 1986)

EPA METHOD 8290
ANALYSIS OF PCDD/PCDF'S

DRAFT

24 May 1987

METHOD 8290

ANALYTICAL PROCEDURES AND QUALITY ASSURANCE

FOR MULTIMEDIA ANALYSIS

OF

POLYCHLORINATED DIBENZO-p-DIOXINS

AND

POLYCHLORINATED DIBENZOFURANS

BY

HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY

(Exhibits D and E)

by

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June 1987

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NOTICE

This document is a preliminary draft. It has not been formally released by the University of Nevada Environmental Research Center or the U.S. Environmental Protection Agency, and it should not at this stage be construed to represent University or Agency policy. It is circulated for comments on its technical merit and policy implications.

FOREWORD

In January 1986, the Environmental Protection Agency published an analytical protocol, Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) (EPA 600/4-86-004), aimed at the determination of part-per-trillion and sub-part-per-trillion levels of 2,3,7,8-TCDD and of total TCDD in soil, sediment and aqueous samples. The January 1986 document was intended to be a stepping stone for the realization of a more comprehensive method that would include all the polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congeners present in a broader spectrum of environmentally significant matrices.

The present report constitutes a draft addressing the analytical procedures (Exhibit D) and quality assurance (Exhibit E, quality assessment and control) requirements sections of the future analytical protocol for the analysis of PCDDs and PCDFs by HRGC/HRMS; i.e., Method 8290. At times, reference to other exhibits (e.g., Exhibit C) are made, even though these sections have not been prepared. The format used for this report is similar to the format used for other EPA TCDD protocols. Figures and tables are, however, grouped at the end of Exhibit D. A final version of Method 8290 is expected following peer review of this draft report and the completion of the single-laboratory evaluation. Elements included in this Method 8290 have been taken from a variety of sources, such as the EPA Region VII low-resolution mass spectrometry (LRMS) TCDD protocol, the aforementioned high-resolution mass

spectrometry TCDD protocol, the RCRA Method 8280 (LRMS) protocol, the method evaluation study final report by the Midwest Research Institute on "Analysis for Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Human Adipose Tissue" (EPA-560/5-86-020), the National Dioxin Study Analytical Procedures and Quality Assurance Plan for the Analysis of 2,3,7,8-TCDD in Tier 3-7 Samples (EPA/600/3-85/019), and the analytical protocol for the analysis for PCDDs and PCDFs by HRGC/HRMS submitted recently for review by Region VII. Also, we wish to acknowledge the contributions from experts in the analysis of PCDDs and PCDFs in environmental samples. The cooperation of P. W. Albro (National Institute of Environmental Health Sciences, Research Triangle Park, NC), L. Alexander (Center for Disease Control, Atlanta, GA), J. R. Hass and D. J. Harvan (Triangle Laboratories, Inc., Research Triangle Park, NC), R. Harless (US EPA, Research Triangle Park, NC), R. D. Kleopfer (US EPA, Region VII, Kansas City, MO), D. W. Kuehl (US EPA, Duluth, MN), M. J. Miille (California Analytical Laboratories, Sacramento, CA), R. W. Noble (Monsanto Company, Dayton, OH), T. M. Sack and J. S. Stanley (Midwest Research Institute, Kansas City, MO), and T. S. Viswanathan (Ecology and Environment, Inc., Kansas City, MO) is particularly appreciated.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS AND SYMBOLS

A	--	Integrated ion abundance
ADC	--	Analogue-to-digital conversion
AX-21	--	Type of carbon adsorbent
C	--	Concentration
CDC	--	Center for Disease Control
CDWG	--	Chlorinated Dioxins Workgroup
° C	--	Degree centigrade
^{13}C	--	Carbon-13 labeled
cm	--	Centimeter
DB-5	--	Type of fused-silica capillary column
DS	--	Data system
EDL	--	Estimated detection limit
EMPC	--	Estimated maximum possible concentration
EMSL-LV	--	Environmental Monitoring System Laboratory, Las Vegas
EPA	--	Environmental Protection Agency
g	--	Gram
GC	--	Gas chromatography or gas chromatograph
GC/MS	--	Gas chromatography/mass spectrometry
HEPA	--	High-efficiency particulate absorbant
HpCDD	--	Heptachlorodibenzodioxin
HpCDF	--	Heptachlorodibenzofuran
HRGC/HRMS	--	High-resolution gas chromatography/high-resolution mass spectrometry
HxCDD	--	Hexachlorodibenzodioxin
HxCDF	--	Hexachlorodibenzofuran
IFB	--	Invitation for Bid
IS	--	Internal Standard
KD	--	Kuderna-Danish
L	--	Liter
MB	--	Method blank
MCL	--	Method calibration limit
mL	--	Milliliter
mm	--	Millimeter
M/ΔM	--	Mass spectrometer resolving power
MS	--	Matrix spike
MSD	--	matrix spike duplicate
OCDD	--	Octachlorodibenzodioxin
OCDF	--	Octachlorodibenzofuran
OSHA	--	Occupational Safety and Health Administration
PCB	--	Polychlorinated biphenyl
PCDD	--	Polychlorinated dibenzodioxin
PCDPE	--	Polychlorinated diphenyl ether
PCDF	--	Polychlorinated dibenzofuran
PE	--	Performance evaluation

PEM	--	Performance evaluation material
PeCDD	--	Pentachlorodibenzodioxin
PeCDF	--	Pentachlorodibenzofuran
PFK	--	Perfluorokerosene
pg	--	Picogram
ppm	--	Part per million
ppt	--	Part per trillion
Q	--	Amount of substance
QA	--	Quality Assurance or Quality Assessment
QA/QC	--	Quality Assessment/Quality Control
rpm	--	Revolutions per minute
RPD	--	Relative percent difference
RRF	--	Relative response factor
$\overline{\text{RRF}}$	--	Mean relative response factor
RRT	--	Relative retention time
RS	--	Recovery standard
S	--	EPA reference standard solution
SAS	--	Special Analytical Service
SES	--	Site evaluation sheet
SICP	--	Selected ion current profile
SIM	--	Selected ion monitoring
SMO	--	Sample Management Office
S/N	--	Signal-to-noise ratio
SOP	--	Standard Operating Procedure
SP-2330	--	Type of fused-silica capillary column
Still-bottom	--	Name of a matrix that is used as a noun
TCDD	--	Tetrachlorodibenzodioxin
TEF	--	Toxicity Equivalency Factor
V	--	Volume
v/v	--	Volume/volume
W	--	Weight or laboratory working standard
WTE	--	Wipe test experiment
uL	--	Microliter

ANALYTICAL METHODS

(EXHIBIT D)

EXHIBIT D

1. Scope and Application

1.1 This method provides procedures for the detection and quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) concentrations. The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based method calibration limits (MCLs) and other germane information. Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL (Table 1). Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than the upper MCL must be analyzed by a protocol designed for such concentration levels. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.

1.2 The sensitivity of this method is dependent upon the level of interferences within a given matrix. Actual limits of detection and quantification will be provided based on the single- or multi-laboratory evaluation of this protocol, and on examining the data gathered by the Sample Management Office (SMO) from Special Analytical Services (SAS) performed over the past few years.

1.3 This method is designed for use by analysts who are experienced with residue analysis and skilled in high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

1.4 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

2. Summary of the Method

2.1 This procedure uses matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. A simplified analysis flow chart is shown in Figure 1.

2.3 A specified amount (see Table 1) of soil, sediment, fly ash, water, sludge (including paper pulp), still-bottom, fuel oil, chemical reactor residue, fish tissue, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs listed in Column 1 of Table 2. The sample is then extracted according to a matrix-specific extraction procedure. The extraction procedures are: a) toluene (or benzene) Soxhlet extraction for soil, sediment and fly ash samples; b) methylene chloride liquid-liquid extraction for water samples; c) toluene (or benzene) Dean-Stark extraction for fuel oils and aqueous sludges; d) toluene (or benzene) extraction for still-bottoms; e) hexane/methylene chloride Soxhlet extraction for fish tissue and paper pulp; and f) methylene chloride extraction for human adipose tissue. The decision for the selection of an extraction procedure for chemical reactor residue samples is based on the appearance (consistency, viscosity) of the samples. Generally, they can be handled according to the procedure used for still-bottom (or chemical sludge) samples.

2.4 The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the residue is cleaned up by column chromatography on neutral alumina and carbon on Celite 545®. The extract from adipose tissue is treated with silica gel impregnated with sulfuric acid before chromatography on acidic silica gel, neutral alumina, and carbon on Celite 545®. Fish tissue and paper pulp are subjected to an acid wash treatment only prior to chromatography or neutral alumina and carbon/Celite. The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding, to the concentrated carbon column

eluate, 10 to 50 uL uL (depending on the matrix type) of a tridecane solution containing 50 pg/uL of each of the two recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners while the latter is used for the determination of hexa-, hepta- and octa-chlorinated PCDD/PCDF congeners percent recoveries.

2.5 One to two uL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.6 The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners (Table 3), for which a ^{13}C-labeled standard is available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (-1 to +3 seconds from the respective internal or recovery standard signal) and the simultaneous detection of the two most abundant ions in the molecular ion region. The remaining six 2,3,7,8-substituted congeners (i.e., 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other identified PCDD/PCDF congeners are identified by their relative retention times falling within their respective PCDD/PCDF retention time windows, as established by using a GC column performance evaluation solution, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time

relative to $^{13}C_{12}$-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation is based on a comparison of the ratio of the integrated ion abundance of the molecular ion species to their theoretical abundance ratio.

2.7 Quantification of the individual congeners, total PCDDs and total PCDFs is achieved in conjunction with the establishment of a multipoint (seven points) calibration curve for each homologue, during which each calibration solution is analyzed once.

3. Definitions

3.1 Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs): Compounds (Figure 2) that contain from one to eight chlorine atoms. The fifteen 2,3,7,8-substituted PCDDs (totaling 75) and PCDFs (totaling 135) are shown in Table 3. The number of isomers at different chlorination levels is shown in Table 4.

3.2 Homologous series: Defined as a group of chlorinated dibenzodioxins or dibenzofurans having a specific number of chlorine atoms.

3.3 Isomer: Defined by the arrangement of chlorine atoms within an homologous series. For example, 2,3,7,8-TCDD is a TCDD isomer.

3.4 Congener: Any isomer of any homologous series.

3.5 Internal Standard: An internal standard is a $^{13}C_{12}$-labeled analogue of a congener chosen from the compounds listed in Table 3 and of OCDD. Internal standards are added to all samples including method blanks and quality control samples before extraction, and they are used to measure the concentration of the analytes. Nine internal standards are used in this method. There is one for each of the dioxin and furan homologues (except for OCDF) with the degree of chlorination ranging from four to eight.

3.6 Recovery Standard: Recovery standards (two) are used to determine the percent recoveries for PCDDs and PCDFs. The $^{13}C_{12}$-1,2,3,4-TCDD is used to measure the percent recoveries of the tetra- and pentachlorinated dioxins and furans while $^{13}C_{12}$-1,2,3,7,8,9-HxCDD permits the recovery determination of the hexa-, hepta- and octachlorinated homologues. They are added to the final sample extract before HRGC/HRMS analysis. Furthermore, $^{13}C_{12}$-1,2,3,7,8,9-HxCDD is used for the identification of the unlabeled analogue present in sample extracts (this exhibit, Section 2.6).

3.7 High-Resolution Concentration Calibration Solutions (Table 5): Solutions (tridecane) containing known amounts of 17 selected PCDDs and PCDFs, nine internal standards ($^{13}C_{12}$-labeled PCDDs/PCDFs), and two carbon-labeled recovery standards (this exhibit, Section 3.6); the set of seven solutions is used to determine the instrument response of the unlabeled analytes relative to the internal standards and of the internal standards relative to the recovery standards.

3.8 Sample Fortification Solution (Table 2): A solution (isooctane) containing the nine internal standards, which is used to spike all samples before extraction and cleanup.

3.9 Recovery Standard Solution (Table 2): A tridecane solution containing the two recovery standards, which is added to the final sample extract before HRGC/HRMS analysis.

3.10 Field Blank: A portion of a sample representative of the matrix under consideration, which is free of any PCDDs/PCDFs.

3.11 Laboratory Method Blank: A blank prepared in the laboratory and carried through all analytical procedure steps except the addition of a sample aliquot to the extraction vessel.

3.12 Rinsate: A portion of solvent used to rinse sampling equipment. The rinsate is analyzed to demonstrate that samples were not contaminated during sampling.

3.13 GC Column Performance Check Mixture: A tridecane solution containing a mixture of selected PCDD/PCDF standards including the first and last eluters for each homologous series, which is used to demonstrate continued acceptable performance of the capillary column (i.e., $\leq$ 25 percent valley separation of 2,3,7,8-TCDD from all the other 21 TCDD isomers) and to define the homologous PCDD/PCDF retention time windows.

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3.14 Performance Evaluation Materials: Representative sample portions containing known amounts of certain unlabeled PCDD/PCDF congeners (in particular the ones having a 2,3,7,8-substitution pattern). Representative interferences may be present. PEMs are obtained from the EPA EMSL-LV and submitted to potential contract laboratories, who must analyze these and obtain acceptable results before being awarded a contract for sample analyses (see IFB Pre-Award Bid Confirmations). PEMSs are also included as unspecified ("blind") quality control (QC) samples in any sample batch submitted to a laboratory for analysis.

3.15 Relative Response Factor: Response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.16 Estimated Level of Method Blank Contamination: The response from a signal occurring in the homologous PCDD/PCDF retention time windows, at any of the masses monitored, is used to calculate the level of contamination in the method blank, as described in Section 14 (this exhibit). The results from such calculations must be reported along with the data obtained on the samples belonging to the batch associated with the method blank.

Reporting a method blank contamination level for any of the 2,3,7,8-substituted congeners except OCDD and OCDF that exceeds 10 percent of the desired detection limit would invalidate the results and require automatic sample reruns (Exhibit C) for all positive samples found in that batch of samples. A positive sample is defined as a sample found to

contain at least one 2,3,7,8-substituted PCDD/PCDF congener (except OCDD and OCDF). A valid method blank run is an analysis during which all internal standard signals are characterized by S/N of at least 10:1.

3.17 Sample Rerun: Extraction of another portion of the sample followed by extract cleanup and extract analysis.

3.18 Extract Reanalysis: Analysis by HRGC/HRMS of another aliquot of the final extract.

3.19 Mass Resolution Check: Standard method used to demonstrate a static resolving power of 10,000 minimum (10 percent valley definition).

3.20 Method Calibration Limits (MCLs): For a given sample size, a final extract volume, and the lowest and highest concentration calibration solutions, the lower and upper MCLs delineate the region of quantification for which the HRGC/HRMS system was calibrated with standard solutions.

3.21 HRGC/HRMS Method Blank (MB): This additional QC check analysis corresponds to a 2-uL injection of the method blank extract into the GC column and a complete (tetra- through octachlorinated congeners) HRGC/HRMS analysis. Such a QC check is required following a calibration run and before the daily analysis of the first sample extract. Acceptable HRGC/HRMS method blanks (see this exhibit, Section 3.16, for guidelines) must be obtained before sample extracts can be analyzed.

3.22 Matrix Spike (MS): A sample which is spiked with a known amount of the matrix spike fortification solution (this exhibit, Section 3.24) prior to the extraction step. The recoveries of the matrix spike compounds are determined; they are used to estimate the effect of the sample matrix upon the analytical methodology.

3.23 Matrix Spike Duplicate (MSD): A second portion of the same sample as used in the matrix spike analysis and which is treated like the matrix spike sample.

3.24 Matrix Spike Fortification Solution: Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes listed in Table 5 at concentrations corresponding to the HRCC 3. The solution also contains all internal standards used in the sample fortification solution at concentrations as shown in Table 2.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data (see references 1 and 2 at the end of this Section). All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks. Analysts should avoid using PVC gloves.

4.2 The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

4.3 Interferents co-extracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated xanthenes that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 8.1.3 (this exhibit). While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

4.4 A high-resolution capillary column (60 m DB-5) is used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all isomers. The use of several capillary columns will, in fact, be necessary during the determination of the toxicity equivalency factors (TEFs) (this exhibit, Section 14.7).

References:

1. "Control of Interferences in the Analysis of Human Adipose Tissue for 2,3,7,8-Tetrachlorodibenzo-p-dioxin". D. G. Patterson et al., Environ. Toxicol. Chem. 5, 355-360 (1986).

2. "Protocol for the Analysis of 2,3,7,8-TCDD by HRGC/HRMS". J. S. Stanley and T. M. Sack, EPA 600/4-86-004.

5. Safety

5.1 The following safety practices are exerpted directly from EPA Method 613, Section 4 (July 1982 version) and amended for use in conjunction with this method.

Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should also wear masks fitted with charcoal filter absorbent media to prevent inhalation of dust.

5.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum by whatever means available. The laboratory is responsible for maintaining 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 should also be made available to all personnel involved in the chemical analysis.

Additional references to laboratory safety are given in references 1-3 (see end of Section 5, this exhibit). Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

5.3 Each laboratory must develop a strict safety program for the handling of 2,3,7,8-TCDD. The laboratory practices listed below are recommended.

5.3.1 Contamination of the laboratory will be minimized by conducting most of the manipulations in a hood.

5.3.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

5.3.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength less than 290 nm for several days (use F 40 BL lamps or equivalent). Using this analytical method, analyze the liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

5.4 Some of the following precautions were issued by Dow Chemical U.S.A. (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory and amended for use in conjunction with this method.

5.4.1 The following statements on safe handling are as complete as possible on

the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to certain kinds of laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

5.4.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and laboratory hood adequate for radioactive work.

5.4.1.2 Training: Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.4.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

5.4.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

5.4.1.5 Waste: Good technique includes minimizing contaminated waste.

Plastic bag liners should be used in waste cans.

5.4.1.6 Disposal of Hazardous Wastes: Refer to the November 7, 1986 issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin-containing wastes.

5.4.1.7 Decontamination: Personnel - any mild soap with plenty of scrubbing action. Glassware, tools and surfaces - Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial sources that are expensive.

5.4.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Laboratory coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

5.4.1.9 Wipe Tests: A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, extract the filter paper and analyze the extract.

NOTE: Appendix A describes a procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory. The results and decision making processes are based on the presence of 2,3,7,8-substituted PCDD/PCDFs.

5.4.1.10 Inhalation: Any procedure that may produce airborne contamination must be carried out with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no significant inhalation hazards except in case of an accident.

5.4.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

References:

1. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910),

Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

3. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety (3rd Edition, 1979.)

6. Apparatus and Equipment

6.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).

6.1.1 The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column 1-ul injections can be used on the 60-m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2-uL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 uL). One-uL injections are allowed; however, laboratories are encouraged to remain consistent throughout the analyses by using the same injection volume at all times.

6.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface--The GC/MS interface components should withstand 350° C. The interface must be designed so

that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. Vespel™ or equivalent ferrules are recommended.

6.1.3 Mass Spectrometer--The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less (this exhibit, Section 9.1.4.1). At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all the descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) is to eliminate, even under high-resolution mass spectrometric conditions, interferences occuring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory. The recommended mass spectrometer tuning conditions (this exhibit, Section 8.2.3) are based on the groups of monitored ions shown in Table 6.

6.1.4 Data System--A dedicated data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass-spectral peak profiles (this exhibit, Section 8.2.4) and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should also permit the measurement of noise on the base line.

NOTE: The detector ADC zero setting must allow peak-to-peak measurement of the noise on the base line of every monitored channel and allow for good estimation of the instrument resolving power. In Figure 3, the effect of different zero settings on the measured resolving power is shown.

6.2 GC Column

In order to have an isomer-specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one

HRGC/HRMS analysis, the 60-m DB-5 fused-silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented (this exhibit, Section 8.1). At the beginning of each 12-hour period (after mass resolution is demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended column are shown in Table 7.

6.3 Miscellaneous Equipment and Materials

The following list of items does not necessarily constitute an exhaustive compendium of the equipment needed for this analytical method.

6.3.1 Nitrogen evaporation apparatus with variable flow rate.

6.3.2 Balances capable of accurately weighing to 0.01 g and 0.0001 g.

6.3.3 Centrifuge.

6.3.4 Water bath, equipped with concentric ring covers and capable of being temperature-controlled within $\pm$ 2° C.

6.3.5 Stainless steel or glass container large enough to hold contents of one-pint sample containers.

6.3.6 Glove box.

6.3.7 Drying oven.

6.3.8 Stainless steel spoons and spatulas.

6.3.9 Laboratory hoods.

6.3.10 Pipets, disposable, Pasteur, 150 mm long x 5 mm ID.

6.3.11 Pipets, disposable, serological, 10 mL, for the preparation of the carbon column specified in Section 7.1.2.

6.3.12 Reacti-vial, 2 mL, silanized amber glass.

6.3.13 Stainless steel meatgrinder with a 3- to 5-mm hole size inner plate.

6.3.14 Separatory funnels, 125 mL.

6.3.15 Kuderna-Danish concentrator, 500 mL, fitted with 10-mL concentrator tube and three-ball Snyder column.

6.3.16 Teflon™ boiling chips (or equivalent), washed with hexane before use.

6.3.17 Chromatographic column, glass, 300 mm x 10.5 mm, fitted with Teflon stopcock.

6.3.18 Adaptors for concentrator tubes.

6.3.19 Glass fiber filters.

6.3.20 Dean-Stark trap, 5 or 10 mL, with T-joints, condenser and 125-mL flask.

6.3.21 Continuous liquid-liquid extractor.

6.3.22 All-glass Soxhlet apparatus, 500-mL flask.

6.3.23 Glass funnels, sized to hold 170 mL of liquid.

6.3.24 Desiccator.

6.3.25 Solvent reservoir (125 mL), Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.

6.3.26 Rotary evaporator with a temperature-controlled water bath.

6.3.27 High-speed tissue homogenizer, equipped with an EN-8 probe or equivalent.

6.3.28 Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.

NOTE: Reuse of glassware should be minimized to avoid the risk of

contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, applying the following procedure: Rinse glassware with the last solvent used in it, then with high-purity acetone and hexane. Wash with hot detergent water. Rinse with copious amounts of tap water and several portions of distilled water. Drain, dry and heat in a muffle furnace at 400° C for 15 to 30 minutes. Volumetric glassware must not be heated in a muffle furnace. Some thermally stable materials (such as PCBs) may not be removed by heating in a muffle furnace. In these cases, rinsing with high-purity acetone and hexane may be substituted for muffle-furnace heating. After the glassware is dry and cool, rinse it with hexane and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.

7. Reagents and Standard Solutions

7.1 Column Chromatography Reagents

7.1.1 Alumina, neutral, Super 1, Woelm®, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

7.1.2 Carbopak C (80 to 100 mesh, Supelco 1-1025) and Celite 545® (Supelco). Preparation of the Carbopak C/Celite 545® column: Thoroughly mix 3.6 g Carbopak C (80 to 100 mesh) and 16.4 g Celite 545® in a 40-mL vial. Activate the mixture at 130° C for 6 hours, then store it in a desiccator. Cut off both ends of a 10-mL disposable serological pipet

to give a 4-inch long column. Fine-polish both ends and flare, if desired. Insert a glass-wool plug at one end, then pack the column with 0.64 g of the activated Carbopak C/Celite 545® mixture to form a 2-cm long absorbant bed. Cap the packing with another glass-wool plug.

7.2 Reagents

7.2.1 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.2.2 Potassium hydroxide, ACS grade, 20 percent (w/v) in distilled water.

7.2.3 Sodium chloride, analytical reagent, 5 percent (w/v) in distilled water.

7.2.4 Potassium carbonate, anyhdrous, analytical reagent.

7.3 Desiccating Agent

7.3.1 Sodium sulfate, granular, anhydrous; use as such.

7.4 Solvents

7.4.1 High-purity, distilled-in-glass or highest available purity: methylene chloride, hexane, benzene, methanol, tridecane, isooctane, toluene, cyclohexane, and acetone.

7.5 Calibration Solutions

7.5.1 High-Resolution Concentration Calibration Solutions (Table 5) -- Seven tridecane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values associated with the tetra- and pentachlorinated dioxins and furans (2.5 pg/uL) and the highest for the octachlorinated congeners (1000 pg/uL).

7.5.2 These high-resolution concentration calibration solutions may be obtained from the Quality Assurance Division, US EPA, Las Vegas, Nevada. However, additional secondary standards must be obtained from commercial sources, and solutions must be prepared in the contractor laboratory. Traceability (Appendix B) of standards must be verified against EPA-supplied standard solutions. Such procedures will be documented by laboratory standard operating procedures (SOP) as required in IFB Preaward Bid Confirmations, part 2.f.(4). It is the responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples. A recommended traceability procedure for PCDD/PCDF standards is described in Appendix B.

7.5.3 Store the concentration calibration solutions in 1-mL minivials at room temperature in the dark.

7.6 GC Column Performance Check Solution

This solution contains the firstand last-eluting isomers for each homologous series from tetra- through hepta-chlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$-2,3,7,8-TCDD is also present. The laboratory is required to use tridecane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/uL per congener. Table 8 summarized the qualitative composition (minimum requirement) of this performance evaluation solution.

NOTE: The use of a PCDD/PCDF-containing fly-ash extract is allowed but the qualitative equivalency of the fly-ash extract to the EPA solution should be demonstrated for each fly-ash extract.

7.7 Sample Fortification Solution

This isooctane solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note that $^{13}C-_{12}$-OCDF is not present in the solution.)

7.8 Recovery Standard Solution

This tridecane solution contains two recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) at a nominal concentration of 50 pg/uL

per compound. Ten to fifty uL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

8. System Performance Criteria

System performance criteria are presented below. The laboratory may use the recommended GC column described in Section 6.2 (this exhibit). It must be documented that all applicable system performance criteria specified in Section 8.1 (this exhibit) were met before analysis of any sample is performed. Table 7 provides recommended GC conditions that can be used to satisfy the required criteria. Figure 4 provides a typical 12-hour analysis sequence whereby the response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period of operation. A GC column performance check is only required at the beginning of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run (this exhibit, Section 3.21) is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

8.1 GC Column Performance

8.1.1 Inject 2 uL (this exhibit, Section 6.1.1) of the column performance check solution (this exhibit, Section 7.6) and acquire selected ion monitoring (SIM) data as described in Section 6.1.3 (this exhibit) within a total cycle time of $\leq$ 1 second (this exhibit, Section 9.1.4.1).

8.1.2 The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of $\leq$ 25 percent (Figure 5), where

$$\text{Valley Percent} = (x/y)\ (100)$$

x = measured as in Figure 5 from the 2,3,7,8-closest TCDD eluting isomer, and

y = the peak height of 2,3,7,8-TCDD.

It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. Their retention times are used to determine the eight homologue retention time windows that are used for qualitative (this exhibit, Section 13.4.1) and quantitative purposes. All peaks (that includes $^{13}C_{12}$-2,3,7,8-TCDD) must be labeled and identified on the chromatograms. Furthermore, all first eluters of a homologous series must be labeled with the letter F, and all last eluters of a homologous series must be labeled with the letter L (Figure 5 shows an example of peak labeling for TCDD isomers). Any individual selected ion current profile (SICP) (for the tetras, this would be the SICP for m/z 322 and m/z 304) or the reconstructed homologue ion current (for the tetras, this would correspond to m/z 320 + m/z 322 + m/z 304 + m/z 306)

constitutes an acceptable form of data presentation. An SICP for the labeled compounds (e.g., m/z 334 for labeled TCDD) is also required.

8.1.3 The retention times for the switching of SIM ions characteristic of one homologous series to the next higher homologous series must be indicated in the SICP. Accurate switching at the appropriate times is absolutely necessary for accurate monitoring of these compounds. Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be excercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60-m DB-5 column. A laboratory with a GC/MS system that is not capable of detecting both congeners (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) within one analysis must indicate in the case narrative of its report which congener (only one is permitted) was missed.

8.2 Mass Spectrometer Performance

8.2.1 The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed (this exhibit, Section 13). Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that a visual check (i.e.,

documentation is not required) of the static resolution be made by using the peak matching unit before and after each analysis. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

8.2.2 Chromatography time for PCDDs and PCDFs exceeds the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on the instrument performances. Therefore, a mass-drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 6 offers some suggestions for the lock-mass ions. However, an acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source resulting in an increase in

downtime for source cleaning.

8.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using the peak matching unit and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 6).

8.2.4 Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation (Figure 6) must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10-percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

9. Calibration

9.1 Initial Calibration

Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration (this exhibit, Section 9.3) does not meet the required criteria listed in Section 9.4 (this exhibit).

9.1.1 All seven high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

9.1.2 Tune the instrument with PFK as described in Section 8.2.3 (this exhibit).

9.1.3 Inject 2 uL of the GC column performance check solution (this exhibit, Section 7.6) and acquire SIM mass spectral data as described earlier in Section 8.1 (this exhibit). The total cycle time must be $\leq$ 1 second. The laboratory must not perform any further analysis until it is demonstrated and documented that the criterion listed in Section 8.1.2 (this exhibit) was met.

9.1.4 By using the same GC (this exhibit, Section 6.2) and mass spectrometer (this exhibit, Section 6.1.3) conditions that produced acceptable results with the column performance check solution, analyze a 2-uL portion of each of the seven concentration calibration solutions once with the following mass spectrometer operating parameters.

9.1.4.1 The total cycle time for data acquisition must be $\leq$ 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

9.1.4.2 Acquire SIM data for all the ions listed in the five descriptors of Table 6.

9.1.4.3 The ratio of integrated ion current for the ions appearing in Table 9 (homologous series quantification ions) must be within the indicated control limits (set for each homologous series).

9.1.4.4 The ratio of integrated ion current for the ions belonging to the carbon-labeled internal and recovery standards must be within the control limits stipulated in Table 9.

NOTE: Sections 9.1.4.3 and 9.1.4.4 (this exhibit) require that 17 ion ratios from Section 9.1.4.3 and 11 ion ratios from Section 9.1.4.4 be within the specified control limits simultaneously in one run. It is the laboratory's responsibility to take corrective action if the ion abundance ratios are outside the limits.

9.1.4.5 For each SICP and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Appendix C describes the procedure to be followed for the measurement of the S/N from conspicuously weak signals. This measurement is required for any GC

peak that has an apparent S/N of less than 5:1. The result of the calculation must appear on the SICP above the GC peak in question.

9.1.4.6 Referring to Table 10, calculate the 17 relative response factors (RRF) for unlabeled target analytes [RRF(n); n = 1 to 17] relative to their appropriate internal standards (Table 5) and the nine RRFs for the labeled $^{13}C_{12}$ internal standards [RRF(m); m = 18 to 26)] relative to the two recovery standards according to the following formulae:

$$RRF(n) = \frac{A_x \cdot Q_{is}}{Q_x \cdot A_{is}}$$

$$RRF(m) = \frac{A_{is} \cdot Q_{rs}}{Q_{is} \cdot A_{rs}}$$

where

A_x = sum of the integrated ion abundances of the quantification ions (Tables 6 and 9) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantification ions (Tables 6 and 9) for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantification ions (Tables 6 and 9) for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg),

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The RRF(n) and RRF(m) are dimensionless quantities; the units used to express Q_{is}, Q_{rs} and Q_x must be the same.

9.1.4.7 *Calculate the* $\overline{RRF}(n)$*s and their respective percent relative standard deviations (%RSD) for the seven calibration solutions:*

$$\overline{RRF}(n) = 1/7 \sum_{j=1}^{7} RRF_j(n) \quad ,$$

where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17; Table 10), and j is the injection number (or calibration solution number; j = 1 to 7).

9.1.4.8 **The relative response factors to be used for the determination of the concentration of total isomers in a homologous series (Table 10) are calculated as follows:**

9.1.4.8.1 **For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the mean $\overline{RRF}$ used**

will be the same as the mean $\overline{RRF}$ determined in Section 9.1.4.7 (this exhibit).

NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard. This is because a minimum resolving power of 12,000 is required to resolve the $[M+6]^+$ ion of $^{13}C_{12}$-OCDF from the $[M+2]^+$ ion of OCDD (and $[M+4]^+$ from $^{13}C_{12}$-OCDF with $[M]^+$ of OCDD). Therefore, the $\overline{RRF}$ for OCDF is calculated relative to $^{13}C_{12}$-OCDD.

9.1.4.8.2 For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the mean $\overline{RRF}$ used for those homologous series will be the mean of the RRFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\overline{RRF}(k) = \frac{1}{t} \sum_{n=1}^{t} RRF_n \ ,$$

where

k = 27 to 30 (Table 10), with 27 = PeCDF; 28 = HxCDF; 29 = HxCDD; and 30 = HpCDF,

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions (Table 5) for each homologous series (e.g., two for PeCDF, four for HxCDF, three for HxCDD, two for HpCDF).

NOTE: Presumably, the HRGC/HRMS response factors of different isomers within a homologous series are different. However, this analytical protocol will make the assumption that the HRGC/HRMS responses of all isomers in a homologous series that do not have the 2,3,7,8-substitution pattern are the same as the responses of one or more of the 2,3,7,8-substituted isomer(s) in that homologous series.

9.1.4.9 Relative response factors [$\overline{RRF}(m)$] to be used for the determination of the percent recoveries for the nine internal standards are calculated as follows:

$$RRF(m) = \frac{A_{is}^{m} \times Q_{rs}}{Q_{is}^{m} \times A_{rs}}$$

$$\overline{RRF}(m) = \frac{1}{7} \sum_{j=1}^{7} RRF_j(m),$$

where:

m = 18 to 26 (congener type) and j = 1 to 7 (injection number),

A_{is}^{m} = sum of the integrated ion abundances of the quantification ions (Tables 6 and 9) for a given internal standard (m = 18 to 26),

A_{rs} = sum of the integrated ion abundances of the quantification ions (Tables 6 and 9) for the appropriate recovery standard (see Table 5, footnotes),

Q_{rs} and Q_{is}^{m} = quantities of, respectively, the recovery standard (rs) and a particular internal standard (is = m) injected (pg),

RRF(m) = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from one injection, and

$\overline{RRF}$(m) = calculated mean relative response factor of a particular internal standard (m) relative to an appropriate recovery standard, as determined from the seven initial calibration injections (j).

9.2 Criteria for Acceptable Calibration

The criteria listed below for acceptable calibration must be met before the analysis is performed.

9.2.1 The percent relative standard deviations for the mean response factors [RRF(n) and RRF(m)] from each of the 26 determinations (17 for the unlabeled standards and 9 for the labeled reference compounds) must be less than 20 percent.

9.2.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be $\geq$ 2.5.

9.2.3 The isotopic ratios (Table 9) must be within the specified control limits.

NOTE: If the criterion for acceptable calibration listed in Section 9.2.1 (this exhibit) is met, the analyte-specific $\overline{RRF}$ can then be considered independent of the analyte quantity for the calibration concentration range. The mean $\overline{RRF}$s will be used for all calculations until the routine calibration criteria (this exhibit, Section 9.4) are no longer met. At such time, new mean $\overline{RRF}$s will be calculated from a new set of injections of the calibration solutions.

9.3 Routine Calibration (Continuing Calibration Check)

Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift.

9.3.1 Inject 2 uL of the concentration calibration solution HRCC-3 containing 10 pg/uL of tetra- and pentachlorinated congeners, 25 pg/uL of hexa- and heptachlorinated congeners, 50 pg/uL of octachlorinated congeners, and the respective internal and recovery standards (Table 5). By using the same HRGC/HRMS conditions as used in Sections 6.1.3 and 6.2 (this exhibit), determine and document an acceptable calibration as provided in Section 9.4 (this exhibit).

9.4 Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed.

If these criteria are not met, corrective action must be taken.

9.4.1 The measured RRFs [RRF(n) for the unlabeled standards] obtained during the routine calibration runs must be within 20 percent of the mean values established during the initial calibration (this exhibit, Section 9.1.4.7).

9.4.2 The measured RRFs [RRF(m) for the labeled standards] obtained during the routine calibration runs must be within 20 percent of the mean values established during the initial calibration (this exhibit, Section 9.1.4.9).

9.4.3 The ion-abundance ratios (Table 9) must be within the allowed control limits.

9.4.4 If either one of the above criteria (this exhibit, Sections 9.4.1 and 9.4.2) is not satisfied, the entire initial calibration process (this exhibit, Section 9.1) must be repeated. If the ion-abundance ratio criterion (this exhibit, Section 9.4.3) is not satisfied, refer to the note in Section 9.1.4.4 (this exhibit) for resolution.

NOTE: An initial calibration must be carried out whenever the HRCC-3, the sample fortification or the recovery standard solution is replaced by a new solution from a different lot.

10. Quality Assessment/Quality Control Procedures

See Exhibit E for QA/QC requirements.

11. Sample Preservation

11.1 The sample collection, shipping, handling, and chain-of-custody procedures are not described in this document. Sample collection personnel will, to the extent possible, homogenize samples in the field before filling the sample containers. This should minimize or eliminate the necessity for sample homogenization in the laboratory. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing. If the sample is clearly inhomogeneous, the entire contents should be transferred to a glass or stainless steel pan for mixing with a stainless steel spoon or spatula before removal of a sample portion for analysis.

11.2 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Sampling equipment must be free of potential sources of contamination.

11.3 Grinding or Blending of Fish Samples.

If not otherwise specified by the EPA, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meatgrinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the EPA. If so requested by the EPA, the above whole fish requirement is superseded.

11.4 With the exception of the fish and adipose tissues, which must be stored at -20° C, all samples must be stored at 4° C, extracted within 30 days and completely analyzed within 45 days of collection.

11.5 Phase Separation - This is a guideline for phase separation on very wet (>25 percent water) soil and sediment samples. Place a 50-g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipet, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent moisture determination, extraction). Return the remaining solid portion to the original sample bottle (empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil and sediment method. Take note of and report the estimated volume of liquid before disposing of the liquid as a liquid waste.

CAUTION: Finely divided soils and sediments contaminated with PCDDs/PCDFs are hazardous because of the potential for inhalation or ingestion of particles containing PCDDs/PCDFs (including 2,3,7,8-TCDD). Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

11.6 Soil, Sediment or Paper Sludge (Pulp) Percent Moisture Determination. The percent moisture of soil or sediment samples showing detectable

levels (see note below) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined according to the following recommended procedure.

Weigh a 9.5- to 10.5-g portion of the soil or sediment sample (± 0.5 g) to three significant figures. Dry it to constant weight at 100° C in an adequately ventilated oven. Allow the sample to cool in a desiccator. Weigh the dried solid to three significant figures. Calculate and report the percent moisture on Form (to be determined). Do not use this solid portion of the sample for extraction, but instead dispose of it as hazardous waste. The pulp sample (10 g) should be dried overnight in a fume hood.

NOTE: Until detection limits are determined (Section 1.2, this exhibit), the lower MCLs (Table 1) may be used to estimate the minimum detectable levels.

$$\text{Percent moisture} = \frac{\text{Weight of wet soil} - \text{Weight of dry soil}}{\text{Weight of wet soil}} \times 100$$

11.7 Fish Tissue Lipid Content Determination

The percent lipid of fish samples showing detectable levels (see Section 11.6 note; this exhibit) of at least one 2,3,7,8-substituted PCDD/PCDF congener is determined as follows:

Use a separate portion (2 g) of the ground frozen fish sample. Blend it

with 6 g anhydrous sodium sulfate, pour the mixture in a 1-cm i.d. glass column and extract the lipids by passing two 25-mL portions of methylene chloride through the column and collecting the extract in a tared 100-mL round-bottom flask. Concentrate the extract on a rotary evaporator until constant weight is attained. The percent lipid is calculated using the following expression:

$$\text{Percent lipid} = \frac{\text{Weight of residue from extraction (in g)}}{\text{Weight of fish tissue portion (in g)}} \times 100$$

Dispose of the lipid residue as a hazardous waste if the results of the analysis indicate the presence of PCDDs or PCDFs.

1.8 Adipose Tissue Lipid Content Determination

Details for the determination of the adipose tissue lipid content are provided in Section 12.11.3 (this exhibit).

12. Extraction and Cleanup Procedures

12.1 Internal standard addition. Use a portion of 1 g to 1000 g (typical sample size requirements for each type of matrix are given in Section 12.2 of this exhibit and in Table 1) of the sample to be analyzed. Transfer the sample portion to a tared flask and determine its weight. Except for adipose tissue, add an appropriate quantity of the sample fortification mixture (this exhibit, Section 3.8) to the sample. All samples should be

spiked with 100 uL of the sample fortification mixture to give internal standard concentrations as indicated in Table 1. As an example, for $^{13}C_{12}$-2,3,7,8-TCDD, a 10-g soil sample requires the addition of 1000 pg of $^{13}C_{12}$-2,3,7,8-TCDD to give the requisite 100 ppt fortification level. For the fortification of soil, sediment, fly ash, water and fish tissue samples, mix the 100 uL sample fortification solution with 1.5 mL acetone. Do not dilute the isooctane solution for the other matrices. The fortification of adipose tissue is carried out at the time of homogenization (this exhibit, Section 12.11.2.3).

12.2 Extraction

The extraction and purification procedures for biological tissue samples are described in Sections 12.10 (fish tissue) and 12.11 (adipose tissue) of this exhibit.

12.2.1 Sludge/Fuel Oil. Extract aqueous sludge samples by refluxing a sample (e.g., 2 g) with 50 mL toluene (or benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed. Cool the sample, filter the toluene (or benzene) extract through a glass-fiber filter, or equivalent, into a 100-mL round-bottom flask. Rinse the filter with 10 mL toluene (or benzene), and combine the extract and rinsate. Concentrate the combined solutions to near dryness on a rotary evaporator at 50° C (toluene) or a Kuderna-Danish (KD) apparatus (benzene). Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 12.2.4 below.

NOTE: If the labeled sludge sample dissolves in toluene, treat it according to the instructions in Section 12.2.2 below. If the labeled sludge sample originates from pulp (paper mills), treat it according to the instructions starting in Section 12.10.1 but without the addition of sodium sulfate.

12.2.2 Still-Bottom. Extract still-bottom samples by mixing a sample portion (e.g., 1.0 g) with 10 mL toluene (or benzene) in a small beaker and filtering the solution through a glass-fiber filter (or equivalent) into a 50-mL round-bottom flask. Rinse the beaker and filter with 10 mL toluene (or benzene). Concentrate the combined toluene (or benzene) solutions to near dryness on a rotary evaporator at 50° C. A KD apparatus can be used if benzene is the extraction solvent. Proceed with Section 12.2.4 below.

12.2.3 Fly Ash. Extract fly ash samples by placing a sample portion (e.g., 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL toluene (or benzene), and extract for 16 hours using a three cycle/hour schedule. Cool and filter the toluene (or benzene) extract through a glass-fiber filter into a 500-mL round-bottom flask. Rinse the filter with 5 mL toluene (or benzene). Concentrate the combined toluene (or benzene) solutions to near dryness on a rotary evaporator (toluene) at 50° C or a KD apparatus (benzene). Proceed with Section 12.2.4 below.

12.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL hexane.

Rinse the flask with two 5-mL portions of hexane and add the rinses to the funnel. Shake two minutes with 50 mL of 5 percent sodium chloride solution, discard the aqueous layer and proceed with Section 12.3 (this exhibit).

12.2.5 Soil. Add 10 g anhydrous sodium sulfate to the soil sample portion (e.g., 10 g) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass-wool plug (the use of an extraction thimble is optional). Add 200 to 250 mL benzene (or toluene) to the Soxhlet apparatus and reflux for 24 hours. The solvent must cycle completely through the system at least three times per hour.

12.2.5.1 Transfer the extract from Section 12.2.5 to a KD apparatus mounted with a three-ball Snyder column (or to a 500-mL round-bottom flask for evaporating the toluene on a rotary evaporator).

12.2.5.2 Add a Teflon™ or an equivalent boiling chip. Concentrate in a 70° C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 minutes.

12.2.5.3 Add 50 mL hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

12.2.5.4 Remove and invert the Snyder column, and rinse it down into the KD

apparatus with two 1-mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125-mL separatory funnel. Rinse the KD apparatus with two additional 5-mL portions of hexane, and add the rinsates to the funnel. Proceed with Section 12.3 (this exhibit).

12.2.6 Aqueous Samples. Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Section 12.2.6.1 (this exhibit).

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered when using a separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinsate to the extractor. Add 200 to 500 mL methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Sections 12.2.6.1 and 12.2.6.2 (this exhibit). Proceed with Section 12.2.6.3 (this exhibit).

12.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal, and shake for

30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride into a KD apparatus (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass-wool plug and 5 g anhydrous sodium sulfate. Repeat the extraction twice with fresh 60-ml portions of methylene chloride. After the third extraction, rinse the sodium sulfate with an additional 30 mL methylene chloride to ensure quantitative transfer. Combine all extracts and the rinsate in the KD apparatus.

12.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid is 5 mL. Remove the KD apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the KD apparatus before proceeding with the second concentration step. Rinse the flask and the lower joint with two 5-mL portions of hexane and combine the rinsates with the extract to give a final volume of about 15 mL.

12.2.6.3 Determine the original sample volume by filling the sample bottle to

the mark with water and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Section 12.3 (this exhibit).

12.3 Partition the extract (15 mL hexane) against 40 mL of 20 percent (w/v) aqueous potassium hydroxide (KOH). Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform a maximum of four base washings). Strong base (KOH) is known to degrade certain PCDDs/PCDFs, so contact time must be minimized.

12.4 Partition the extract (15 mL hexane) against 40 mL of 5 percent (w/v) aqueous sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom).

12.5 Partition the extract against 40 mL concentrated sulfuric acid. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

12.6 Partition the extract against 40 mL of five percent (w/v) sodium chloride. Shake for two minutes. Remove and discard the aqueous layer (bottom). Dry the extract by pouring it through a funnel containing anhydrous sodium sulfate and collect it in a 50-mL round-bottom flask. Rinse the sodium sulfate with two 15-mL portions of hexane, add the rinsates to the 50-mL flask, and concentrate the hexane solution to near dryness on a

rotary evaporator (35° C water bath), making sure all traces of toluene (when applicable) are removed. (Use of blow-down with an inert gas to concentrate the extract is also permitted.)

12.7 Pack a gravity column (glass, 300 mm x 10.5 mm), fitted with a Teflon™ stopcock, in the following manner: Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm® Super 1 neutral alumina. Tap the top of the column gently. Woelm® Super 1 neutral alumina need not be activated or cleaned before use, but it should be stored in a sealed desiccator. Add a 4-g layer of anhydrous sodium sulfate to cover the alumina. Elute with 10 mL hexane and close the stopcock just before exposure of the sodium sulfate layer to air. Discard the eluate. Check the column for channeling. If channeling is present, discard the column. Do not tap a wetted column.

12.8 Dissolve the residue from Section 12.6 (this exhibit) in 2 mL hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluate.

12.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane.

12.8.2 Elute the PCDDs and PCDFs from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15 mL) concentrator tube.

12.9 Carbon Column Cleanup

Prepare a Carbopak C/Celite 545® column as described in Section 7.1.2 (this exhibit).

12.9.1 With a carefully regulated stream of nitrogen, concentrate the 60-percent fraction (this exhibit, Section 12.8.2) to about 2 mL. Rinse the Carbopak C/Celite 545® with 5 mL toluene followed by 2 mL of 75:20:5 methylene chloride/methanol/benzene, 1 mL of 1:1 cyclohexane/ methylene chloride, and 5 mL hexane. The flow rate should be less than 0.5 mL/min. Discard the rinsates. While the column is still wet with hexane, add the sample concentrate to the top of the column. Rinse the concentrator tube which contained the sample concentrate twice with 1 mL hexane and add the rinsates to the top of the column. Elute the column sequentiallly with two 2-mL portions of hexane, 2 mL cyclohexane/ methylene chloride (50:50, v/v), and 2 mL methylene chloride/methanol/ benzene (75:20:5, v/v). Combine these eluates; this combined fraction may be used as a check on column efficiency. Now turn the column upside down and elute the PCDD/PCDF fraction with 20 mL toluene. Verify that no carbon fines are present in the eluate.

12.9.2 Concentrate the toluene fraction to about 1 mL on a rotary evaporator by using a water bath at 50° C. Carefully transfer the concentrate into a 1-mL minivial and, again at elevated temperature (50° C), reduce the volume to about 100 uL using a stream of nitrogen and a sand bath. Rinse the rotary evaporator flask three times with 300 uL of a solution

of 1 percent toluene in methylene chloride. Add 10 uL for soil, sediment, and water, or 50 uL for sludge, still-bottom and fly ash of the tridecane recovery standard solution. Store the sample at room temperature in the dark.

12.10 Extraction and Purification Procedures for Fish and Paper Pulp Samples

12.10.1 Add 30 g anhydrous sodium sulfate to a 10-g portion of a homogeneous fish sample (this exhibit, Section 11.3) and mix thoroughly with a stainless steel spatula. After breaking up any lumps, place the fish/sodium sulfate mixture in the Soxhlet apparatus on top of a glass-wool plug. Add 200 mL hexane/methylene chloride (1:1) to the Soxhlet apparatus and reflux for 12 hours. The solvent must cycle completely through the system at least three times per hour. Follow the same procedure for the dried (this exhibit, Section 11.6) paper pulp samples.

12.10.2 Transfer the fish or paper pulp extract from Section 12.10.1 to a KD apparatus equipped with a Snyder column.

12.10.3 Add a Teflon™ or an equivalent boiling chip. Concentrate the extract in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

12.10.4 Add 50 mL isooctane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 5 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

NOTE: The methylene chloride must have been completely removed before proceeding with the next step.

12.10.5 Remove and invert the Snyder Column and rinse it into the KD apparatus with two 1-mL portions of hexane. Decant the contents of the KD apparatus and concentrator tube into a 125-mL separatory funnel. Rinse the KD apparatus with two additional 5-mL portions of hexane and add the rinsates to the funnel. Proceed with the cleanup according to the instructions starting in Section 12.5 (this exhibit).

12.11 Extraction and Purification Procedures for Human Adipose Tissue

12.11.1 Human adipose tissue samples must be stored at -20° C from the time of collection until the time of analysis. The use of chlorinated materials during the collection of the sample must be avoided. Samples are handled with stainless steel forceps, spatulas, or scissors. All sample bottles (glass) are cleaned as specified in the note appearing in Section 6.3 (this exhibit). Teflon™-lined caps should be used.

12.11.2 Adipose Tissue Extraction Procedure

12.11.2.1 Weigh to the nearest 0.01 g a 10-g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

NOTE: The sample size may be smaller, depending on availability. In such a situation, the analyst is required to adjust the volume of

the internal standard solution added to the sample to meet the fortification level stipulated in Table 1.

12.11.2.2 Allow the adipose tissue specimen to reach room temperature (up to 2 hours).

12.11.2.3 Add 10 mL methylene chloride and 100 uL of the sample fortification solution. Homogenize the mixture for approximately 1 minute with a tissue homogenizer.

12.11.2.4 Allow the mixture to separate, and remove the methylene chloride extract from the residual solid material with a disposable pipet. Percolate the methylene chloride through a filter funnel containing a clean glass-wool plug and 10 g anhydrous sodium sulfate. Collect the dried extract in a graduated 100-mL volumetric flask.

12.11.2.5 Add a second 10-mL portion of methylene chloride to the sample and homogenize for 1 minute. Decant the solvent, dry it, and transfer it to the 100-mL volumetric flask (this exhibit, Section 12.11.2.4).

12.11.2.6 Rinse the culture tube with at least two additional portions of methylene chloride (10 mL each), and transfer the entire contents to the filter funnel containing the anhydrous sodium sulfate. Rinse the filter funnel and the anhydrous sodium sulfate contents with additional methylene chloride (20 to 40 mL) into the 100-mL flask. Discard the sodium sulfate.

12.11.2.7 Adjust the volume to the 100-mL mark with methylene chloride.

12.11.3 Adipose Tissue Lipid Content Determination

12.11.3.1 Preweigh a clean 1-dram glass vial to the nearest 0.0001 g on an analytical balance tared to zero.

12.11.3.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Section 12.11.2.6 (this exhibit) to the 1-dram vial. Reduce the volume of the extract on a water bath (50-60° C) by a gentle stream of purified nitrogen until an oily residue remains. Nitrogen blow-down is continued until a constant weight is achieved.

12.11.3.3 Accurately weigh the 1-dram vial with the residue to the nearest 0.0001 g and calculate the weight of the lipid present in the vial based on the difference of the weights.

12.11.3.4 Calculate the percent lipid content of the original sample to the nearest 0.1 percent as shown below:

$$\text{Lipid Content, LC (\%)} = \frac{W_{lr} \times V_{ext}}{W_{at} \times V_{al}} \times 100$$

where

W_{lr} = weight of the lipid residue to the nearest 0.0001 g calculated from Section 12.11.3.3 (this exhibit),

V_{ext} = total volume (100 mL) of the extract in mL from Section 12.11.2.6 (this exhibit)

W_{at} = weight of the original adipose tissue sample to the nearest 0.01 g from Section 12.11.2.1 (this exhibit), and

V_{al} = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL).

12.11.3.5 Record the lipid residue measured in Section 12.11.3.3 (this exhibit) and the percent lipid content from Section 12.11.3.4 (this exhibit).

12.11.4 Adipose Tissue Extract Concentration

12.11.4.1 Quantitatively transfer the remaining extract volume (99.0 mL) to a 500-mL round-bottom flask. Rinse the volumetric flask with 20 to 30 mL of additional methylene chloride to ensure quantitative transfer.

12.11.4.2 Concentrate the extract on a rotary evaporator and a water bath at 40°C until an oily residue remains.

12.11.5 Adipose Tissue Extract Cleanup Procedures

12.11.5.1 Add 200 mL hexane to the lipid residue in the 500-mL Erlenmeyer

flask and swirl the flask to dissolve the residue.

12.11.5.2 Slowly add, with stirring, 100 g of 40-percent w/w sulfuric-acid-impregnated silica gel. Stir with a magnetic stirrer for two hours at room temperature.

12.11.5.3 Allow the solid phase to settle and decant the liquid through a powder funnel containing 20 g anhydrous sodium sulfate into another 500-mL Erlenmeyer flask.

12.11.5.4 Rinse the solid phase with two 50-mL portions of hexane. Stir each rinse for 15 minutes, decant, and dry as described under Section 12.11.5.3. Combine the hexane extracts from Section 12.11.5.3 (this exhibit) with the rinses.

12.11.5.5 Rinse the sodium sulfate in the powder funnel with an additional 25 mL hexane and combine this rinse with the hexane extracts from Section 12.11.5.4 (this exhibit).

12.11.5.6 Prepare an acidic silica column as follows: Pack a 2-cm x 10-cm chromatographic column with a glass-wool plug, add approximately 20 mL hexane, add 4 g silica gel and allow to settle, then add 16 g of 40-percent w/w sulfuric-acid-impregnated-silica gel and allow to settle. Elute the excess hexane from the column until the solvent level reaches the top of the chromatographic packing. Verify that the column does not have any air bubbles and channels.

12.11.5.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (this exhibit, Sections 12.11.5.3 through 12.11.5.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect the eluate in a 500-mL KD apparatus.

12.11.5.8 Complete the elution by percolating 50 mL hexane through the column into the KD apparatus. Concentrate the eluate on a steam bath to approximately 5 mL. Use nitrogen blow-down to bring the final volume to about 100 uL.

NOTE: If the silica gel impregnated with 40-percent sulfuric acid is highly discolored throughout the length of the adsorbent bed, the cleaning procedure must be repeated beginning with Section 12.11.5.1 (this exhibit).

12.11.5.9 The extract is ready for the alumina and carbon cleanups described in Sections 12.7 through 12.9.2 (this exhibit).

13. Analytical Procedures.

13.1 Remove the sample extract or blank from storage. With a stream of dry, purified nitrogen, reduce the extract volume to 10 uL or 50 uL (the volume of the tridecane recovery standard solution) as stipulated above (this exhibit, Section 12.9.2).

13.2 Inject a 2-uL aliquot of the extract into the GC, operated under the

conditions previously used (this exhibit, Section 6.2) to produce acceptable results with the performance check solution.

13.3 Acquire SIM data according to Section 6.1.3 (this exhibit). Use the same acquisition and mass spectrometer operating conditions previously used to determine the relative response factors (this exhibit, Sections 9.1.4.6 through 9.1.4.9). Ions characteristic for polychlorinated diphenyl ethers are included in the descriptors listed in Table 6. Their presence is to monitor their interference during the characterization of PCDFs.

NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined (Section 8.1, this exhibit). Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package as deliverables. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run. (See this exhibit, Section 8.2.2 for the proper level of reference compound to be metered into the ion chamber.) It is recommended to examine the lock-mass ion SICP for obvious basic sensitivity and stability changes of the instrument during the GC/MS run that could affect the measurements [Y. Tondeur et al., Anal. Chem. 56, 1344 (1984)]. Report any discrepancies in the case narrative.

13.4 Identification Criteria

For a gas chromatographic peak to be identified as a PCDD or PCDF, it

must meet all of the following criteria:

13.4.1 Relative Retention Times.

13.4.1.1 For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD; Tables 2 and 3), the relative retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantification purposes listed in Table 6) must be within -1 and +3 seconds of the retention time of the peak for the isotopically labeled internal or recovery standard at m/z corresponding to the first characteristic ion (of the set of two; Table 6) to obtain a positive identification of these nine 2,3,7,8-substituted PCDDs/PCDFs and OCDD.

13.4.1.2 For 2,3,7,8-substituted compounds, that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners; Table 3), the relative retention time must fall within the established homologous retention time windows by analyzing the column performance check solution (this exhibit, Section 8.1.3). Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

13.4.1.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding

homologous retention time windows established by analyzing the column performance check solution (this exhibit, Section 8.1.3).

13.4.1.4 The ion current responses for both ions used for quantitative purposes (e.g., for TCDDs: m/z 319.8465 and 321.8936) must reach maximum simultaneously (± 2 seconds).

13.4.1.5 The ion current responses for both ions used for the labeled standards (e.g., for $^{13}C_{12}$-TCDD: m/z 331.9368 and m/z 333.9339) must reach maximum simultaneously (± 2 seconds).

NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF (this exhibit, Section 8.1.3) in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to report that observation with the results associated with the sample batch as it may indicate a potential problem with the ability to detect all the PCDDs/PCDFs.

13.4.2 Ion Abundance Ratios

13.4.2.1 The integrated ion current for the two ions used for quantification purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned. See Sections 9.1.4.3 and 9.1.4.4 (this exhibit) and Table 9 for details.

13.4.3 Signal-to-Noise Ratio

13.4.3.1 All ion current intensities must be $\geq$ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers. Appendix C describes the procedure to be followed for the determination of the S/N.

13.4.4 Polychlorinated Diphenyl Ether Interferences

13.4.4.1 In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected, at the same retention time ($\pm$ 2 seconds), in the corresponding PCDPE channel.

14. Calculations

14.1 For gas chromatographic peaks that have met the criteria outlined in Sections 13.4.1.1 through 13.4.3.1 (this exhibit), calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantification ions (Table 6) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantification ions (Table 6) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight, in g, of the sample (solid or liquid), and

$\overline{RRF}(n)$ = calculated mean relative response factor for the analyte [$\overline{RRF}(n)$ with n = 1 to 17; Section 9.1.4.7, this exhibit].

If the analyte is identified as one of the 2,3,7,8-substituted PCDDs or PCDFs, $\overline{RRF}(n)$ is the value calculated using the equation in Section 9.1.4.7 (this exhibit). However, if it is a non-2,3,7,8-substituted congener, the $\overline{RRF}(k)$ value is the one calculated using the equation in Section 9.1.4.8.2 (this exhibit). [$\overline{RRF}(k)$ with k = 27 to 30.]

14.2 Calculate the percent recovery of the nine internal standards measured in the sample extract, using the formula:

$$\text{Internal standard percent recoverr} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RRF}(m)} \times 100$$

where

A_{is} = sum of the integrated ion abundances of the quantification ions (Table 6) for the labeled internal standard,

A_{rs} = sum of the integrated ion abundances of the quantification ions (Table 6) for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners (see Table 5, footnotes),

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and

$\overline{RRF}(m)$ = calculated mean relative response factor for the labeled internal standard relative to the appropriate (see Table 5, footnotes) recovery standard. This represents the mean obtained in Section 9.1.4.9 (this exhibit) [$\overline{RRF}(m)$ with m = 18 to 26].

NOTE: For human adipose tissue, adjust the percent recoveries by adding 1 percent to the calculated value.

14.3 If the concentration in the 10-uL or 50-uL final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds (Table 3) exceeds the upper method calibration limits (MCL) listed in Table 1 (e.g., 200 pg/uL.

for TCDD in soil), the linear range of response versus concentration may have been exceeded, and, after contacting EPA/SMO, a reanalysis of the sample (using one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation (this exhibit, Sections 12.1 to 12.9.3). For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

14.4 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report.

14.5 Sample-Specific Estimated Detection Limit

The sample-specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

14.5.1 Samples giving a response for both quantification ions (Tables 6 and 9) that is less than 2.5 times the background level.

14.5.1.1 Use the expression for EDL (specific 2,3,7,8-substituted PCDD/PCDF) below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF (i.e., S/N < 2.5). The background level is determined by measuring the range of the noise (peak to peak) for the two quantification ions (Table 6) of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that product height.

Use the formula:

$$\text{EDL (specific 2,3,7,8 subst.-PCDD/PCDF)} = \frac{2.5 \times A_x \times Q_{is}}{A_{is} \times W \times \overline{RRF}(n)}$$

where

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

A_x, A_{is}, W, $\overline{RRF}(n)$, and Q_{is} retain the same meanings as defined in Section 14.1.

14.5.2 Samples characterized by a response above the background level with a S/N of at least 2.5 for at least one of the quantification ions (Tables 6 and 9).

14.5.2.1 When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria listed in Section 13.4, calculate the "Estimated Maximum Possible Concentration" (EMPC) according to the expression shown in Section 14.1.

14.6 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{| S_1 - S_2 |}{(S_1 + S_2) / 2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

14.7 The 2,3,7,8-TCDD toxic equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, only at the data user's request, according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs (Table 3) and the non-2,3,7,8-substituted compounds as shown in Table 11. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds

listed in Table 11. The exclusion of other homologous series such as mono-, di-, tri- and octachlorinated dibenzodioxins and dibenzofurans does not mean that they are non-toxic. Their toxicity, as known at this time, is much less than the toxicity of the compounds listed in Table 11. The above procedure for calculating the 2,3,7,8-TCDD toxic equivalents is not claimed by the CDWG to be based on a thoroughly established scientific foundation. The procedure, rather, represents a "Consensus recommendation on science policy". Since the procedure may be changed in the future, reporting requirements for PCDD and PCDF data would still include the reporting of the analyte concentrations of the PCDD/PCDF congener as calculated in Sections 14.1 and 14.4.

14.7.1 Two-GC Column TEF Determination

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60-m DB-5 GC column alone. In order tc determine the proper concentrations of the individual 2,3,7,8-substituted congeners, the sample extract must be reanalyzed on a 60-m SP-2330 (or SP-2331) GC column.

14.7.1.1 The concentrations of 2,3,7,8-TCDD (see note below), 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8HpCDD, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,7,8,9-HpCDF are calculated from the analysis of the sample extract on the 60-m DB-5 fused-silica column. The experimental conditions remain the same as the conditions described previously in Section 13 (this exhibit), and the calculations are performed as outlined in Section 14 (this exhibit).

14.7.1.2 The concentrations of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD and -PeCDF, 1,2,3,4,7,8-HxCDD and -HxCDF, 1,2,3,6,7,8-HxCDD and -HxCDF, 1,2,3,7,8,9-HxCDD and -HxCDF, and 2,3,4,6,7,8-HxCDF are obtained from the analysis of the sample extract on the second fused-silica capillary column (confirmation GC column: 60 m SP-2330). However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (i.e., tetra-, penta-, and hexachlorinated congeners) of Table 6 are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The concentration calculations are performed as outlined in Section 14 (this exhibit).

NOTE: The confirmation and quantification of 2,3,7,8-TCDD (this exhibit, Section 14.7.1.1) may be accomplished on the SP-2330 GC column instead of the DB-5 column, provided the criteria listed in Section 8.1.2 (this exhibit) are met and the requirements described in Section 2.2 (Exhibit E) are followed.

14.7.1.3 For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria listed in Sections 13.4.2 and 13.4.3 (this exhibit), respectively. In addition, the retention time identification criterion described in Section 13.4.1.1 (this exhibit) applies here for congeners for which a carbon-labeled analogue is available in the sample extract. However, the relative retention

time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT. Experimentally, this is accomplished by using the attributions described in Table 12 and the results from the routine calibration run on the SP-2330 column.

APPENDICES

APPENDIX A

Procedure for the Collection, Handling, Analysis, and Reporting Requirements of Wipe Tests Performed within the Laboratory

This procedure is designed for the periodic evaluation of potential contamination by 2,3,7,8-substituted PCDD/PCDF congeners of the working areas inside the laboratory.

PERFORMING WIPE TEST

Perform the wipe tests on surface areas of two inches by one foot with laboratory wipers saturated with distilled-in-glass acetone using a pair of clean stainless steel forceps. Use one wiper for each of the designated areas. Combine the wipers to one composite sample in an extraction jar containing 200 mL distilled-in-glass acetone. Place an equal number of unused wipers in 200 mL acetone and use this as a control.

COMPOSITE SAMPLE PREPARATION

Close the jar containing the wipers and 200 mL acetone and extract for 20 minutes using a wrist-action shaker. Transfer the extract into a KD apparatus fitted with a concentration tube and a three-ball Snyder column. Add two Teflon™ or Carborundum™ boiling chips and concentrate the extract to an apparent volume of 1.0 mL on a steam bath. Rinse the Snyder column and the KD assembly with two 1-mL portions of hexane into the concentrator tube. Add 100 uL of the sample fortification solution to the concentrator tube (Section 3.8, this exhibit), and concentrate its contents to near dryness with a gentle stream of nitrogen. Add 1.0 mL hexane to the concentrator tube, and swirl the solvent on the walls.

Prepare a neutral alumina column as described in Section 12.7 (this exhibit) and follow the steps outlined in Sections 12.8 thru 12.8.2 (this exhibit).

Add 10 uL of the recovery standard solution as described in Section 12.9.2 (this exhibit).

EXTRACT ANALYSIS

Concentrate the contents of the vial to a final volume of 10 uL (either in a minivial or in a capillary tube). Inject two uL of each extract (wipe and control) onto a capillary column and analyze for 2,3,7,8-substituted PCDDs/PCDFs as specified in the analytical method Section 13 (this exhibit). Perform calculations according to Section 14 (this exhibit).

REPORTING FORMAT

Report the presence of 2,3,7,8-substituted PCDDs and PCDFs as a quantity (pg or ng) per wipe test experiment (WTE). Under the conditions outlined in this analytical protocol, a lower limit of calibration of 25 pg/WTE is expected for 2,3,7,8-TCDD. A positive response for the blank (control) is defined as a signal in the TCDD retention time window at any of the masses monitored which is equivalent to or above 8 pg of 2,3,7,8-TCDD per WTE. For other congeners, use the multiplication factors listed in Table 1, footnote (a) (e.g., for OCDD, the lower MCL is 25 x 5 = 125 pg/WTE and the positive response for the blank

would be 8 x 5 = 40 pg). Also, report the recoveries of the internal standards during the simplified cleanup procedure.

FREQUENCY OF WIPE TESTS

At a minimum, wipe tests should be performed when there is evidence of contamination in the method blanks.

CORRECTIVE ACTION

An upper limit of 25 pg per TCDD isomer and per wipe test experiment is allowed. (Use multiplication factors listed in footnote (a) from Table 1 for other congeners.) This value corresponds to the lower calibration limit of the analytical method. Steps to correct the contamination must be taken whenever these levels are exceeded. To that effect, first vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high-efficiency particulate absorbant (HEPA) filter and then wash with a detergent. A new set of wipes should be analyzed before anyone is allowed to work in the dioxin area of the laboratory.

APPENDIX B

Standards Traceability Procedure

NOTE: The content of this appendix is based on the assumption that EPA will have within its repository a mixture (named S2) containing known concentrations (e.g., 100 pg/uL) of the eight ^{13}C-labeled 2,3,7,8-substituted PCDD/PCDF congeners marked with an asterisk in Table 3 of this exhibit, and a second solution (named S1, with the same concentration as used for S2) containing the eight corresponding unlabeled analogues.

All laboratories are expected to maintain traceability of their standard solutions by verifying that all standard solutions used for direct quantification of samples agree in chemical identity and concentration with the EPA primary standard solutions. The specific procedures are described below:

Each time a new laboratory working standard solution (W) is prepared, the identities and concentrations of the components of this solution must be verified. Verifications of the identities of the compounds are to be carried out by HRGC/HRMS. The EPA reference standard (S) and the laboratory working standard (W) are to be analyzed under the instrumental conditions described in this exhibit, which are appropriate for the analysis of PCDDs and PCDFs. Two criteria must be satisfied to verify the identifications:

- Elution of the component(s) of the laboratory working standard must be at the same retention time(s) as those of the component(s) of the EPA reference standard solution.

- Concentration(s) of the laboratory working standard component(s) must be equal to or less than 20 percent different from the EPA reference standard component(s).

Qualitative Characterization

Due to the complexity brought by the large number of possible PCDD and PCDF congeners, the requirement for qualitative verification by comparison of the retention times applies only to the eight 2,3,7,8-substituted PCDD/PCDF

congeners marked with an asterisk in Table 3 and for which a carbon-labeled analogue is available. Two situations need to be considered:

a) The laboratory is required to trace back its unlabeled PCDD/PCDF standards to EPA standards. This is accomplished by adding an appropriate aliquot of the EPA ^{13}C-labeled standard solution (S2) to an aliquot of the laboratory working solution (W1) so that the concentrations are comparable; the new mixture is then analyzed by HRGC/HRMS. The retention times of the eight unlabeled PCDDs/PCDFs discussed above must fall within -1 to +3 seconds of the EPA ^{13}C-labeled analogues.

b) In addition to a), the laboratory is required to trace back its ^{13}C-labeled standards to EPA standards. Proceed as follows: Add an aliquot of the laboratory working standard solution (W2) containing the carbon-labeled compounds to an aliquot of the EPA standard solution (S1) containing the eight unlabeled 2,3,7,8-substituted PCDD/PCDF congeners discussed above, and analyze by HRGC/HRMS. The concentrations must be comparable. The retention times for the eight carbon-labeled compounds must fall within -3 to +1 seconds of the EPA unlabeled analogues.

Quantitative Characterization

To establish that the concentration of the laboratory working standard is correct with respect to the EPA reference standard, the relative response factors (RRFs) for the eight 2,3,7,8-substituted PCDD/PCDF congeners (marked with asterisks in Table 3) must be determined as described in this exhibit.

The concentrations of the EPA reference and laboratory working standards should be approximately the same (e.g., 50 pg/uL/congener). Proceed as follows:

1) Mix equal portions of the two EPA standard solutions (S1 and S2) and analyze by HRGC/HRMS. Calculate two RRFs for each of the eight analytes as shown below:

Response factor of unlabeled congener (i) relative to carbon-labeled analogue (j):

$$RRF\ (S1,i) = \frac{A_i \times Q_j}{Q_i \times A_j}$$

Response factor of carbon-labeled congener (j) relative to unlabeled analogue (i):

$$RRF\ (S2,j) = \frac{A_j \times Q_i}{Q_j \times A_i}$$

where A_i and A_j represent the integrated ion abundances of, respectively, the unlabeled congener and carbon-labeled congener, and Q_i and Q_j the quantities of, respectively, the unlabeled congener and carbon-labeled congener, with $i = 1$ to 8, $j = 1$ to 8.

2) Add an appropriate aliquot of the laboratory working solution W1 (or W2) to an aliquot of the EPA solution S2 (or S1). Analyze the mixture by HRGC/HRMS and calculate the corresponding response factors as indicated below:

$$RRF\ (W1,i) = \frac{A_i \times Q_j}{Q_i \times A_j}$$

or

$$RRF\ (W2,j) = \frac{A_j \times Q_i}{Q_j \times A_i}$$

A and Q have the same meanings as in (1).

3) When the percent difference between each congener relative response factor -- RRF (S1,i) and RRF (W1,i), and RRF (S2,j) and RRF (W2,j) -- does not exceed 20 percent, the concentration of the laboratory working standard is correct. (RPD = relative percent difference.)

$$RPD = \frac{|\ RRF\ (S1,i) - RRF\ (W1,i)\ |}{RRF\ (S1,\ i)} \times 100$$

and

$$RPD = \frac{|\ RRF\ (S2,j) - RRF(W2,j)\ |}{RRF\ (S2,j)} \times 100$$

Traceability Requirements

If any or all of the above conditions for qualitative and quantitative verifications for the laboratory working standard are not met, the standard is not traceable to the EPA reference standard and can therefore not be used for the analysis of samples.

NOTE: The procedure outlined above is required for laboratories which use different batches of analytical standard compounds in the preparation of the sample fortification and recovery standard solutions and in the preparation of the HRCC solutions. Laboratories which use the same batch of analytical standards during the preparation of the sample fortification and recovery standard solutions and the HRCC solutions are exempt from following the above procedure, provided proper traceability documentation is available.

In addition, the records pertaining to the above qualitative and quantitative requirements, records of all verifications, documentation of the preparation, and all inventory must be kept for all contract laboratory primary, secondary, and working standards that are generated for the purpose of analyzing samples for EPA. These records should include the signed and dated logbooks containing the information pertaining to the preparation of the laboratory standards (weight of compound(s), volume and nature of the solvent, laboratory code name, EPA reference standard lot number) and of any modification made to the EPA reference standard. All standards should be used on a first in, first out basis. The raw data, quantification reports and calculations must be kept on file.

APPENDIX C

Signal-to-Noise Ratio Determination

SIGNAL-TO-NOISE RATIO DETERMINATION

MANUAL DETERMINATION

This method describes a manual determination of the signal-to-noise ratio (S/N) from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 7 for the following discussion.)

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E1 and E2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown on Figure 7. In addition, the signal offset (O) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.

2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.

3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E3 and E4.

4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

FIGURES CAPTIONS

1. Method flow chart for sample extraction and cleanup as used for the analysis of PCDDs and PCDFs in complex waste and biological samples.

2. General structures of dibenzodioxin and dibenzofuran.

3. Peak profile displays demonstrating the effect of the detector zero on the measured resolving power. In this example, the true resolving power is 5,600.

   A) The zero was set too high; no effect is observed upon the measurement of the resolving power. (Not aesthetic.)

   B) The zero was adjusted properly.

   C) The zero was set too low; this results in overestimating the actual resolving power because the peak-to-peak noise cannot be measured accurately.

4. Typical 12-hour analysis sequence of events.

5. Selected ion current profile for m/z 322 (TCDDs) produced by MS analysis of the GC performance check solution on a 60-m DB-5 fused-silica capillary column under the conditions listed in Table 7.

6. Peak profiles representing two PFK reference ions at m/z 305 and 381. The resolution of the high-mass signal is 95 ppm at 5 percent of the peak height; this corresponds to a resolving power $M/\Delta M$ of 10,500 (10 percent valley definition).

7. Manual determination of S/N.

   The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E1 and E2, and between the apex average noise extremes, E3 and E4, at the apex of the signal. Note, it is imperative that the instrument interface amplifier electronic zero offset be set high enough such that negative-going baseline noise is recorded.

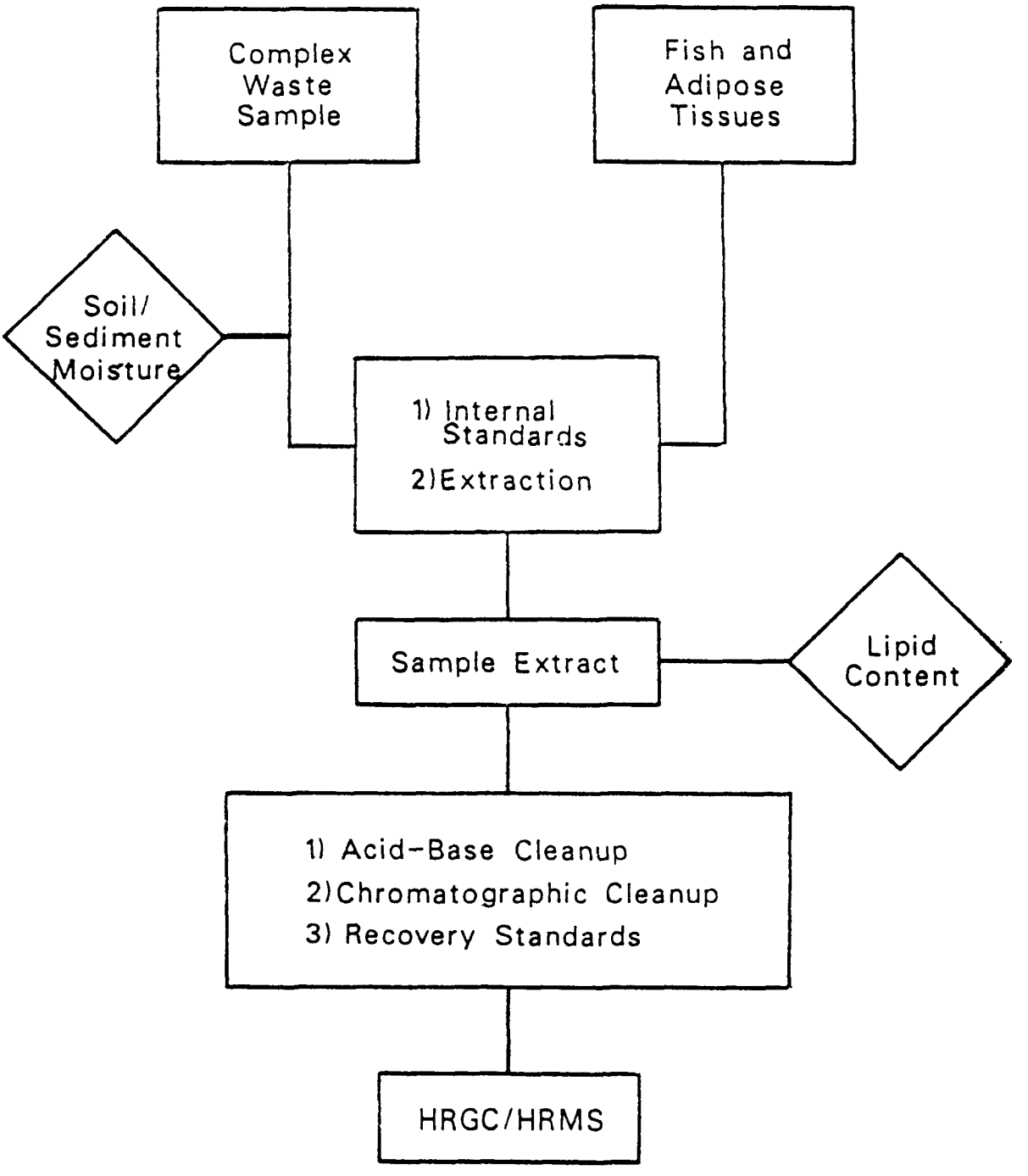
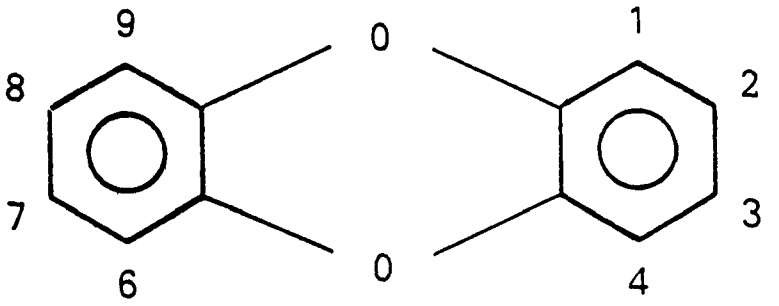
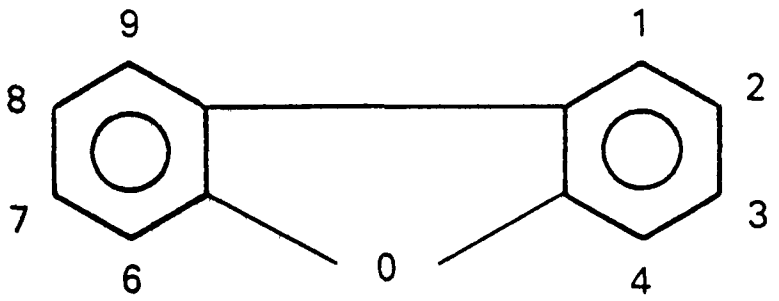

Complex Waste Sample
Fish and Adipose Tissues
Soil/ Sediment Moisture
1) Internal Standards
2) Extraction
Sample Extract
Lipid Content
1) Acid-Base Cleanup
2) Chromatographic Cleanup
3) Recovery Standards
HRGC/HRMS

Figure 1

D-87



Dibenzodioxin



Dibenzofuran

Figure 2

D-88

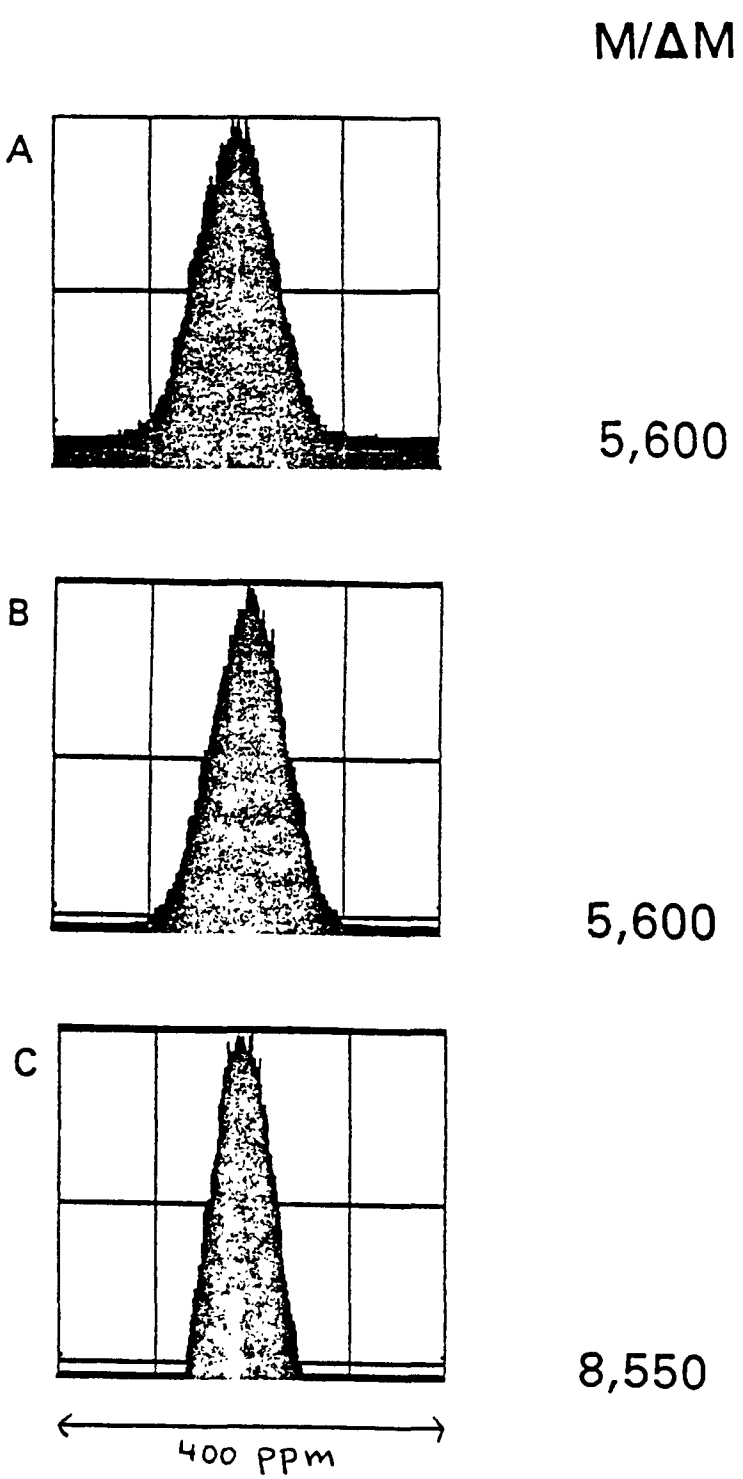


Figure 3

D-89

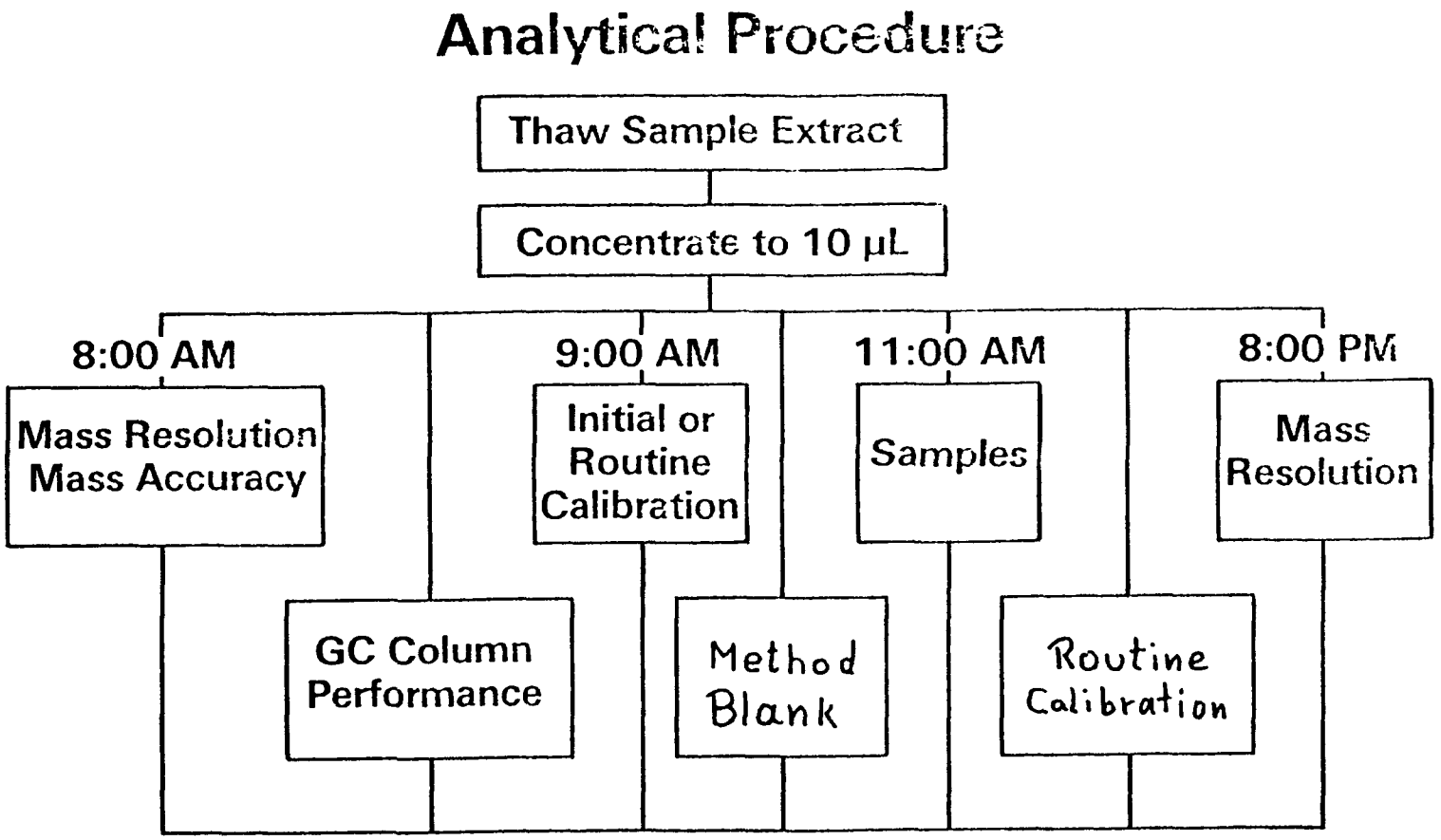

Analytical Procedure
Thaw Sample Extract
Concentrate to 10 µL
8:00 AM
9:00 AM
11:00 AM
8:00 PM
Mass Resolution
Mass Accuracy
Initial or
Routine
Calibration
Samples
Mass
Resolution
GC Column
Performance
Method
Blank
Routine
Calibration

Figure 4

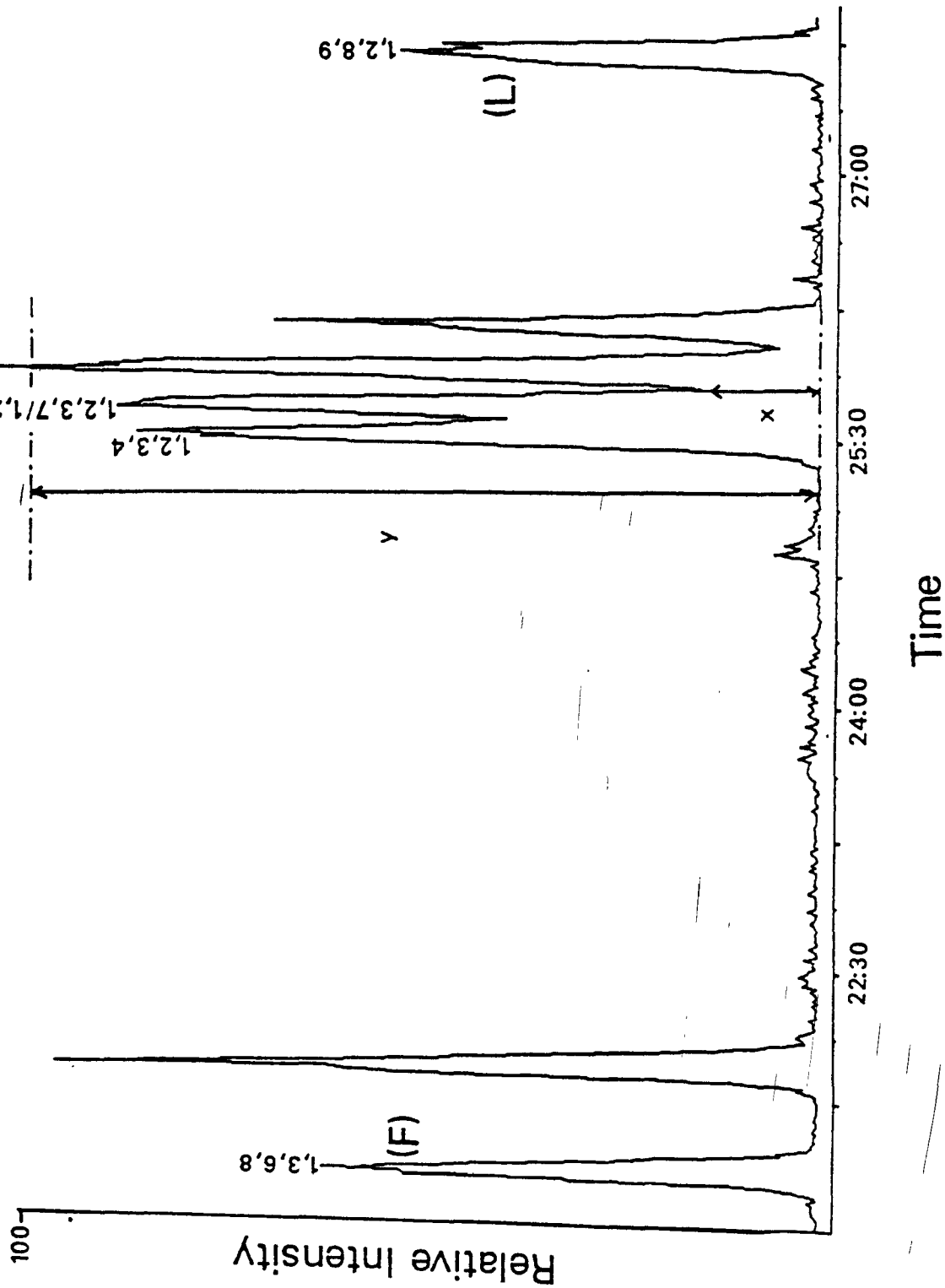
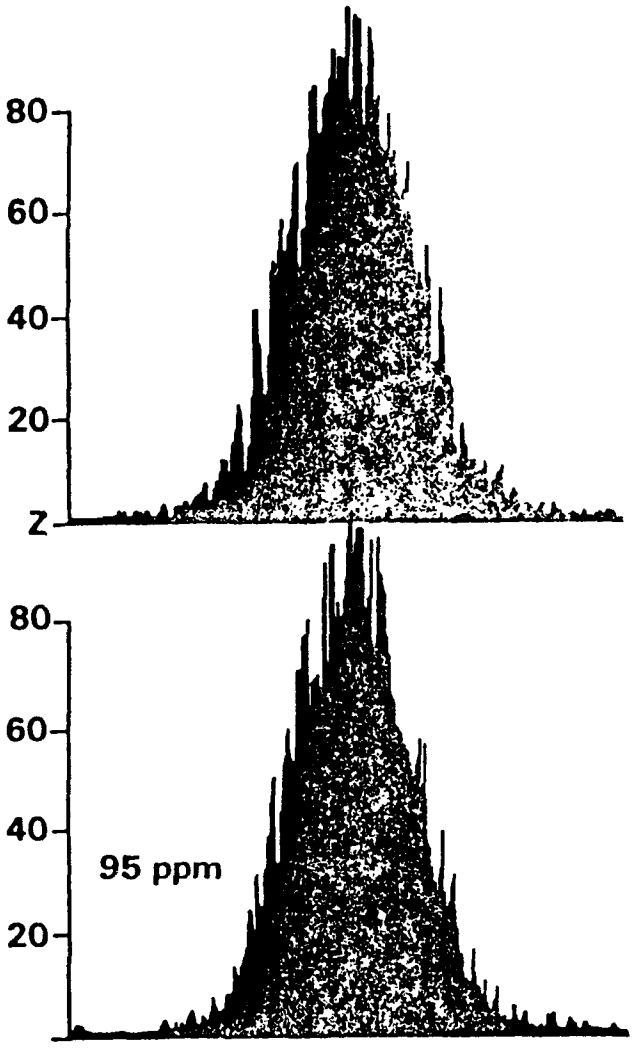

Relative Intensity
100
(F)
1,3,6,8
(L)
1,2,8,9
22:30
24:00
25:30
27:00
Time
x
y
1,2,3,4
1,2,3,7/1,2,3,8
2,3,7

Figure 5



Ref. mass 304.9824 Peak top
Span. 200 ppm

System file name	YVES150
Data file name	A:85Z567
Resolution	10000
Group number	1
Ionization mode	EI+
Switching	VOLTAGE
Ref. masses	304.9824 380.9260

M/M Δ M ~10,500

Channel B 380.9260 Lock mass
Span 200 ppm

Figure 6

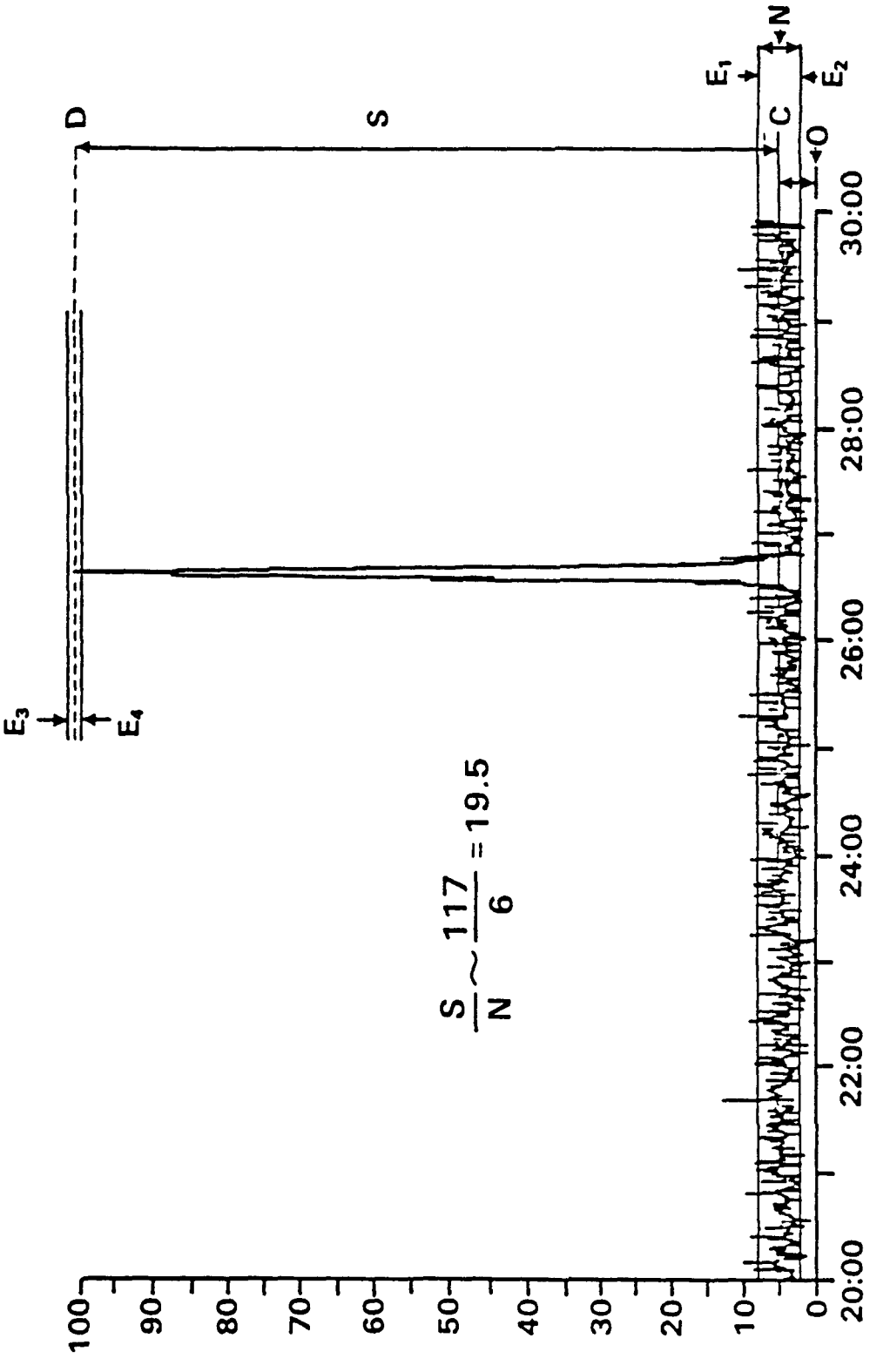

D
S
E1
N
E2
C
O
E3
E4
S/N ~ 117/6 = 19.5
100
90
80
70
60
50
40
30
20
10
0
20:00
22:00
24:00
26:00
28:00
30:00

Figure 7

Table 1. Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (Parts per Trillion)

	Soil Sediment	Fly Ash	Water	Sludges Fuel Oil	Still-Bottom	Fish Tissue Paper Pulp	Human Adipose Tissue
Lower MCL[a]	2.5	2.5	0.025	12.5	25	2.5	2.5
Upper MCL[a]	200	200	2	1000	2000	200	200
Weight (g)	10	10	1000	2	1	10	10
IS Spiking Levels (ppt)	100	100	1	500	1000	100	100
Final Extr. Vol. (uL)	10	50	10	50	50	10	10

[a]For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

NOTE: Chemical reactor residues are treated as still-bottoms if their appearances suggest so.

Table 2. Composition of the Sample Fortification and Recovery Standard Solutions

Analyte	Sample Fortification Solution Concentration (pg/uL; Solvent: Isooctane)	Recovery Standard Solution Concentration (pg/uL; Solvent: Tridecane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

Table 3. The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(*)The ^{13}C-labeled analogue is used as an internal standard.
(+)The ^{13}C-labeled analogue is used as a recovery standard.

Table 4. Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	---	4	---
2	10	---	16	---
3	14	---	28	---
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

Table 5. High-Resolution Concentration Calibration Solutions

Compound	HRCC	Concentration (pg/uL) 7	6	5	4	3	2	1
Unlabeled Analytes								
2,3,7,8-TCDD		200	100	50	25	10	5	2.5
2,3,7,8-TCDF		200	100	50	25	10	5	2.5
1,2,3,7,8-PeCDD		200	100	50	25	10	5	2.5
1,2,3,7,8-PeCDF		200	100	50	25	10	5	2.5
2,3,4,7,8-PeCDF		200	100	50	25	10	5	2.5
1,2,3,4,7,8-HxCDD		500	250	125	62.5	25	12.5	6.25
1,2,3,6,7,8-HxCDD		500	250	125	62.5	25	12.5	6.25
1,2,3,7,8,9-HxCDD		500	250	125	62.5	25	12.5	6.25
1,2,3,4,7,8-HxCDF		500	250	125	62.5	25	12.5	6.25
1,2,3,6,7,8-HxCDF		500	250	125	62.5	25	12.5	6.25
1,2,3,7,8,9-HxCDF		500	250	125	62.5	25	12.5	6.25
2,3,4,6,7,8-HxCDF		500	250	125	62.5	25	12.5	6.25
1,2,3,4,6,7,8-HpCDD		500	250	125	62.5	25	12.5	6.25
1,2,3,4,6,7,8-HpCDF		500	250	125	62.5	25	12.5	6.25
1,2,3,4,7,8,9-HpCDF		500	250	125	62.5	25	12.5	6.25
OCDD		1,000	500	250	125	50	25	12.5
OCDF		1,000	500	250	125	50	25	12.5
Internal Standards								
$^{13}C_{12}$-2,3,7,8-TCDD		50	50	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF		50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD		50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF		50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD		125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF		125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD		125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF		125	125	125	125	125	125	125
$^{13}C_{12}$-OCDD		250	250	250	250	250	250	250
Recovery Standards								
$^{13}C_{12}$-1,2,3,4-TCDD[a]		50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]		125	125	125	125	125	125	125

[a]Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.

[b]Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF, and OCDD internal standards.

Table 6. Ions Monitored for HRGC/HRMS analysis of PCDD/PCDFs
(S = internal/recovery standard)

Descriptor	Accurate(a) Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_6O$	HxCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_7O$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK

(Continued)

Table 6. Continued

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8642	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

(Continued)

Table 6. Continued

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK

(a)The following nuclidic masses were used:

H = 1.007825	O = 15.994915
C = 12.000000	^{35}Cl = 34.968853
13C = 13.003355	^{37}Cl = 36.965903

Table 7. Recommended GC Operating Conditions

Column coating	DB-5
Film thickness	0.25 um
Column dimension	60 m x 0.32 mm
Injector temperature	270° C
Splitless valve time	45 s
Interface temperature	Function of the final temperature

Temperature program

Stage	Init. Temp. (° C)	Init. Hold. Time (min)	Temp. Ramp (° C/min)	Fin. Temp. (° C)	Fin. Hol. Time
1	200	2	5	220	16
2			5	235	7
3			5	330	5
			Total time: 60 min		

Table 8. PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60-m DB-5 Column

No. of Chlorine Atoms	PCDD-Positional Isomer		PCDF-Positional Isomer	
	Early Eluter	Late Eluter	Early Eluter	Late Eluter
4[a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/ 1,2,4,7,9	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
6	1,2,3,4,6,8	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
7	1,2,3,4,6,7,8	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,9
8	1,2,3,4,6,7,8,9		1,2,3,4,6,7,8,9	

[a] In addition to these two PCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8-, and 1,2,3,9-TCDD isomers must also be present.

Table 9. Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Control Limits upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.24	1.86
6	$\frac{M+2}{M+4}$	1.24	1.05	1.43
6(a)	$\frac{M}{M+2}$	0.51	0.43	0.59
7(b)	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	0.89

(a)Used only for ^{13}C-HxCDF (IS).
(b)Used only for ^{13}C-HpCDF (IS).

Table 10. Relative Response Factor [RRF (number)] Attributions

Number	Specific Congener Name
1	2,3,7,8-TCDD (and total TCDDs)
2	2,3,7,8-TCDF (and total TCDFs)
3	1,2,3,7,8-PeCDD (and total PeCDDs)
4	1,2,3,7,8-PeCDF
5	2,3,4,7,8-PeCDF
6	1,2,3,4,7,8-HxCDD
7	1,2,3,6,7,8-HxCDD
8	1,2,3,7,8,9-HxCDD
9	1,2,3,4,7,8-HxCDF
10	1,2,3,6,7,8-HxCDF
11	1,2,3,7,8,9-HxCDF
12	2,3,4,6,7,8-HxCDF
13	1,2,3,4,6,7,8-HpCDD (and total HpCDDs)
14	1,2,3,4,6,7,8-HpCDF
15	1,2,3,4,7,8,9-HpCDF
16	OCDD
17	OCDF
18	$^{13}C_{12}$-2,3,7,8-TCDD
19	$^{13}C_{12}$-2,3,7,8-TCDF
20	$^{13}C_{12}$-1,2,3,7,8-PeCDD
21	$^{13}C_{12}$-1,2,3,7,8-PeCDF
22	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
23	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
24	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
25	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
26	$^{13}C_{12}$-OCDD
27	Total PeCDFs
28	Total HxCDFs
29	Total HxCDDs
30	Total HpCDFs

TABLE 11. 2,3,7,8-TCDD Equivalent Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.04
4	1, 2,3,7,8,9-HxCDD	0.04
5	1, 2,3,4,7,8-HxCDD	0.04
6	1, 2,3,4,6,7,8-HpCDD	0.001
7	* Total - TCDD	0.01
8	* Total - PeCDD	0.005
9	* Total - HxCDD	0.0004
10	* Total - HpCDD	0.00001
11	2,3,7,8-TCDF	0.10
12	1,2,3,7,8-PeCDF	0.10
13	2,3,4,7,8-PeCDF	0.10
14	1,2,3,6,7,8-HxCDF	0.01
15	1,2,3,7,8,9-HxCDF	0.01
16	1,2,3,4,7,8-HpCDF	0.01
17	2,3,4,6,7,8-HxCDF	0.01
18	1,2,3,4,6,7,8-HpCDF	0.001
19	1,2,3,4,7,8,9-HpCDF	0.001
20	* Total - TCDF	0.001
21	* Total - PeCDF	0.001
22	* Total - HxCDF	0.0001
23	* Total - HpCDF	0.00001

*Excluding the 2,3,7,8-substituted congeners.

Table 12. Toxicity Equivalency Factor: Analyte Relative Retention Time Reference Attributions

Analyte	Analyte RRT Reference[a]
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF

(a) The retention time of 2,3,4,7,8-PeCDF on the DB-5 column is measured relative to $^{13}C_{12}$-1,3,7,8-PeCDF and the retention time of 1,2,3,4,7,8,9-HpCDF relative to $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF.

QUALITY ASSURANCE REQUIREMENTS

(Quality Assessment and Quality Control)

(Exhibit E)

1. SUMMARY OF QA/QC ANALYSES

- Initial and periodic calibration and instrument performance checks.

- HRGC/HRMS method blank analysis.

- Field blank analyses (Section 2.4.2, this exhibit); a minimum of one fortified field blank shall be analyzed with each sample batch; an additional fortified field blank must be analyzed when a new lot of absorbent or solvent is used. A matrix spike may be used in place of a fortified field blank.

- Analysis of a batch of samples with accompanying QA/QC analyses:

  Sample Batch -- $\leq$ 24 samples, including field blank and rinsate sample(s).

  Additional QA/QC analyses per batch:

Fortified field blank or matrix spike (MS)	1
Method blank (MB)	1
Duplicate sample or matrix spike duplicate (MSD)	1
Total	3

- "Blind" QC samples (soil, sediment, water) may be submitted to the laboratory as ordinary samples included in the sample batch.

Blind samples include:

Uncontaminated soil, sediment, or water samples

Split samples,

Unidentified duplicates, and

Performance evaluation samples.

2. QUALITY ASSESSMENT/QUALITY CONTROL

2.1 Performance Evaluation Samples -- Included among the samples in all batches will be samples (blind or double blind) containing known amounts of unlabeled 2,3,7,8-substituted PCDDs/PCDFs or other PCDD/PCDF congeners.

2.2 Performance Check Solutions

2.2.1 At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3) shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound (PFK is recommended).

These procedures are described in Section 8 of Exhibit D. If the required criteria are not met, remedial action must be taken before any

samples are analyzed.

2.2.2 To validate positive sample data, the routine or continuing calibration (HRCC-3) and the mass resolution check must be performed also at the end of each 12-hour period during which samples are analyzed. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

2.2.2.1 If the laboratory operates only during one period (shift) each day of 12 hours or less, the GC performance check solution must be analyzed only once (at the beginning of the period) to validate the data acquired during the period. However, the mass resolution and continuing calibration checks must be performed at the beginning as well as at the end of the period.

2.2.2.2 If the laboratory operates during consecutive 12-hour periods (shifts), analysis of the GC performance check solution must be performed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

2.2.3 Results of at least one analysis of the GC column performance check solution and of two mass resolution and continuing calibration checks must be reported with the sample data collected during a 12-hour period.

2.2.4 Deviations from criteria specified for the GC performance check or for

the mass resolution check (Section 8, Exhibit D) invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed (Exhibit C).

If the routine calibration run fails at the beginning of a 12-hour shift, the instructions in Exhibit D, Section 9.4.4 must be followed. If the continuing calibration check performed at the end of a 12-hour period fails by no more than 25 percent RPD, use the mean $\overline{RRF}$s from the two daily routine calibration runs to compute the analyte concentrations, instead of the $\overline{RRF}$s obtained from the initial calibration. A new initial calibration (new $\overline{RRF}$s) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent. Failure to perform a new initial calibration immediately following the analysis of the samples will automatically require reanalysis of all positive sample extracts analyzed before the failed end-of-shift continuing calibration check.

2.3 The GC column performance check mixture, high-resolution concentration calibration solutions, and the sample fortification solutions may be obtained from the EMSL-LV. However, if not available from the EMSL-LV, standards can be obtained from other sources, and solutions can be prepared in the laboratory. Concentrations of all solutions containing 2,3,7,8-substituted PCDDs/PCDFs, which are not obtained from the EMSL-LV, must be verified by comparison with the EPA standard solutions that

are available from the EMSL-LV. (Refer to Appendix B, Exhibit D, for details on the recommended standards traceability procedure.)

2.4 Blanks

2.4.1 Method Blank

One method blank is required per batch of samples. To that effect, perform all steps detailed in the analytical procedure (Section 12, Exhibit D) using all reagents, standards, equipment, apparatus, glassware and solvents that would be used for a sample analysis, but omit addition of the soil, aqueous or any other matrix sample portion.

2.4.1.1 The method blank must contain the same amount of $^{13}C_{12}$-labeled internal standards that is added to samples before extraction.

2.4.1.2 An acceptable method blank exhibits no positive response as stated in Section 3.16, Exhibit D. If the method blank, which was extracted along with a batch of samples, is contaminated, all positive samples must be rerun (Exhibit C).

2.4.1.2.1 If the above criterion is not met, check solvents, reagents, fortification solutions, apparatus and glassware to locate and eliminate the source of contamination before any further samples are extracted and analyzed.

2.4.1.2.2 If new batches of reagents or solvents contain interfering

contaminants, purify or discard them.

2.4.2 Field Blanks

Each batch of samples contains a field blank sample of uncontaminated soil, sediment or water that is to be fortified before analysis according to Section 2.4.2.1 (this exhibit). In addition to this field blank, a batch of samples may include a rinsate, which is a portion of the solvent (usually trichloroethylene) that was used to rinse sampling equipment. The rinsate is analyzed to assure that the samples were not contaminated by the sampling equipment.

2.4.2.1 Fortified Field Blank

2.4.2.1.1 Weigh a 10-g portion or use 1 L (for aqueous samples) of the specified field blank sample and add 100 uL of the solution containing the nine internal standards (Table 2, Exhibit D) diluted with 1.5 mL acetone (Section 12.1, Exhibit D).

2.4.2.1.2 Extract by using the procedures beginning in Sections 12.2.5 or 12.2.6 of Exhibit D, as applicable, add 10 uL of the recovery standard solution (Section 12.9.2, Exhibit D) and analyze a 2-uL aliquot of the concentrated extract.

2.4.2.1.3 Calculate the concentration (Section 14.1, Exhibit D) of 2,3,7,8-substituted PCDDs/PCDFs and the percent recovery of the internal standards (Section 14.2, Exhibit D). If the percent recovery at the

measured concentration of any 2,3,7,8-substituted PCDD/PCDF congener is <40 percent or >120 percent, report the results to SMO before proceeding with the samples.

2.4.2.1.4 Extract and analyze a new simulated fortified field blank whenever new lots of solvents or reagents are used for sample extraction or for column chromatographic procedures.

2.4.2.2 Rinsate Sample

2.4.2.2.1 The rinsate sample must be fortified like a regular sample.

2.4.2.2.2 Take a 100-mL (± 0.5 mL) portion of the sampling equipment rinse solvent (rinsate sample), filter, if necessary, and add 100 uL of the solution containing the nine internal standards (Table 2, Exhibit D).

2.4.2.2.3 Using a Kuderna-Danish appparatus, concentrate to approximately 5 mL.

2.4.2.2.4 Transfer the 5-mL concentrate from the K-D concentrator tube in 1-mL portions to a 1-mL minivial, reducing the volume in the minivial as necessary with a gentle stream of dry nitrogen.

2.4.2.2.5 Rinse the K-D concentrator tube with two 0.5-mL portions of hexane and transfer the rinses to the 1-mL minivial. Blow down with dry nitrogen as necessary.

2.4.2.2.6 Just before analysis, add 10 uL tridecane recovery standard solution (Table 2, Exhibit D), and reduce the volume to a final volume of 10 uL, or 50 uL, as necessary (Section 12.9.2, Exhibit D). No column chromatography is required.

2.4.2.2.7 Analyze an aliquot following the same procedures used to analyze samples (Section 13, Exhibit D).

2.4.2.2.8 Report percent recovery of the internal standard and the presence of any PCDD/PCDF compounds on Form (to be determined) in pg/mL of rinsate solvent.

2.5 Duplicate Analyses

2.5.1 In each batch of samples, locate the sample specified for duplicate analysis, and analyze a second 10-g soil or sediment sample portion or 1-L water sample, or an appropriate amount of the type of matrix under consideration.

2.5.1.1 The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) must agree within 25 percent relative difference (difference expressed as percentage of the mean). If the relative difference is >25 percent for any one of the fifteen 2,3,7,8-substituted PCDDs/PCDFs, the laboratory shall immediately contact the Sample Management Office for resolution of the problem. Report all results.

2.5.1.2 Recommended actions to help locate problems:

2.5.1.2.1 Verify satisfactory instrument performance (Section 8, Exhibit D).

2.5.1.2.2 If possible, verify that no error was made while weighing the sample portions.

2.5.1.2.3 Review the analytical procedures with the performing laboratory personnel.

2.6 Matrix Spike and Matrix Spike Duplicate

2.6.1 Locate the sample for the MS and MSD analyses (the sample may be labeled "double volume").

2.6.2 Add on appropriate volume of the matrix spike fortification solution (Exhibit D, Section 3.24), adjusting the fortification level as specified in Exhibit D, Table 1, under IS Spiking Levels.

2.6.3 Analyze the MS and MSD samples as described in Exhibit D, Section 12.

2.6.4 The results obtained from the MS and MSD samples (percent recovery and concentrations of 2,3,7,8-substituted PCDDs/PCDFs) must agree within 20 percent relative difference.

2.7 Percent Recovery of the Internal Standards

For each sample, method blank and rinsate, calculate the percent recovery (Section 14.2, Exhibit D). It is recommended that the percent recovery be >40 percent and <120 percent for all 2,3,7,8-substituted internal standards.

NOTE: A low or high percent recovery for a blank does not require discarding the analytical data but it may indicate a potential problem with future analytical data.

2.8 Identification Criteria

2.8.1 If either one of the identification criteria appearing in Sections 13.4.1.1 through 13.4.1.4, Exhibit D, is not met for an homologous series, it is reported that the sample does not contain unlabeled 2,3,7,8-substituted PCDD/PCDF isomers for that homologous series at the calculated detection limit (Section 14.5, Exhibit D).

2.8.2 If the first initial identification criteria (Sections 13.4.1.1 through 13.4.1.4) are met, but the criteria appearing in Sections 13.4.1.5 and 13.4.2.1, Exhibit D, are not met, that sample is presumed to contain interfering contaminants. This must be noted on the analytical report form, and the sample must be rerun or the extract reanalyzed. Detailed sample rerun and extract reanalysis requirements are presented in Exhibit C.

2.9 Blind QA/QC Samples

Included among soil, sediment and aqueous samples may be QA/QC samples

that are not specified as such to the performing laboratory. Types that may be included are:

2.9.1 Uncontaminated soil, sediment, or water.

2.9.1.1 If a false positive is reported for such a sample, the laboratory shall be required to rerun the entire associated batch of samples (Section to be determined, Exhibit C).

2.9.2 Split samples -- composited sample portions sent to more than one laboratory.

2.9.3 Unlabeled field duplicates -- two portions of a composited sample.

2.9.4 Performance evaluation samples -- soil/sediment or water samples containing a known amount of unlabeled 2,3,7,8-substituted PCDDs/PCDFs and/or other PCDD/PCDF compounds.

2.9.4.1 If the performance evaluation sample result falls outside the acceptance windows established by the EPA, the laboratory shall be required to rerun the entire associated batch of samples (Exhibit C).

NOTE: EPA acceptance windows are based on previously generated data.

2.10 Quality Control Charts

The performance of the entire measurement system (i.e., from the extraction

of the sample to the mass spectrometric determination) must be documented by using germane control charts. The selection and design of a specific measurement control chart must be accomplished in a rational manner so that the measurement process can be adequately surveyed. By using the standard deviations obtained from control samples or control runs, the laboratory must delineate control limits, i.e., statistically congruous extreme values, which should warn the operator of possible problems. It is recommended to consider the values corresponding to two standard deviations as warning limits and the values from three standard deviations as control limits (i.e., corrective actions are required). For some particular applications, however, the control limits must not exceed the limits set forth by the EPA (e.g., ion-abundance ratios). [Specific and required QC charts, such as mass and GC resolutions, ion abundance ratios, RRF values, etc., will be described in the final version of this protocol.]

2.11 Standard Operating Procedures (SOPs)

As part of the quality assurance program, the laboratory must use in-house SOPs describing how the basic operations executed within the laboratory are done.

2.12 Internal Audits

Internal audits of records, instrumentation performances and calibration data are highly encouraged in order to identify defects that could compromise the quality of the results.

2.13 Records

At each laboratory, records must be maintained on site for six months after contract completion to document the quality of all data generated during the contract period. Before any records are disposed, written concurrence from the Contracting Officer must be obtained.

2.14 Unused portions of samples and sample extracts must be preserved for six months after sample receipt; appropriate samples may be selected by EPA personnel for further analyses.

2.15 Reuse of glassware is to be minimized to avoid the risk of contamination.

3. Laboratory Evaluation Procedures

3.1 On a quarterly basis, the EPA Project Officer or his/her designated representatives may conduct an evaluation of the laboratory to ascertain that the laboratory is meeting contract requirements. This section outlines the procedures which may be used by the Project Officer or his/her authorized representative in order to conduct a successful evaluation of laboratories conducting dioxin analyses according to this protocol. The evaluation process consists of the following steps: 1) analysis of a performance evaluation (PE) sample, and 2) on-site evaluation of the laboratory to verify continuity of personnel, instrumentation, and quality assurance/quality control functions. The following is a description of these two steps.

3.2 Performance Evaluation (PE) Sample Analysis

3.2.1 The PE sample set will be sent to a participating laboratory to verify the laboratory's continuing ability to produce acceptable analytical results. The PE sample will be representative of the types of samples that will be analyzed under this contract.

3.2.2 When the PE sample results are received, they are scored using the PE Sample Score Sheet shown in Figure (to be determined). If a false positive (e.g., a PE sample not containing 2,3,7,8-TCDD or other PCDD/PCDF but reported by the laboratory to contain it or them) is reported, the laboratory has failed the PE analysis requirement. The Project Officer will notify the laboratory immediately if such an event occurs.

3.2.3 As a general rule, a laboratory should achieve 75 percent or more of the total possible points for all three categories listed on the PE Sample Score Sheet, and 75 percent or more of the maximum possible points in each category, to be considered acceptable for this program. However, the Government reserves the right to accept scores of less than 75 percent.

3.2.4 If unanticipated difficulties with the PE samples are encountered, the total points may be adjusted by the Government evaluator in an impartial and equitable manner for all participating laboratories.

3.3 On-site Laboratory Evaluation

3.3.1 An on-site laboratory evaluation is performed to verify that (1) the laboratory is maintaining the necessary minimum level in instrumentation and levels of experience in personnel committed to the contract and (2) that the necessary quality assurance activities are being carried out. It also serves as a mechanism for discussing laboratory weaknesses identified through routine data audits, PE sample analyses results, and prior on-site evaluations. Photographs may be taken during the on-site laboratory evaluation tour.

3.3.2 The sequence of events for the on-site evaluations is shown in Figure (to be determined). A Site Evaluation Sheet (SES) is used to document the results of the evaluation.

EPA METHOD 3050
ACID DIGESTION OF SEDIMENTS, SLUDGES AND SOILS

Modifications: **a) Sb digestion *not* to exceed 95° C**
b) HCl reflux for ICP fraction

METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Paragraph 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mo, Pb, Ni, K, Na, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V. A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers: 250-mL.
4.2 Watch glasses.
4.3 Drying ovens: That can be maintained at 30°C.
4.4 Thermometer: That covers range of 0 to 200°C.
4.5 Whatman No. 41 filter paper (or equivalent).
4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.4 Hydrogen peroxide (30%) (H_2O_2): Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqeuous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation.

Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.
NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.5.2 **Centrifugation:** Centrifugation at 2,000-3,000 rpm for 10 min is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.6.2 **Centrifugation:** Centrifugation at 2,000-3,000 for 10 min is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations:

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, preparation blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

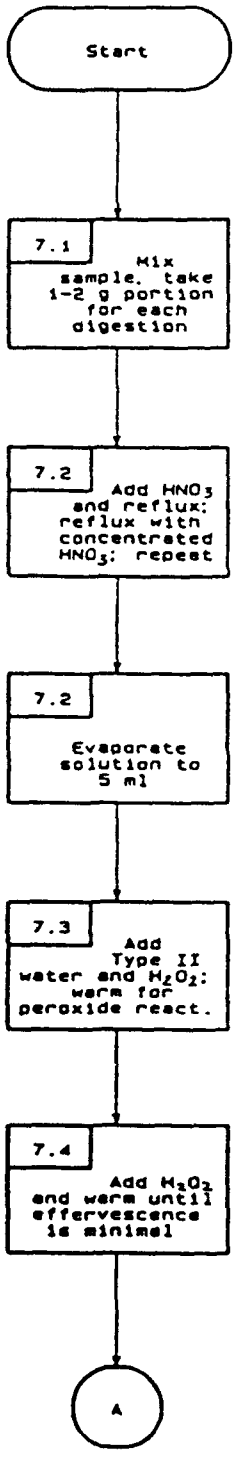
8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

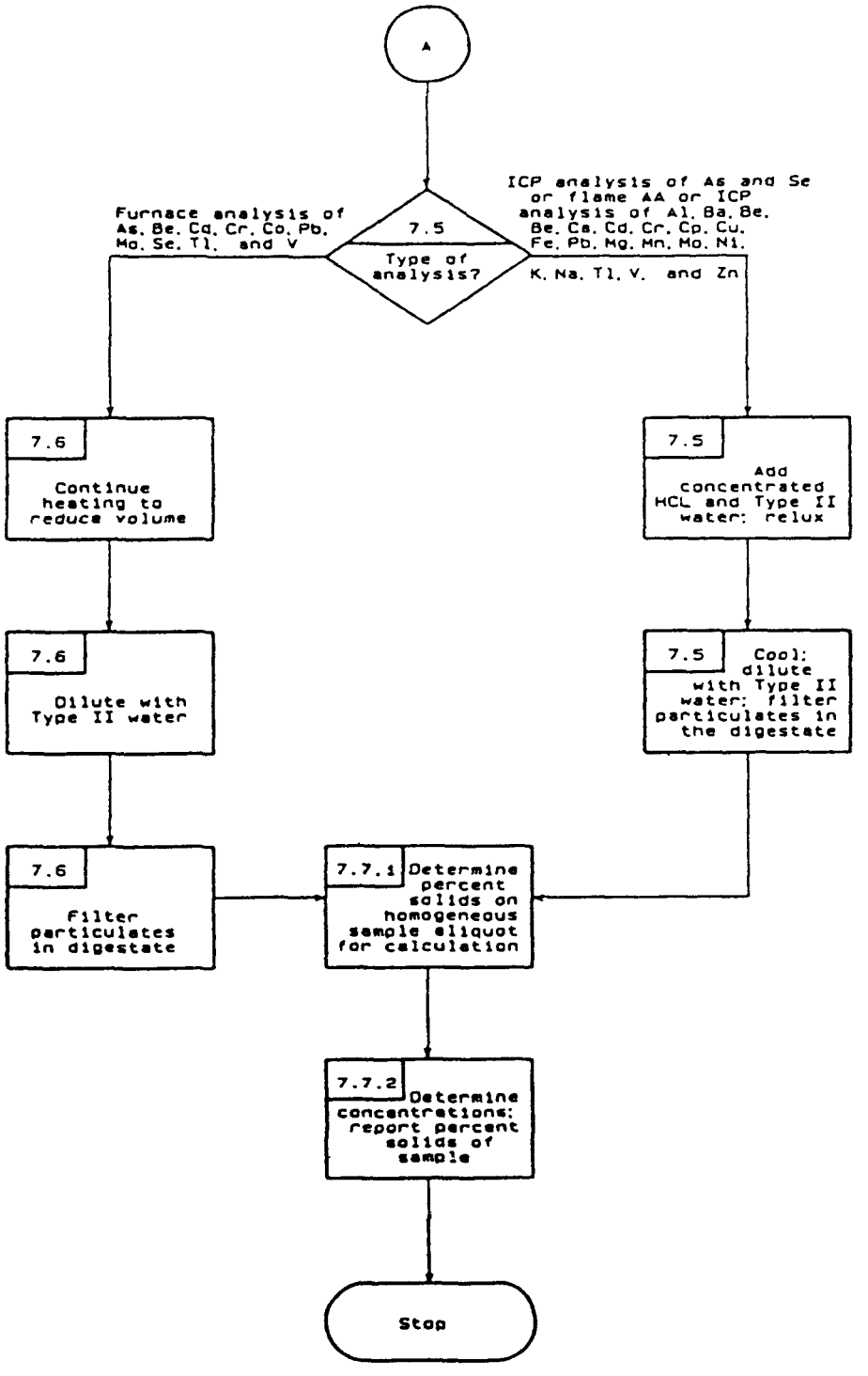


Revision 0
Date September 1986

METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

(Continued)



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Date September 1986

3.3 METHODS FOR DETERMINATION OF METALS

This manual contains six analytical techniques for trace metal determinations: inductively coupled argon plasma emission spectrometry (ICP), direct-aspiration or flame atomic absorption spectrometry (FAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA.

Flame AAS (FLAA) determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

EPA METHOD 204.2
ANTIMONY
ATOMIC ABSORPTION, FURNACE TECHNIQUE

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 20–300 *ug/l*
Detection Limit: 3 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual. .

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

EPA METHOD 206.2
ARSENIC
ATOMIC ABSORPTION, FURNACE TECHNIQUE

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/l).

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100ml.

3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.

2. Cool and bring back to 50 ml with deionized distilled water.

3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30%H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 ug/1 and spiked with concentrations of 2, 10 and 25 ug/1, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were ±8.8%, ±8.2%, ±5.4% and ±8.7%, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 ug As/1, the standard deviations were ±0.7, ±1.1 and ±1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

EPA METHOD 270.2
SELENIUM
ATOMIC ABSORPTION, FURNACE TECHNIQUE

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 2 *ug/l*

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Approved for NPDES and SDWA
Issued 1978

Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides ($>$ 800 mg/1) and sulfate ($>$ 200 mg/1). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/1, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing $<$ 2 *ug*/1 and spiked with a concentration of 20 *ug*/1, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 *ug*/1 level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 *ug*/1, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 *ug* Se/1, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

EPA METHOD 279.2
THALLIUM
ATOMIC ABSORPTION, FURNACE TECHNIQUE

THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 5–100 ug/l
Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

EPA 245.5
MERCURY IN SEDIMENT
MANUAL COLD VAPOR TECHNIQUE

MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
   1.1 This procedure[1] measures total mercury (organic † inorganic) in soils, sediments, bottom deposits and sludge type materials.
   1.2 The range of the method is 0.2 to 5 *ug/g*. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
   2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
   2.2 An alternate digestion[2] involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
   3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
   3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
   4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
   4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the **BOD** bottle should be purged before the addition of stannous sulfate.
5. Apparatus
   5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

   NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

Issued 1974

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the

working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass value and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass value, remove the fritted tubing from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a **BOD** bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-

hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation
   9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.
   9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\,Hg/g = \frac{ug\,Hg \text{ in the aliquot}}{\text{wt of the aliquot in gms}}$$

   9.3 Report mercury concentrations as follows: Below 0.1 *ug*/gm, <0.1; between 0.1 and 1 *ug*/gm, to the nearest 0.01 *ug*; between 1 and 10 *ug*/gm, to nearest 0.1 *ug*; above 10 *ug*/gm, to nearest *ug*.
10. Precision and Accuracy
   10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 *ug*/g ±0.02 and 0.82 *ug*/g ±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
2. Salma, M., private communication, EPA Cal/Nev Basin Office, Almeda, California.

EPA METHOD 200.7
INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES METHOD

Modification: + 42 Element Screen

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes—Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects (See 5)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary In time, other elements may be added as more information becomes available and as required

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP) The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes The photocurrents from the photomultiplier tubes are processed and controlled by a computer system A background correction technique is required to compensate for variable background contribution to the

determination of trace elements Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5 1 (and tests for their presence as described in 5 2) should also be recognized and appropriate corrections made

3. Definitions

3.1 Dissolved — Those elements which will pass through a 0 45 μm membrane filter.

3.2 Suspended — Those elements which are retained by a 0 45 μm membrane filter

3.3 Total — The concentration determined on an unfiltered sample following vigorous digestion (9 3), or the sum of the dissolved plus suspended concentrations (9 1 plus 9 2.)

3.4 Total recoverable — The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (9 4)

3.5 Instrumental detection limit — The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength

3.6 Sensitivity — The slope of the analytical curve, i e functional relationship between emission intensity and concentration

3.7 Instrument check standard — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis (See 7 6 1)

3.8 Interference check sample — A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7 6 2)

3.9 Quality control sample — A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 Calibration standards — a series of know standard solutions used by the analyst for calibration of the instrument (i e , preparation of the analytical curve). (See 7 4)

3.11 Linear dynamic range — The concentration range over which the analytical curve remains linear

3.12 Reagent blank — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme (See 7 5 2)

3.13 Calibration blank — A volume of deionized, distilled water acidified with HNO_3 and HCl (See 7 5 1)

3.14 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard (See 10 6 1)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis Additional references to laboratory safety are available and have been identified (14 7, 14 8 and 14 9) for the information of the analyst

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements They can be summarized as follows

5 1 1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element, 2) unresolved overlap of molecular band spectra, 3) background contribution from continuous or recombination phenomena, and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1 The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed

The interference information, which was collected at the Ames Laboratory,[1] is expressed at analyte concentration equivalents (i e, false analyte concentrations) arising from 100 mg L of the interferent element The suggested use of this information is as follows Assume that arsenic (at 193 696 nm) is to be determined in a sample containing approximately 10 mg L of aluminum According to Table 2, 100 mg L of aluminum would yield a false signal for arsenic equivalent to approximately 1 3 mg L Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0 13 mg L The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3 Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 5% of the peaks generated by the

Ames Laboratory, USDOE, Iowa State University, Ames, Iowa 50011

analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766 491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aersol flow-rate causing instrumental drift Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures These types of interferences can be highly dependent on matrix type and the specific analyte element

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5 2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 % of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix) If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect *Caution:* The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See 5 2.3)

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer

6.1.1 Computer controlled atomic emission spectrometer with background correction

6.1.2 Radiofrequency generator

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions — Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent Redistilled acids are acceptable

7.1.1 Acetic acid, conc. (sp gr 1.06).

7.1.2 Hydrochloric acid, conc. (sp gr 1.19)

7.1.3 Hydrochloric acid, (1+1). Add 500 mL conc HCl (sp gr 1.19) to 400 mL deionized, distrilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc (sp gr 1.41).

7.1.5 Nitric acid,(1+1): Add 500 mL conc HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 *Dionized, distilled water:* Prepare by passing distilled water through a mixed bed of cation and anion exchange resins Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals All salts must be dried for 1 h at 105°C unless otherwise specified (CAUTION Many metal salts are extremely toxic and may be fatal if swallowed Wash hands thoroughly after handling) Typical stock solution preparation procedures follow

7.3.1 Aluminum solution, stock, 1 mL = 100 μg Al· Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water

7.3.2 Antimony solution stock, 1 mL = 100 μg Sb Dissolve 0.2669 g K(SbO) $C_4H_4O_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water

7.3.3 Arsenic solution, stock, 1 mL = 100 μg As. Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.4 Barium solution, stock, 1 mL = 100 μg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water

7.3.5 Beryllium solution, stock, 1 mL = 100 μg Be: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4\ 4H_2O$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.6 Boron solution, stock, 1 mL = 100 μg B. *Do not dry.* Dissolve 0.5716 g anhydrous H_3BO_3 in deionized distilled water dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture

7.3.7 Cadmium solution, stock, 1 mL = 100 μg Cd: Dissolve 0 1142 g CdO in a minimum amount of (1+1) HNO_3 Heat to increase rate of dissolution. Add 10.0 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 Calcium solution, stock, 1 mL = 100 μg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3 Add 10 0 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.9 Chromium solution, stock, 1 mL = 100 μg Cr Dissolve 0 1923 g of CrO_3 in deionized, distilled water When solution is complete, acidify with 10 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.10 Cobalt solution, stock, 1 mL = 100 μg Co Dissolve 0 1000 g of cobalt metal in a minimum amount of (1+1) HNO_3 Add 10 0 mL (1+1) HCl and dilute to 1,000 mL with deionized distilled water

7.3.11 Copper solution, stock, 1 mL = 100 μg Cu Dissolve 0 1252 g CuO in a minimum amount of (1+1) HNO_3 Add 10 0 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.12 Iron solution, stock, 1 mL = 100 μg Fe Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.13 Lead solution, stock, 1 mL = 100 μg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.14 Magnesium solution, stock, 1 mL = 100 μg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.15 Manganese solution, stock, 1 mL = 100 μg Mn Dissolve 0 1000 g of manganese metal in the acid mixture 10 mL conc HCl and 1 mL conc HNO_3, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 Molybdenum solution, stock, 1 mL = 100 μg Mo: Dissolve 0 2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 Nickel solution, stock, 1 mL = 100 μg Ni Dissolve 0.1000 g of nickel metal in 10 mL hot conc HNO_3, cool and dilute to 1,000 mL with deionized, distilled water

7.3.18 Potassium solution, stock, 1 mL = 100 μg K Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water dilute to 1,000 mL

7 3.19 Selenium solution, stock, 1 mL = 100 μg Se *Do not dry* Dissolve 0 1727 g H_2SeO_3 (actual assay 94 6%) in deionized, distilled water and dilute to 1,000 mL

7.3.20 Silica solution, stock, 1 mL = 100 μg SiO_2 *Do not dry* Dissolve 0 4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water Add 10 0 mL conc HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.21 Silver solution, stock, 1 mL = 100 μg Ag Dissolve 0 1575 g $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL conc HNO_3 Dilute to 1,000 mL with deionized, distilled water

7 3 22 Sodium solution, stock, 1 mL = 100 μg Na Dissolve 0 2542 g NaCl in deionized, distilled water Add 10 0 mL conc HNO_3 and dilute to 1 000 mL with deionized, distilled water

7.3.23 Thallium solution, stock, 1 mL = 100 μg Tl. Dissolve 0 1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 Vanadium solution, stock, 1 mL = 100 μg V· Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3 Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.3.25 Zinc solution, stock, 1 mL = 100 μg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10 0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water

7.4 *Mixed calibration standard solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (See 7.4 1 thru 7 4.5) Add 2 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water (See Notes 1 and 6) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities Care should be taken when preparing the mixed standards that the elements are compatible and stable Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7 6 3) Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1

7.4.1 Mixed standard solution I— Manganese, beryllium, cadmium, lead, and zinc

7 4.2 Mixed standard solution II – Barium, copper, iron, vanadium and cobalt

7 4 3 Mixed standard solution III – Molybdenum silica arsenic and selenium

7 4 4 Mixed standard solution IV – Calcium sodium potassium aluminum chromium and nickel

7.4.5 *Mixed standard solution V*—Antimony, boron, magnesium, silver, and thallium

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 *The calibration blank* is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 *The reagent blank* must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent 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.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

7.6.1 The *instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1.)

7.6.2 The *interference check sample* is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest by known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/L or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2.)

7.6.3 The *quality control sample* should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3.)

8. Sample handling an preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order. (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware, however, the analyst should be be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chomic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc HNO_3. Cover the

beaker with a watch glass and heat gently The warm acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3 Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min to dissolve any precipitated or residue material Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer (See Note 4.) Adjust the volume based on the expected concentrations of elements present This volume will vary depending on the elements to be determined (See Note 6) The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended"

NOTE 4 In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

9.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (See Note 5) Add 3 mL of conc HNO_3 Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry Cool the beaker and add another 5 mL portion of conc HNO_3 Cover the beaker with a watch glass and return to the hot plate Increase the temperature of the hot plate so that a gentle reflux action occurs Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing) Again, evaporate to near dryness and cool the beaker Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min to dissolve any precipitate or residue resulting from evaporation Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer (See Note 4) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

NOTE 5 If low determinations of boron are critical, quartz glassware should be use.

NOTE 6. If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker (See Note 5) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4) Adjust the volume to 100 mL and mix The sample is now ready for analysis Concentrations so determined shall be reported as "total"

10. Procedure

10.1 Set up instrument with proper operating parameters established in 6 2 The instrument must be allowed to become thermally stable before beginning This usually requires at least 30 min of operation prior to calibration

10.2 Initiate appropriate operating configuration of computer

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in 7 4 Flush the system with the calibration blank (7 5.1) between each standard (See Note 7) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error)

NOTE 7 For boron concentrations greater than 500 µg/L extended flush times of 1 to 2 min may be required

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower) If they do, follow the recommendations of the instrument manufacturer to correct for this condition

10.5 Begin the sample run flushing the system with the calibration blank solution (7 5.1) between each sample (See Note 7) Analyze the instrument check standard (7 6 1) and the calibration blank (7 5 1) each 10 samples

10.6 If it has been found that method of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14 2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards It will not correct for additive interference which causes a baseline shift The simplest version of this technique is the single-addition method The procedure is as follows Two identical aliquots of the sample solution, each of volume V_x, are taken To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s To the second (labeled B) is added the same volume V_s of the solvent The analytical signals of A and B are measured and corrected for nonanalyte signals The unknown sample concentration c_x is calculated

$$c_x = \frac{S_B V_S c_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively V_S and c_S should be chosen so that S_A is roughly twice S_B on the average It is best if V_S is made much less than V_x, and thus c_S is much greater than c_x, to avoid excess dilution of the sample matrix If a separation or concentration step is used, the additions are best made first and carried through the entire procedure For the results from this technique to be valid, the following limitations must be taken into consideration

1 The analytical curve must be linear

2 The chemical form of the analyte added must respond the same as the analyte in the sample

3 The interference effect must be constant over the working range of concern
4. The signal must be corrected for any additive interference

11. Calculation

11.1 Reagent blanks (7 5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow.

12.1.1 Analyze an appropriate instrument check standard (7 6 1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ±5% of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated

Analyze the calibration blank (7 5 1) at a frequency of 10% The result should be within the established control limits of two standard deviations of the mean value If not, repeat the analysis two more times and average the three results If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7 6 2) at the beginning, end, and at periodic intervals throughout the sample run Results should fall within the established control limits of 1 5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument

12.1.3 A quality control sample (7 6 3) obtained from an outside source must first be used for the initial verification of the calibration standards A fresh dilution of this sample shall be anlayzed every week thereafter to monitor their stability If the results are not within ±5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration

Precision and Accuracy

13.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation

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Table 1. Recommended Wavelengths [1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, µg/L[2]
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249 773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231 604	15
Potassium	766.491	see[3]
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[1] *The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1 1.).*

[2] *The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines, "EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.*

[3] *Highly dependent on operating conditions and plasma position.*

Table 2. *Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level*

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1 4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455 403	—	—	—	—	—	—	—	—	—	—
Beryllium	313 042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226 502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317 933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267 716	—	—	—	—	0.003	—	0.04	—	—	0 04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0 03	0.15	—
Copper	324 754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279 079	—	0.02	0 11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257.610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202.030	0 05	—	—	—	0.03	—	—	—	—	—
Nickel	231 604	—	—	—	—	—	—	—	—	—	—
Selenium	196 026	0 23	—	—	—	0.09	—	—	—	—	—
Silicon	288 158	—	—	0 07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0 08	—
Thallium	190.864	0 30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0 05	—	0 005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0 14	—	—	—	0 29	—	—

Table 3. *Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2.*

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

Table 4. ICP Precision and Accuracy Data

	Sample # 1			Sample #2			Sample #3		
Element	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3 3
V	750	749	1.8	70	69	2.9	170	169	1 1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3 3
Cu	250	235	5.1	11	11	40	70	67	7 9
Fe	600	594	3.0	20	19	15	180	178	6 0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9 4
Se	40	32	21.9	6	8.5	42	10	8 5	8 3

Not all elements were analyzed by all laboratories.

MODIFICATION TO EPA METHOD 200.7 FOR 42 ELEMENT ICP SCREEN

Attached is a table of recommended wavelengths and minimum levels for this procedure. This procedure requires a sequential ICP instrument (2 channel minimum) interfaced with a computerized data system capable of the short sampling times and narrow survey windows necessary to perform a semi-quantitative ICP screen.

ICP SCREEN ELEMENTS, WAVELENGTHS, & LTL

Requested Element	Symbol	Wavelength*	LTL (mg/l)** (Note: LTL = Minimum Level)
[illegible]	Al-SS	396.152	0.1
[illegible]	Sb-SS	206.833	1
[illegible]	As-SS	197.197	1
[illegible]	Ba-SS	455.403	0.1
[illegible]	Be-SS	313.042	0.1
Bismuth	Bi-SS	223.061	0.5
[illegible]	B-SS	249.773	0.1
[illegible]	Cd-SS	214.438	0.1
[illegible]	Ca-SS	393.366	0.1
Cerium	Ce-SS	413.765	1
[illegible]	Cr-SS	205.552	0.1
[illegible]	Co-SS	238.892	0.1
[illegible]	Cu-SS	324.754	0.1
Dysprosium	Dy-SS	353.170	0.1
Erbium	Er-SS	349.910	0.1
Europium	Eu-SS	381.967	0.1
Gadolinium	Gd-SS	342.247	0.5
Gallium	Ga-SS	294.364	0.5
Germanium	Ge-SS	265.118	0.5
Gold	Au-SS	242.765	1
Hafnium	Hf-SS	277.336	1
Holminum	Ho-SS	345.600	0.5
Indium	In-SS	230.606	1
Iodine	I-SS	183.038	1
Iridium	Ir-SS	224.268	1
[illegible]	Fe-SS	238.204	0.1
Lanthanum	La-SS	379.478	0.1
[illegible]	Pb-SS	220.353	0.5
Lithium	Li-SS	670.781	0.1
Lutetium	Lu-SS	261.542	0.1
[illegible]	Mg-SS	279.553	0.1
[illegible]	Mn-SS	257.610	0.1
[illegible]	Hg-SS	194.232	0.5
[illegible]	Mo-SS	202.030	0.5
Neodymium	Nd-SS	309.418	0.5
[illegible]	Ni-SS	231.604	0.1
Niobium	Nb-SS	401.225	1
Osmium	Os-SS	228.226	0.1
Palladium	Pd-SS	340.458	0.5
Phosphorus	P-SS	213.618	1
Platinum	Pt-SS	214.423	1
Potassium	K-SS	766.490	1
Praseodymium	Pr-SS	390.844	1
Rhenium	Re-SS	221.426	1
Rhodium	Rh-SS	233.477	1
Ruthenium	Ru-SS	240.272	1
Samarium	Sm-SS	359.260	0.5
Scandium	Sc-SS	361.384	0.1
[illegible]	Se-SS	196.079	1
Silicon	Si-SS	251.611	0.1
[illegible]	Ag-SS	328.068	0.1
[illegible]	Na-SS	589.595	0.1
Strontium	Sr-SS	407.771	0.1
Sulfur	S-SS	180.731	1
Tantalium	Ta-SS	226.230	0.5
Tellurium	Te-SS	214.281	1
Terbium	Tb-SS	350.917	0.5
[illegible]	Tl-SS	334.941	1
Thorium	Th-SS	283.730	1
Thulium	Tm-SS	313.126	0.5
[illegible]	Sn-SS	189.989	0.5
[illegible]	Ti-SS	334.941	0.1
Tungston	W-SS	207.911	1
Uranium	U-SS	385.958	1
[illegible]	V-SS	292.402	0.5
Ytterbium	Yb-SS	328.937	0.1
[illegible]	Y-SS	371.030	0.1
[illegible]	Zn-SS	213.856	0.1
Zirconium	Zr-SS	343.823	0.1

* Wavelength: Most sensitived line for analysis. Line choic is dependent on sample matrtix. Use of secondary lines is necessary for some elements for spectral interference confirmation.

** LTL: Lower Threshold Limit. Based upon Signal-to-Noise Ratio for each element; expressed as mg/l. Lower levels would be recorded as ND. The LTL for each analyte is highly dependent upon sample matrix and subject to change on a sample-by-sample basis.

EPA METHOD 160.3
RESIDUE, TOTAL
GRAVIMETRIC, DRIED AT 103-105°C

RESIDUE, TOTAL

Method 160.3 (Gravimetric, Dried at 103–105°C)

STORET NO. 00500

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is from 10 mg/1 to 20,000 mg/1.
2. Summary of Method
   2.1 A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103–105°C.
3. Definitions
   3.1 Total Residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.
4. Sample Handling and Preservation
   4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   5.1 Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.
6. Apparatus
   6.1 Evaporating dishes, porcelain, 90 mm, 100 ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)
7. Procedure
   7.1 Heat the clean evaporating dish to 103–105°C for one hour, if Volatile Residue is to be measured, heat at 550 ±50°C for one hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.
   7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.
      7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.
      7.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

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7.3 Dry the evaporated sample for at least 1 hour at 103–105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103–105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total residue as follows:

$$\text{Total residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of sample + dish in mg
B = weight of dish in mg
C = volume of sample in ml

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

Bibliography

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EPA METHOD 335.2
CYANIDE, TOTAL
TITRIMETRIC, SPECTROPHOTOMETRIC

CYANIDE, TOTAL

Method 335.2 (Titrimetric; Spectrophotometric)

STORET NO. 00720

1. Scope and Application
   - 1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/1 (0.25 mg/250 ml of absorbing liquid).
   - 1.3 The colorimetric procedure is used for concentrations below 1 mg/1 of cyanide and is sensitive to about 0.02 mg/1.
2. Summary of Method
   - 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
   - 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
   - 2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.
3. Definitions
   - 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.
4. Sample Handling and Preservation
   - 4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
   - 4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

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Technical Revision 1980

4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.

4.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1, 8.2 and 8.3.

5.2 Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in Procedure 8.2. The apparatus for this procedure is shown in Figure 3.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1 + 9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

5.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask same as 6.1. The sulfide scrubber may be a Wheaton Bubbler #709682 with 29/42 joints, size 100 ml. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube should be fritted.

6.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-161-50).

7. Reagents

7.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Lead acetate: Dissolve 30 g of $Pb(C_2H_3O_2)\cdot 3H_2O$ in 950 ml of distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.

7.5 Sulfuric acid; 18N: Slowly add 500 ml of concentrated H_2SO_4 to 500 ml of distilled water.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4\cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100.0 ug).

7.9 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh daily.

7.13 Color Reagent — One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Magnesium chloride solution: Weight 510 g of $MgCl_2\cdot 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

7.15 Sulfamic acid.

8. Procedure

8.1 For samples without sulfide.

8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube. Proceed to 8.4.

8.2 For samples that contain sulfide.

8.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (7.1) to the absorbing tube. Add 25 ml of lead acetate (7.2) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber in the train. (Figure 3) The flow meter is connected to the outlet tube of the cyanide absorber.

8.2.2 Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enters the boiling flask through the air inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 8.4.

8.3 If samples contain NO_3 and or NO_2 add 2 g of sulfamic acid solution (7.15) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

8.4 Slowly add 50 ml 18N sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 20 ml of magnesium chloride (7.14) into the air inlet and wash down with a stream of water.

8.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

8.7 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25N sodium hydroxide solution (7.4). Add 15.0 ml of sodium phosphate solution (7.6) and mix.

8.7.1 Pyridine-barbituric acid method: Add 2 ml of chloramine T (7.12) and mix. See Note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.7.2 Pyridine-pyrazolene method: Add 0.5 ml of chloramine T (7.12) and mix. See Note 1 and 2. After 1 to 2 minutes add 5 ml of pyridine-pyrazolone solution

(7.13.1) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE 1: Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 ml of chlorine T. After one minute, recheck the sample.

NOTE 2: More than 05. ml of chloramine T will prevent the color from developing with pyridine-pyrazolone.

8.8 Standard curve for samples without sulfide.

8.8.1 Prepare a series of standards by pipeting suitable volumes of standard solution (7.9) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

ML of Working Standard Solution (1 ml = 10 μg CN)	Conc. μg CN per 250 ml
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

8.8.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards the analyst should find the cause of the apparent error before proceeding.

8.8.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to 500 ml of sample to insure a level of 20 μg/l. Proceed with the analysis as in Procedure (8.1.1).

8.9 Standard curve for samples with sulfide.

8.9.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

8.9.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.10 Titrimetric method.

8.10.1 If the sample contains more than 1 mg/l of CN, transfer the distillate or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.10.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples.

9. Calculation

9.1 If the colorimetric procedure is used, calculate the cyanide, in ug/l, in the original sample as follows:

$$\text{CN, ug/l} = \frac{A \times 1{,}000}{B} \times \frac{50}{C}$$

where:

A = ug CN read from standard curve
B = ml of original sample for distillation
C = ml taken for colorimetric analysis

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B)1{,}000}{\text{ml orig. sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy
    10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ±0.005, ±0.007, ±0.031 and ±0.094, respectively.
    10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

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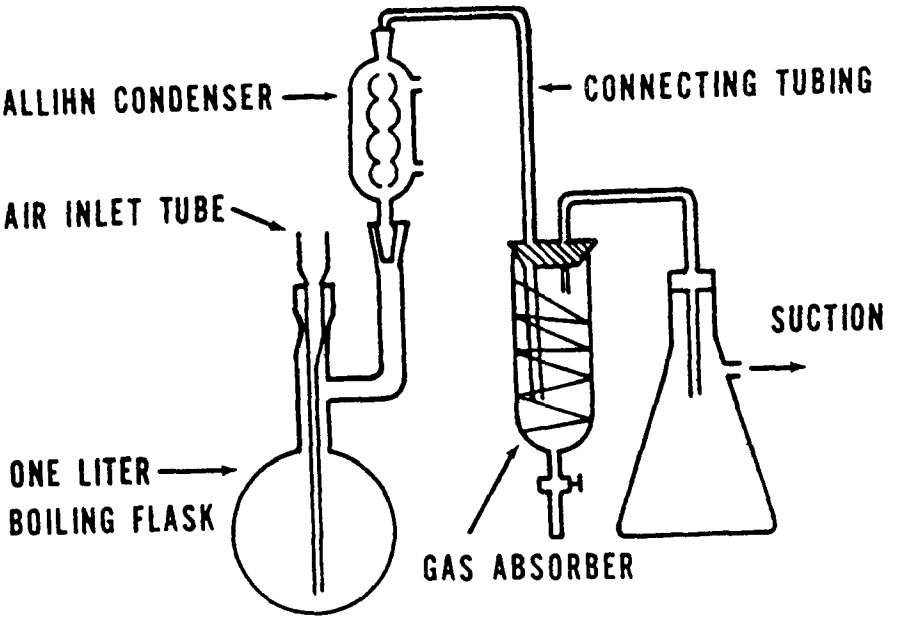

FIGURE 1

CYANIDE DISTILLATION APPARATUS

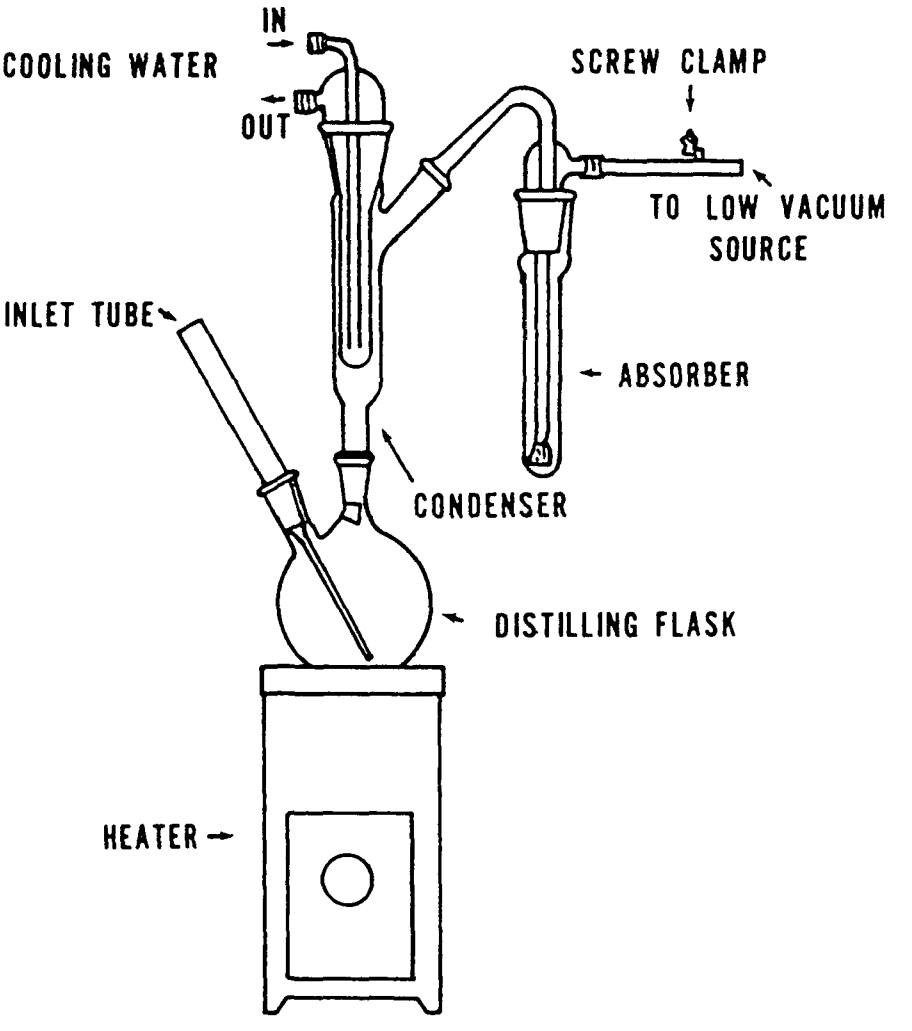

FIGURE 2

CYANIDE DISTILLATION APPARATUS

EPA METHOD 340.2
FLUORIDE
POTENTIOMETRIC, ION SELECTIVE ELECTRODE

FLUORIDE

Method 340.2 (Potentiometric, Ion Selective Electrode)

STORET NO: Total 00951
Dissolved 00950

1. Scope and Application
   - 1.1 This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
   - 1.3 For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.
2. Summary of Method
   - 2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
   - 2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/
3. Interferences
   - 3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
   - 4.1 No special requirements.
5. Apparatus
   - 5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
   - 5.2 Fluoride Ion Activity Electrode, such as Orion No. 94–09[1]
   - 5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90–01, Beckman No. 40454, or Corning No. 476010.
   - 5.4 Magnetic Mixer, Teflon-coated stirring bar.

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6. Reagents

6.1 Buffer solution, pH 5.0–5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA[2]. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/1 by diluting appropriate volumes to 50.0 ml. The following series may be used:

Millimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential

reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy
   - 9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/l with a standard deviation of ±0.03 was obtained.
   - 9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ±0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179–72, Method B, p 312 (1976).

EPA METHOD 351.2
NITROGEN, KJELDAHL, TOTAL
COLORIMETRIC, SEMI-AUTOMATED BLOCK DIGESTER, AAII

NITROGEN, KJELDAHL, TOTAL

Method 351.2 (Colorimetric, Semi-Automated Block Digester, AAII)

STORET NO. 00625

1. Scope and Application
   1.1 This method covers the determination of total Kjeldahl nitrogen in drinking and surface waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogeneous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines. The applicable range of this method is 0.1 to 20 mg/1 TKN. The range may be extended with sample dilution.
2. Summary of Method
   2.1 The sample is heated in the presence of sulfuric acid, K_2SO_4 and $HgSO_4$ for two and one half hours. The residue is cooled, diluted to 25 ml and placed on the AutoAnalyzer for ammonia determination. This digested sample may also be used for phosphorus determination.
3. Definitions
   3.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.
   3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value.
4. Sample Handling and Preservation
   4.1 Samples may be preserved by addition of 2 ml of conc H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Therefore, samples should be analyzed as soon as possible.
5. Apparatus
   5.1 Block Digestor–40
   5.2 Technicon Manifold for Ammonia (Figure 1)
   5.3 Chemware TFE (Teflon boiling stones), Markson Science, Inc., Box 767, Delmar, CA 92014)
6. Reagents
   6.1 Mercuric Sulfate: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10 ml conc H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water.
   6.2 Digestion Solution: (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of K_2SO_4 in 700 ml of distilled water and 200 ml of conc H_2SO_4. Add 25 ml of mercuric sulfate solution and dilute to 1 liter.

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6.3 Sulfuric Acid Solution (4%): Add 40 ml of conc. sulfuric acid to 800 ml of ammonia free distilled water, cool and dilute to 1 liter.

6.4 Stock Sodium Hydroxide (20%): Dissolve 200 g of sodium hydroxide in 900 ml of ammonia-free distilled water and dilute to 1 liter.

6.5 Stock Sodium Potassium Tartrate Solution (20%): Dissolve 200 g sodium potassium tartrate in about 800 ml of ammonia-free distilled water and dilute to 1 liter.

6.6 Stock Buffer Solution: Dissolve 134.0 g of sodium phosphate, dibasic (Na_2HPO_4) in about 800 ml of ammonia free water. Add 20 g of sodium hydroxide and dilute to 1 liter.

6.7 Working Buffer Solution: Combine the reagents in the stated order; add 250 ml of stock sodium potassium tartrate solution (6.5) to 200 ml of stock buffer solution (6.6) and mix. Add xx ml sodium hydroxide solution (6.4) and dilute to 1 liter. See concentration ranges, Table I, for composition of working buffer.

6.8 Sodium Salicylate/Sodium Nitroprusside Solution: Dissolve 150 g of sodium salicylate and 0.3 g of sodium nitroprusside in about 600 ml of ammonia free water and dilute to 1 liter.

6.9 Sodium Hypochlorite Solution: Dilute 6.0 ml sodium hypochlorite solution (clorox) to 100 ml with ammonia free distilled water.

6.10 Ammonium chloride, stock solution: Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask. 1 ml = 1.0 mg NH_3-N.

7. Procedure

Digestion

7.1 To 20 or 25 ml of sample, add 5 ml of digestion solution (6.2) and mix (use a vortex mixer).

7.2 Add (4–8) Teflon boiling stones (5.3). Too many boiling chips will cause the sample to boil over.

7.3 With Block Digestor in manual mode set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digestor and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set timer for 2 1/2 hours.

7.4 Cool sample and dilute to 25 ml with ammonia free water.

Colorimetric Analysis

7.5 Check the level of all reagent containers to ensure an adequate supply.

7.6 Excluding the salicylate line, place all reagent lines in their respective containers, connect the sample probe to the Sampler IV and start the proportioning pump.

7.7 Flush the Sampler IV wash receptacle with about 25 ml of 4.0% sulfuric acid (6.3).

7.8 When reagents have been pumping for at least five minutes, place the salicylate line in its respective container and allow the system to equilibrate. If a precipitate forms after the addition of salicylate, the pH is too low. Immediately stop the proportioning pump and flush the coils with water using a syringe. Before restarting the system, check the concentration of the sulfuric acid solutions and/or the working buffer solution.

TABLE I

CONCENTRATION RANGES (NITROGEN)

No.	Dilution loops: Initial sample — Sample line	Initial sample — Diluent line	Resample — Resample line	Resample — Diluent line	Approx. std. cal. setting	Range PPM N (±10%)	ml stock NaOH per liter working buffer solution
1	.80 (RED/RED)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	700	0–0.5	250
2	.80 (RED/RED)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	100	0–1.5	250
3	.16 (ORN/YEL)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	700	0–1	120
4	.16 (ORN/YEL)	.80 (RED/RED)	.32 (BLK/BLK)	.80 (RED/RED)	100	0–5	120
5	.16 (ORN/YEL)	.80 (RED/RED)	.16 (ORN/YEL)	.80 (RED/RED)	700	0–2	80
6	.16 (ORN/YEL)	.80 (RED/RED)	.16 (ORN/YEL)	80 (RED/RED)	100	0–10	80

7.9 To prevent precipitation of sodium salicylate in the waste tray, which can clog the tray outlet, keep the nitrogen flowcell pump tube and the nitrogen Colorimeter "To Waste" tube separate from all other lines or keep tap water flowing in the waste tray.

7.10 After a stable baseline has been obtained start the Sampler.

8. Calculations

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentrations by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples of concentrations of 1.2, 2.6, and 1.7 mg N/1, the precision was ±0.07, ±0.03 and ±0.15, respectively.

9.2 In a single laboratory (EMSL), using sewage samples of concentrations of 4.7 and 8.74 mg N/1, the recoveries were 99 and 99%, respectively.

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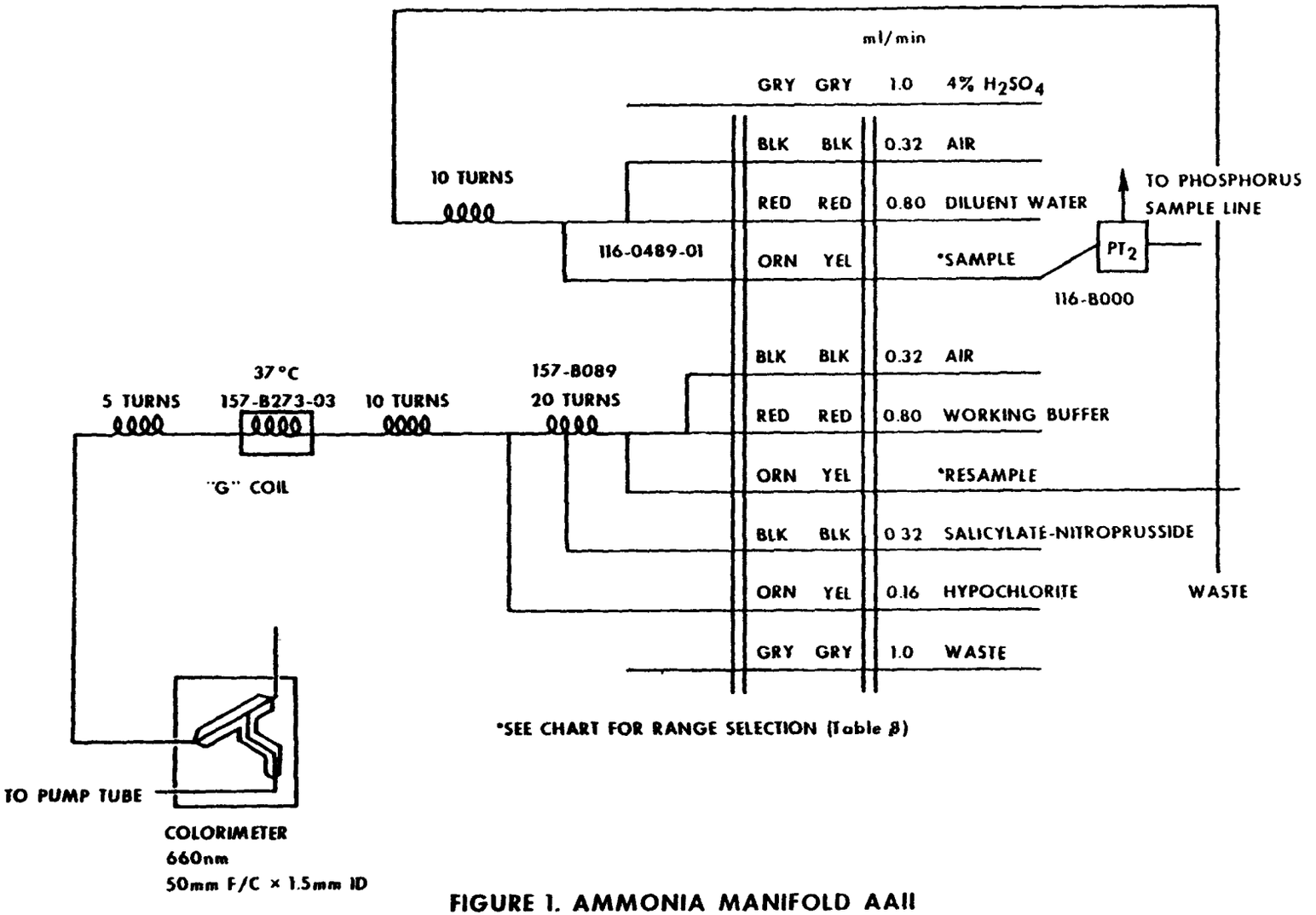

FIGURE 1. AMMONIA MANIFOLD AAII

EPA METHOD 353.2
NITROGEN, NITRATE-NITRITE
COLORIMETRIC, AUTOMATED, CADMIUM REDUCTION

NITROGEN, NITRATE-NITRITE

Method 353.2 (Colorimetric, Automated, Cadmium Reduction;

STORET NO. Total 00630

1. Scope and Application
   1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigeration.
   Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
5. Apparatus
   5.1 Technicon AutoAnalyzer (AAI or AAII) consisting of the following components.
      5.1.1 Sampler.
      5.1.2 Manifold (AAI) or analytical cartridge (AAII).
      5.1.3 Proportioning Pump
      5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filter.
      5.1.5 Recorder.

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5.1.6 Digital printer for AAII (Optional).

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:

6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.

6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.

6.4 Preparation of reduction column AAII: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper-cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.

NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.

6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

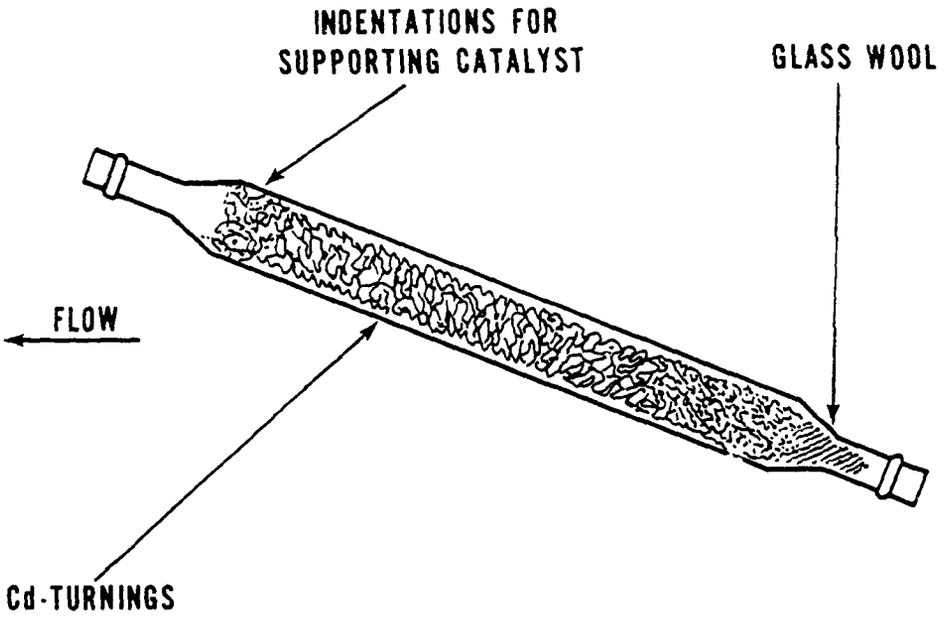
6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.8 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with H_2SO_4, use 2 ml H_2SO_4 per liter of wash water.

6.10 Ammonium chloride–EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 ml Brij-35 (available from Technicon Corporation).



TILT COLUMN TO 20° POSTION

FIGURE 1. COPPER CADMIUM REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

6.11 Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3–N.

6.12 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg NO_2–N.

6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg NO_3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg NO_2-N. Solution is unstable; prepare as required.

6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Conc., mgNO_2–N or NO_3-N/l	ml Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0.
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl - 24.53 g/l	$MgCl_2$ - 5.20 g/l	Na_2SO_4 - 4.09 g/l
$CaCl_2$ - 1.16 g/l	KCl - 0.70 g/l	$NaHCO_3$ - 0.20 g/l
KBr - 0.10 g/l	H_3BO_3 - 0.03 g/l	$SrCl_2$ - 0.03 g/l
NaF - 0.003 g/l		

7. Procedure

7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH.

7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20° incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

NOTE 3: Condition column by running 1 mg/l standard for 10 minutes if a new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAII, use a 40/hr, 4:1 cam and a common wash.

7.6 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO_2 and/or NO_3 standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	− 2.69	−0.067

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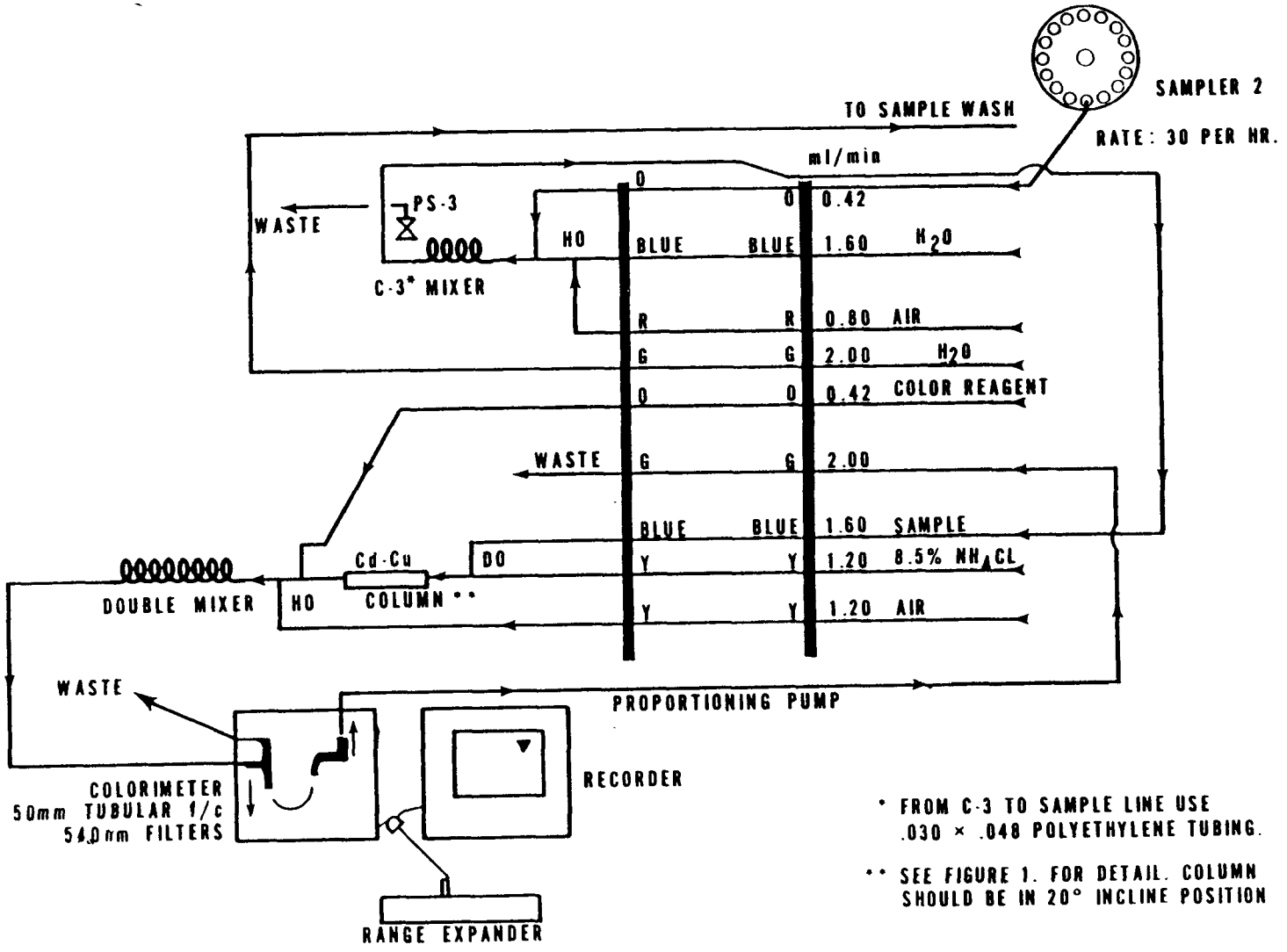

FIGURE 2. NITRATE - NITRITE MANIFOLD AA-I

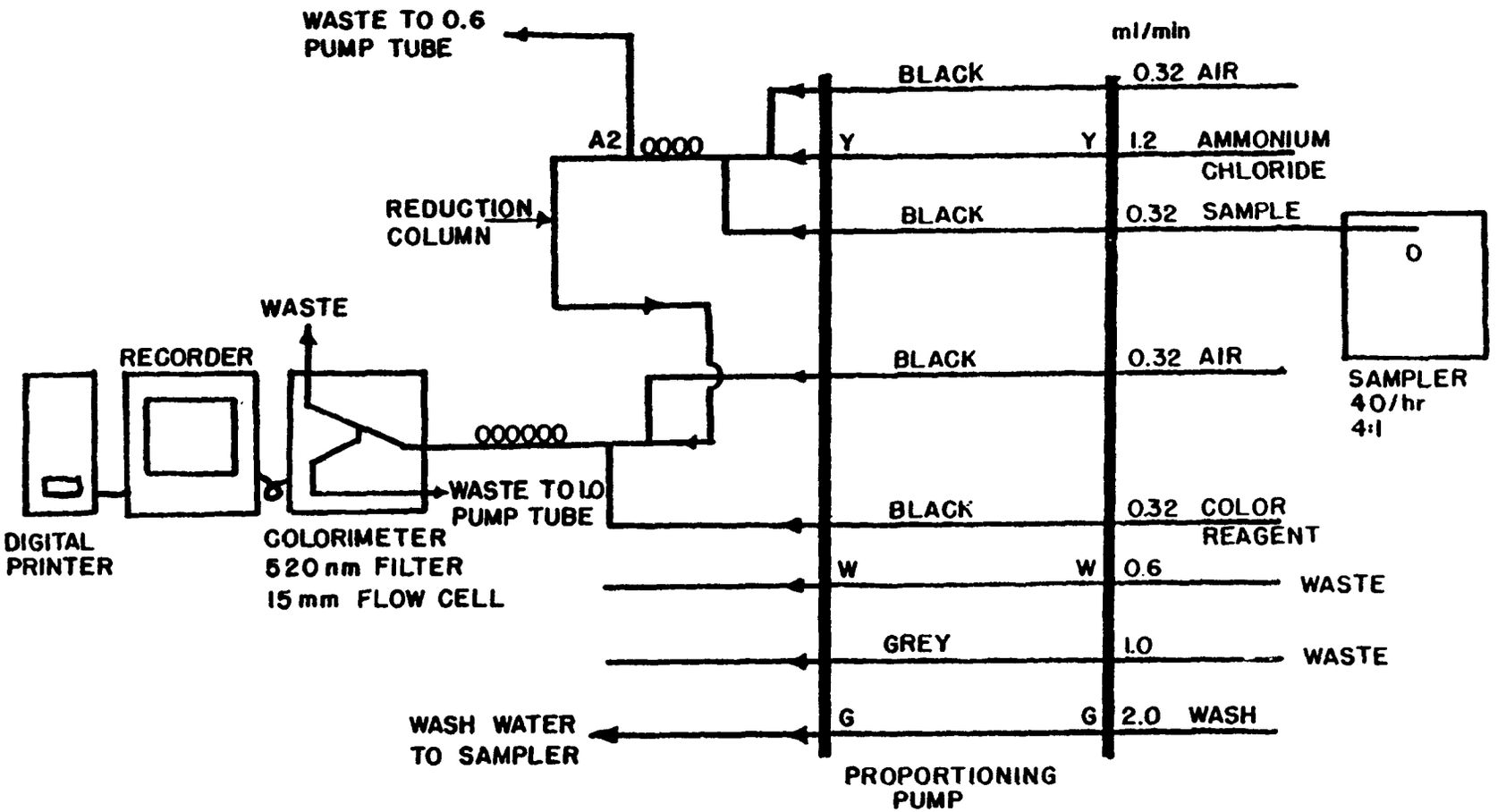

FIGURE 3 NITRATE-NITRITE MANIFOLD AA II

EPA METHOD 365.2
PHOSPHOROUS, ALL FORMS
COLORIMETRIC, ASCORBIC ACID, SINGLE REAGENT

PHOSPHORUS, ALL FORMS

Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent)

STORET NO. See Section 4

1. Scope and Application
   - 1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.
     - 1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.
   - 1.3 The methods are usable in the 0.01 to 0.5 mg P/l range.
2. Summary of Method
   - 2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.
   - 2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion[2].
3. Sample Handling and Preservation
   - 3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
   - 3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.
   - 3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Definitions and Storet Numbers
   - 4.1 Total Phosphorus (P) — all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)
     - 4.1.1 Total Orthophosphate (P, ortho) — inorganic phosphorus [$(PO_4)^{-3}$] in the sample as measured by the direct colorimetric analysis procedure. (70507)
     - 4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphates. [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

Approved for NPDES
Issued 1971

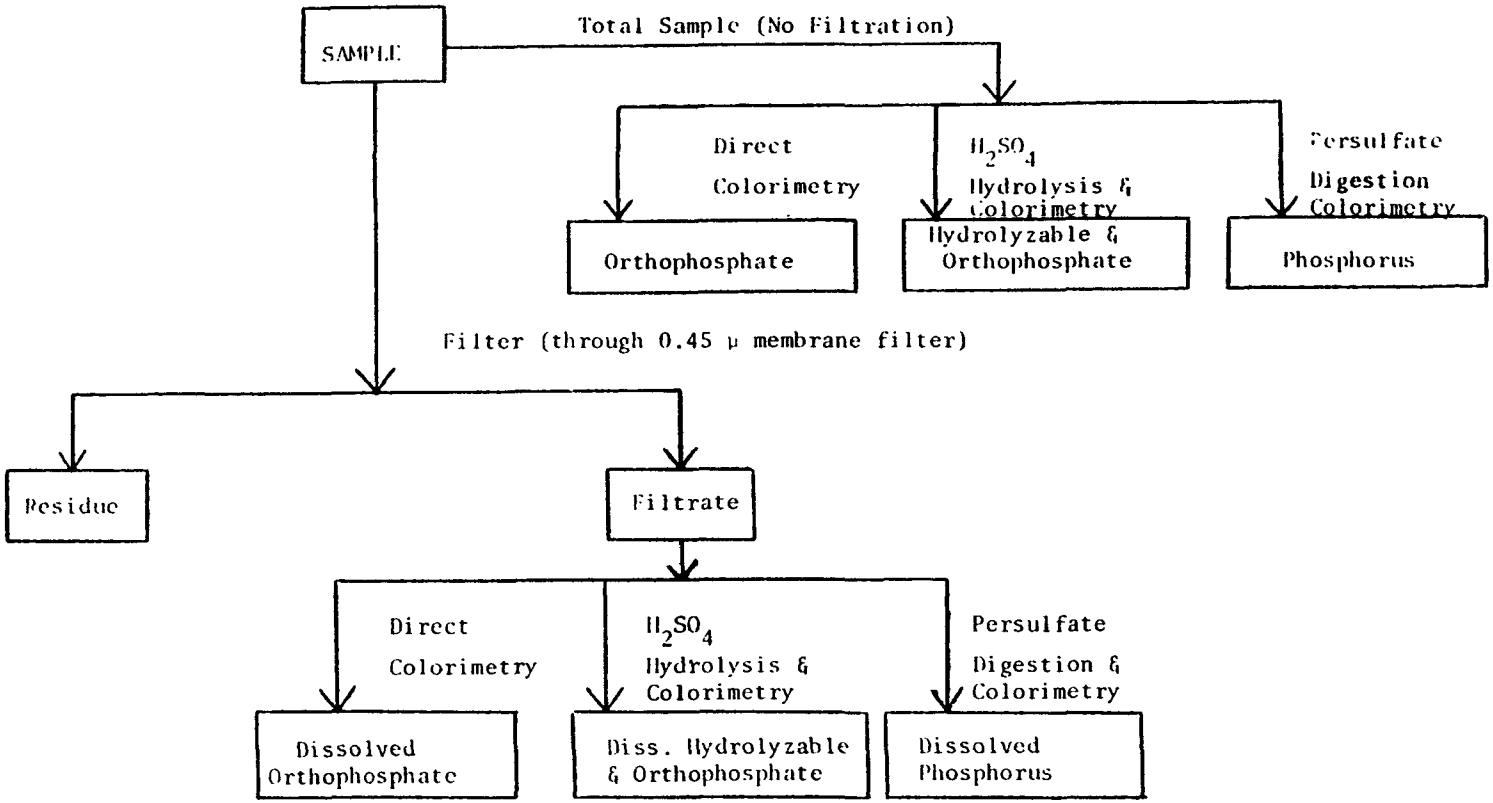

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

4.1.3 Total Organic Phosphorus (P, org) — phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) — all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) — as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) — as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) — as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I)=(P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho)=(P, ortho)-(P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P-I, hydro)=(P, hydro)-(P-D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P-I, org)=(P, org) – (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/l, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

6. Apparatus

6.1 Photometer – A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and

kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 ml = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 ml of stock phosphorus solution (7.8) to 1000 ml with distilled water; 1.0 ml = 0.5 *ug* P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

ml of Standard Phosphorus Solution (7.9)	Conc., mg/l
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0 10
20.0	0.20
30.0	0.30
40 0	0.40
50 0	0 50

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 ml distilled water. Cool and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.1.4 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with 1 N NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.2.3 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 The pH of the sample must be adjusted to 7±0.2 using a pH meter.

8.3.2 Add 8.0 ml of combined reagent (7.5) to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution.
NOTE 1: If the same volume of sodium hydroxide solution is not used to adjust the pH of the standards and samples, a volume correction has to be employed.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/1. SEE **NOTE 1.**

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias mg P/liter
0.110	0.033	+3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+2.96	+0.023
0.882	0.128	-0.92	-0.008

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias, mg P/liter
0.029	0.010	-4.95	-0.001
0.038	0.008	-6.00	-0.002
0.335	0.018	-2.75	-0.009
0.383	0.023	-1.76	-0.007

(FWPCA Method Study 2, Nutrient Analyses)

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