

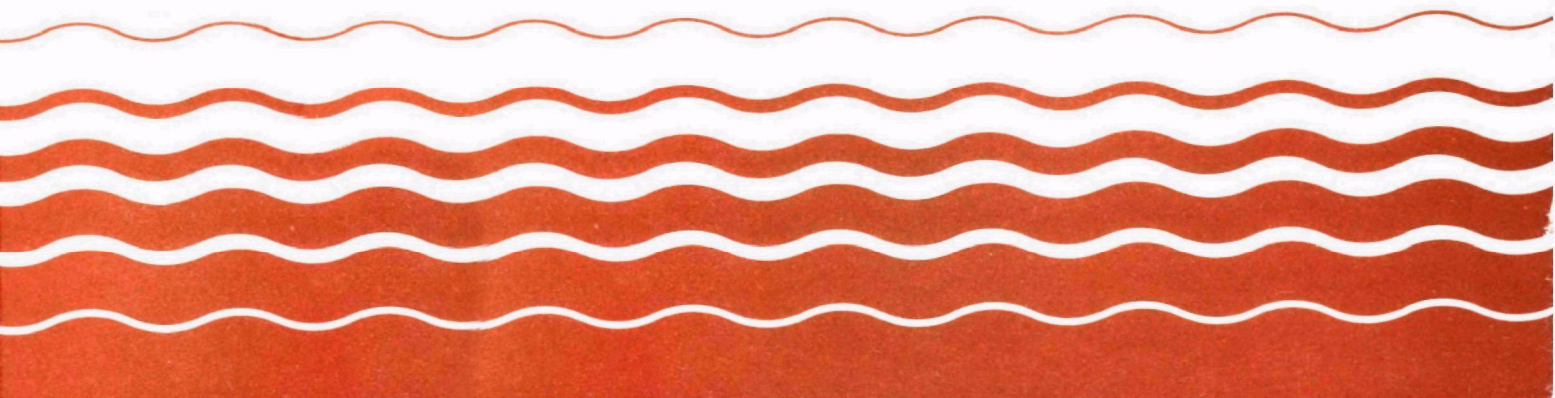


United States Environmental Protection Agency  
Office of Water Regulations and Standards  
Industrial Technology Division

Office of Water

Revision A August 1989

# 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) used in the National Sewage Sludge Survey.

These methods have been compiled from OWRS Industrial Technology Division (ITD) methods and from "Methods for Chemical Analysis of Water and Wastes (MCAWW), USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-79-020 (Revised March 1983). MCAWW is available from the National Technical Information Service, Springfield, VA 22161, PB84-128677.

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# ANALYTICAL METHODS FOR THE NATIONAL SEWAGE SLUDGE SURVEY

## TABLE OF CONTENTS

CATEGORY	METHOD	ANALYTE	TECHNIQUE	PAGE
ORGANIC	1624C	Volatiles (VOA)	GCMS .....	1
	1625C	Semivolatiles (ABN)	GCMS .....	33
	1618	Pesticides/Herbicides	GC .....	81
	1613	Dioxins/Furans	GCMS .....	121
METALS	1620	25 elements	ICP .....	165
		Antimony	GFAA	
		Arsenic	GFAA	
		Selenium	GFAA	
		Thallium	GFAA	
		Mercury	CVAA	
		42 elements	ICP/Semiquantitative screen	
CLASSICALS	160.3	Residue	Gravimetric .....	209
	335.2	Cyanide	Spectrophotometric .....	213
	340.2	Fluoride	Electrode .....	225
	351.3	TKN	Potentiometric .....	235
	353.2	Nitrate-Nitrite	Cd Reduction .....	243
	365.2	Phosphorous	Ascorbic Acid Reduction .....	253



**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 the United States Environmental Protection Agency's (USEPA) Office of Water Regulations and Standards (OWRS) 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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## Volatile Organic Compounds by Isotope Dilution GCMS

## 1 SCOPE AND APPLICATION

1.1 This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the volatile toxic organic pollutants associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); and other compounds amenable to purge and trap gas chromatography-mass spectrometry (GCMS).

1.2 The chemical compounds listed in Tables 1 and 2 may be determined in waters, soils, and municipal sludges by the method.

1.3 The detection limits of the method are usually dependent on the level of interferences rather than instrumental limitations. The levels in Table 3 typify the minimum quantities that can be detected with no interferences present.

1.4 The GCMS portions of the method are for use only by analysts experienced with GCMS

Table 1  
VOLATILE ORGANIC COMPOUNDS DETERMINED BY GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

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

or under the close supervision of such qualified persons. Laboratories unfamiliar with analysis 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. (See Table 2). 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 (see Section 12).

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

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

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



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 The quality of the analysis 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

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 may serve 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.

Table 3  
GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
245	chloromethane-d <sub>3</sub>	147	181	0.141 - 0.270	50		
345	chloromethane	148	245	0.922 - 1.210	50	207*	13
246	bromomethane-d <sub>3</sub>	243	181	0.233 - 0.423	50		
346	bromomethane	246	246	0.898 - 1.195	50	148*	11
288	vinyl chloride-d <sub>3</sub>	301	181	0.286 - 0.501	50		
388	vinyl chloride	304	288	0.946 - 1.023	10	190*	11
216	chloroethane-d <sub>5</sub>	378	181	0.373 - 0.620	50		
316	chloroethane	386	216	0.999 - 1.060	50	789*	24
244	methylene chloride-d <sub>2</sub>	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 <sub>6</sub>	554	181	0.628 - 0.889	50		
716	acetone	565	616	0.984 - 1.019	50	3561*	322*
202	acrolein-d <sub>4</sub>	564	181	0.641 - 0.903	(5)	50	

Table 3 (continued)  
GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
302	acrolein	566	202	0.984 - 1.018 (5)	50	377*	18
203	acrylonitrile-d <sub>3</sub>	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 <sub>2</sub>	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 <sub>3</sub>	778	181	1.031 - 1.119	10		
313	1,1-dichloroethane	786	213	0.999 - 1.014	10	16	1
615	diethyl ether-d <sub>10</sub>	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 <sub>2</sub>	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 <sub>3</sub>	840	181	0.646 - 1.202	50		
714	methyl ethyl ketone	848	614	0.992 - 1.055	50	241*	80*
223	chloroform- <sup>13</sup> C <sub>1</sub>	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 <sub>4</sub>	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- <sup>13</sup> C <sub>2</sub>	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 <sub>8</sub>	982	181	1.262 - 1.448 (5)	50		
727	p-dioxane	1001	627	1.008 - 1.040 (5)	50	--	140*
206	carbon tetrachloride- <sup>13</sup> C <sub>1</sub>	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- <sup>13</sup> C <sub>1</sub>	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 <sub>6</sub>	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- <sup>13</sup> C <sub>2</sub>	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 <sub>6</sub>	1200	182	0.888 - 0.952	10		
304	benzene	1212	204	1.002 - 1.026	10	23	8
251	chlorodibromomethane- <sup>13</sup> C <sub>1</sub>	1222	182	0.915 - 0.949	10		
351	chlorodibromomethane	1222	251	0.989 - 1.030	10	15	2
214	1,1,2-trichloroethane- <sup>13</sup> C <sub>2</sub>	1224	182	0.922 - 0.953	10		
314	1,1,2-trichloroethane	1224	214	0.975 - 1.027	10	26	1

Table 3 (continued)  
GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
233	trans-1,3-dichloropropene-d <sub>4</sub>	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- <sup>13</sup> C <sub>1</sub>	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 <sub>2</sub>	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- <sup>13</sup> C <sub>2</sub>	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 <sub>8</sub>	1603	183	1.016 - 1.054	10		
386	toluene	1619	286	1.001 - 1.019	10	27	4
207	chlorobenzene-d <sub>5</sub>	1679	183	1.066 - 1.135	10		
307	chlorobenzene	1679	207	0.914 - 1.019	10	21	58*
238	ethylbenzene-d <sub>10</sub>	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 Carbowax 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.

- 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  $>105^{\circ}\text{C}$  for one hr minimum before use.

- 5.1.2 Septum--Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at  $100 - 200^{\circ}\text{C}$  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.

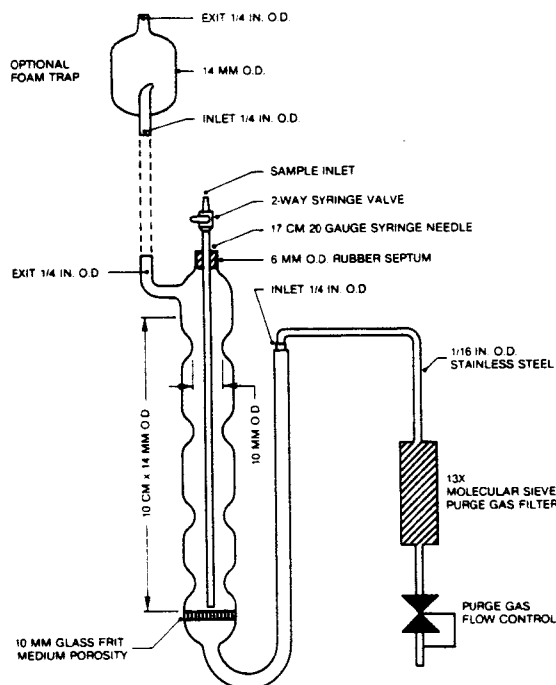


FIGURE 1 Purging Device for Waters

- 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 ( $20 - 25^{\circ}\text{C}$ ) and of being controlled at temperatures of  $40 \pm 2^{\circ}\text{C}$  and  $80 \pm 5^{\circ}\text{C}$  while the sample is being purged. The purging device shown in Figure 2 meets these criteria.

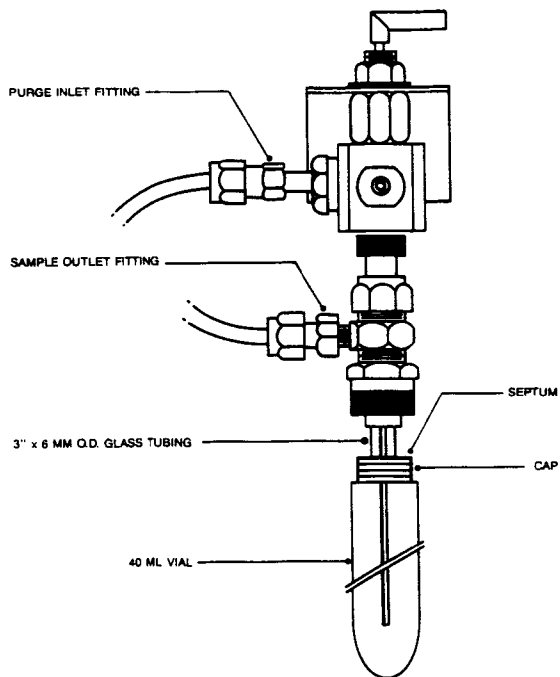


FIGURE 2 Purging Device for Soils or Waters

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  $\pm$  0.2 cm, 3 percent OV-1 on 60/80 mesh Chromosorb W, or equivalent.

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

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

5.2.3 Desorber--shall heat the trap to  $175 \pm 5$  °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.

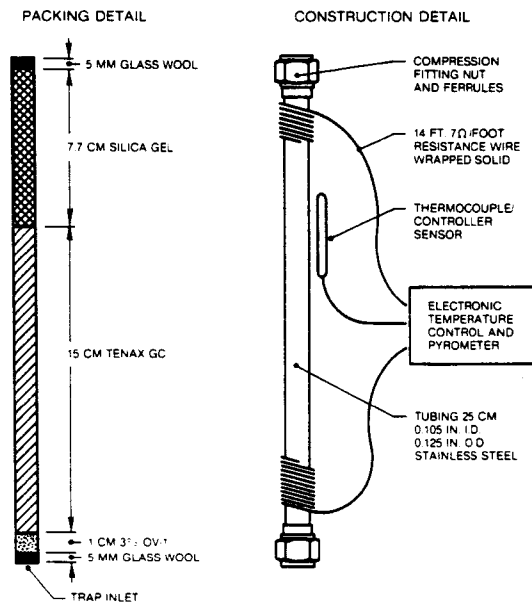


FIGURE 3 Trap Construction and Packings

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

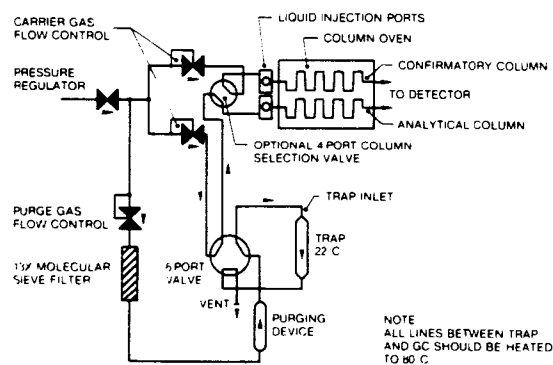


FIGURE 4 Schematic of Purge and Trap Device--Purge Mode

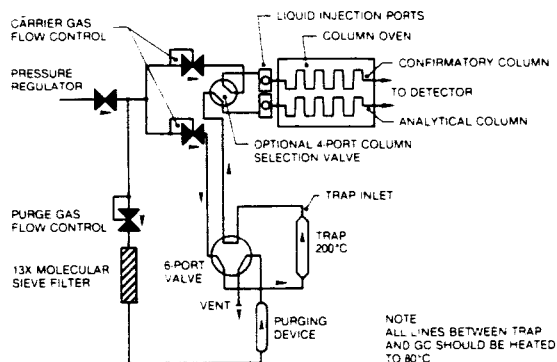


FIGURE 5 Schematic of Purge and Trap Device--Desorb Mode

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 174
176	95 to 101 percent of m/z 174
177	5 to 9 percent of m/z 176

- 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-- $2.8 \pm 0.4$  m x  $2 \pm 0.5$  mm i.d. glass, packed with one percent SP-1000 on Carbowax 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 preclude condensation of less volatile compounds.
- 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-loc tips.
- 5.7 Micro syringes--10, 25, and 100  $\mu$ L.

- 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  $110 \pm 5$  °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 µL 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 (µg/µL) 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  $\mu\text{L}$  spike into each 5 mL sample, blank, or aqueous standard analyzed will result in a concentration of 20  $\mu\text{g/L}$  of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, p-dioxane, and MEK), a concentration of 100  $\mu\text{g/L}$  may be used. Include the internal standards (Section 7.5) in this solution so that a concentration of 20  $\mu\text{g/L}$  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  $\mu\text{g/mL}$ . For the gases and water soluble compounds (Section 6.6), a concentration of 2.5  $\text{mg/mL}$  may be used.
- 6.7.1 Aqueous calibration standards--using a 25  $\mu\text{L}$  syringe, add 20  $\mu\text{L}$  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  $\mu\text{g/L}$ , 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  $\mu\text{g/L}$  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  $\mu\text{g/L}$  of the labeled and pollutant gases and water soluble compounds, 10  $\mu\text{g/L}$  BFB, and 20  $\mu\text{g/L}$  of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20  $\mu\text{g/L}$  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  $\mu\text{g/mL}$  or 500  $\mu\text{g/mL}$  of the gases and water soluble compounds, and 100  $\mu\text{g/mL}$  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. Examine the spectrum to determine that only a single compound is present. 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.

7.2.2 The authentic reference spectrum is obtained under BFB tuning conditions (Section 7.1 and Table 4) to normalize it to spectra from other instruments.

7.2.3 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.

7.2.4 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 7.2.3, if necessary.

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

Table 5  
VOLATILE ORGANIC COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled Analog	Primary m/z (1)	Reference compound (2)	Response factor at purge temp. of:	
				20 °C	80 °C
acetone	d <sub>6</sub>	58/64			
acrolein	d <sub>4</sub>	56/60			
acrylonitrile	d <sub>3</sub>	53/56			
allyl alcohol		57	181	(3)	0.20
benzene	d <sub>6</sub>	78/84			
2-bromo-1-chloropropane (4)		77			
bromochloromethane (4)		128			
bromodichloromethane	<sup>13</sup> C	83/86			
bromoform	<sup>13</sup> C	173/176			
bromomethane	d <sub>3</sub>	96/99			
carbon disulfide		76	181	1.93	2.02
carbon tetrachloride	<sup>13</sup> C	47/48			
2-chloro-1,3-butadiene		53	182	0.29	0.50
chloroacetonitrile		75	181	(3)	1.12
chlorobenzene	d <sub>5</sub>	112/117			
chloroethane	d <sub>5</sub>	64/71			
2-chloroethylvinyl ether	d <sub>7</sub>	106/113			

Table 5 (continued)  
VOLATILE ORGANIC COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled Analog	Primary m/z (1)	Reference compound (2)	Response factor at purge temp. of	
				20 °C	80 °C
chloroform	$^{13}\text{C}$	85/86			
chloromethane	$\text{d}_3$	50/53			
3-chloropropene		76	181	0.43	0.63
crotonaldehyde		70	182	(3)	0.090
dibromochloromethane	$^{13}\text{C}$	129/130			
1,2-dibromoethane		107	182	0.86	0.68
dibromomethane		93	181	1.35	1.91
1,4-dichlorobutane (4)		55			
trans-1,4-dichloro-2-butene		75	183	0.093	0.14
1,1-dichloroethane	$\text{d}_3$	63/66			
1,2-dichloroethane	$\text{d}_4$	62/67			
1,1-dichloroethene	$\text{d}_2$	61/65			
trans-1,2-dichloroethene	$\text{d}_2$	61/65			
1,2-dichloropropane	$\text{d}_6$	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	$\text{d}_4$	75/79			
diethyl ether	$\text{d}_{10}$	74/84			
p-dioxane	$\text{d}_8$	88/96			
ethyl cyanide		54	181	(3)	1.26
ethyl methacrylate		69	183	0.69	0.52
ethylbenzene	$\text{d}_{10}$	106/116			
2-hexanone		58	183	0.076	0.33
iodomethane		142	181	4.55	2.55
isobutyl alcohol		74	181	(3)	0.22
methylene chloride	$\text{d}_2$	84/88			
methyl ethyl ketone	$\text{d}_8$	72/80			
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	$\text{d}_2$	83/84			
tetrachloroethene	$^{13}\text{C}_2$	164/172			
toluene	$\text{d}_8$	92/100			
1,1,1-trichloroethane	$\text{d}_3$	97/102			
1,1,2-trichloroethane	$^{13}\text{C}_3$	83/84			
trichloroethene	$^{13}\text{C}_2$	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	$\text{d}_3$	62/65			
m-xylene		106	183	1.69	-
o- + p-xylene		106	183	3.33	-

(1) native/labeled

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

(3) not detected at a purge temperature of 20 °C

(4) internal standard

NOTE: Because the composition and purity of commercially-supplied isotopically labeled standards may vary, the primary m/z of the labeled analogs given in this table should be used as guidance. The appropriate m/z of the labeled analogs should be determined prior to use for sample analysis. Deviations from the m/z's listed here must be documented by the laboratory and submitted with the data.

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 ( $\mu\text{g/L}$ ) 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.

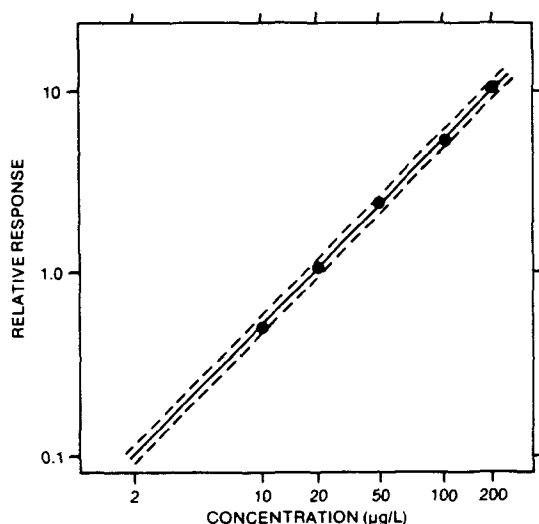


FIGURE 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window

Also shown are the  $\pm 10$  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).

- 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).

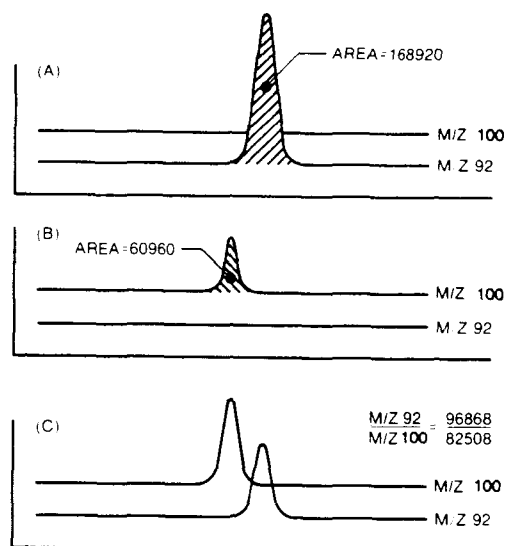


FIGURE 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene- $d_8$ , and (C) a Mixture of Toluene and Toluene- $d_8$

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 data from these analyses are reported to three significant figures (see Section 13.6). In order to prevent rounding errors from affecting the values to be reported, all calculations performed prior to the final determination of concentrations should be carried out using at least four significant figures. Therefore, the calculation of R above is rounded to four significant figures.

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:

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

$$R_y = \frac{1}{60960} = 0.0001640$$

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

The RR for the above data is then calculated using the equation given in Section 7.4.1. For the example, rounded to four significant figures,  $RR = 1.174$ . Not all labeled compounds elute before their pollutant analogs.

- 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 bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluting 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  $40 \pm 2$  °C (Section 10). For these samples, the analytical system may be calibrated using a purge temperature of  $40 \pm 2$  °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 ongoing 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 ( $\bar{X}$ ) 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  $\bar{X}$  with the corresponding limits for initial precision and accuracy found in Table 6. If  $s$  and  $\bar{X}$  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  $\bar{X}$  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  $\bar{X}$  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 ( $\bar{P}$ ) 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  $\bar{P} - 2s_p$  to  $\bar{P} + 2s_p$ . For example, if  $\bar{P} = 90\%$  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.

Table 6  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. (1)	Compound	Acceptance criteria at 20 ug/L or as noted			
		Labeled and native compound initial precision and accuracy (Sect. 8.2.3)		Labeled compound recovery (Sect. 8.3 and 14.2)	Labeled and native compound on-going accuracy (Sect. 11.5)
		s (ug/L)	X (ug/L)	P (%)	R (ug/L)
516	acetone*	51.0	77 - 153	35 - 165	55 - 145
002	acrolein*	72.0	32 - 168	37 - 163	7 - 190
003	acrylonitrile*	16.0	70 - 132	ns - 204	58 - 144
004	benzene	9.0	13 - 28	ns - 196	4 - 33
048	bromodichloromethane	8.2	7 - 32	ns - 199	4 - 34
047	bromoform	7.0	7 - 35	ns - 214	6 - 36
046	bromomethane	25.0	d - 54	ns - 414	d - 61
006	carbon tetrachloride	6.9	16 - 25	42 - 165	12 - 30
007	chlorobenzene	8.2	14 - 30	ns - 205	4 - 35
016	chloroethane	15.0	d - 47	ns - 308	d - 51
019	2-chloroethylvinyl ether	36.0	d - 70	ns - 554	d - 79
023	chloroform	7.9	12 - 26	18 - 172	8 - 30
045	chloromethane	26.0	d - 56	ns - 410	d - 64
051	dibromochloromethane	7.9	11 - 29	16 - 185	8 - 32
013	1,1-dichloroethane	6.7	11 - 31	23 - 191	9 - 33
010	1,2-dichloroethane	7.7	12 - 30	12 - 192	8 - 33
029	1,1-dichloroethene	12.0	d - 50	ns - 315	d - 52
030	trans-1,2-dichloroethene	7.4	11 - 32	15 - 195	8 - 34
032	1,2-dichloropropane	19.0	d - 47	ns - 343	d - 51
033	trans-1,3-dichloropropene	15.0	d - 40	ns - 284	d - 44
515	diethyl ether*	44.0	75 - 146	44 - 156	55 - 145
527	p-dioxane*	7.2	13 - 27	ns - 239	11 - 29
038	ethylbenzene	9.6	16 - 29	ns - 203	5 - 35
044	methylene chloride	9.7	d - 50	ns - 316	d - 50
514	methyl ethyl ketone*	57.0	66 - 159	36 - 164	42 - 158
015	1,1,2,2-tetrachloroethane	9.6	11 - 30	5 - 199	7 - 34
085	tetrachloroethene	6.6	15 - 29	31 - 181	11 - 32
086	toluene	6.3	15 - 29	4 - 193	6 - 33
011	1,1,1-trichloroethane	5.9	11 - 33	12 - 200	8 - 35
014	1,1,2-trichloroethane	7.1	12 - 30	21 - 184	9 - 32
087	trichloroethene	8.9	17 - 30	35 - 196	12 - 34
088	vinyl chloride	28.0	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.

(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.

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 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 utilizing one of two methods, depending on the levels of pollutants in the sample. Samples containing one percent solids or greater, and low to moderate levels of pollutants are analyzed by purging a known weight of sample added to 5 mL of reagent water (Section 10.5). Samples containing one percent solids or greater, and high levels of pollutants are extracted with methanol, and an aliquot of the methanol extract is added to reagent water and purged (Section 10.6).



- 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  $110 \pm 5$  °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  $40 \pm 4$  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  $5.0 \pm 0.1$  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 10.7.
- 10.5 Samples containing one percent solids or greater, and low to moderate levels of pollutants.
- 10.5.1 Mix the sample thoroughly using a clean spatula.
- 10.5.2 Weigh  $5 \pm 1$  grams of sample into a purging vessel (Figure 2). Record the weight to three significant figures.
- 10.5.3 Add  $5.0 \pm 0.1$  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 shake vigorously to further disperse the sample. Attach the purge vessel to the purging device, and purge the sample per Section 10.7.
- 10.6 Samples containing one percent solids or greater, and high levels of pollutants, or samples requiring dilution by a factor of more than 100 (see Section 13.4).
- 10.6.1 Mix the sample thoroughly using a clean spatula.
- 10.6.2 Weigh  $5 \pm 1$  grams of sample into a calibrated 15 - 25 mL centrifuge tube. Record the weight of the sample to three significant figures.
- 10.6.3 Add 10.0 mL of methanol to the centrifuge tube. Cap the tube and shake it vigorously for 15 - 20 seconds to disperse the sample in the methanol. Allow the sample to settle in the tube. If necessary, centrifuge the sample to settle suspended particles.
- 10.6.4 Remove approximately 0.1 percent of the volume of the supernatant methanol using a 15 - 25 uL syringe. This volume will be in the range of 10 - 15 uL.
- 10.6.5 Add this volume of the methanol extract to 5 mL reagent water in a 5 mL syringe, and analyze per Section 10.4.1.
- 10.6.6 For further dilutions, dilute 1 mL of the supernatant methanol (10.6.4) to 10 mL, 100 mL, 1000 mL, etc., in reagent water. Remove a volume of this methanol extract/reagent water mixture equivalent to the volume in Step 10.6.4, add it to 5

mL reagent water in a 5 mL syringe, and analyze per Section 10.4.1.

- 10.7 Purge the sample for  $11.0 \pm 0.1$  minutes at  $20 - 25^\circ\text{C}$  for samples containing less than one percent solids. Purge samples containing one percent solids or greater at  $40 \pm 2^\circ\text{C}$ . If the compounds in Table 2 that do not purge at  $20 - 40^\circ\text{C}$  are to be determined, a purge temperature of  $80 \pm 5^\circ\text{C}$  is used.
- 10.8 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  $170 - 180^\circ\text{C}$  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.
- 10.9 After desorbing the sample for four minutes, recondition the trap by purging with purge gas while maintaining the trap temperature at  $170 - 180^\circ\text{C}$ . 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.
- 10.10 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  $150^\circ\text{C}$ .

## 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 which has no labeled analog by the internal standard method (Section 7.5). Compute the concentrations of the labeled compounds themselves 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 ongoing 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).

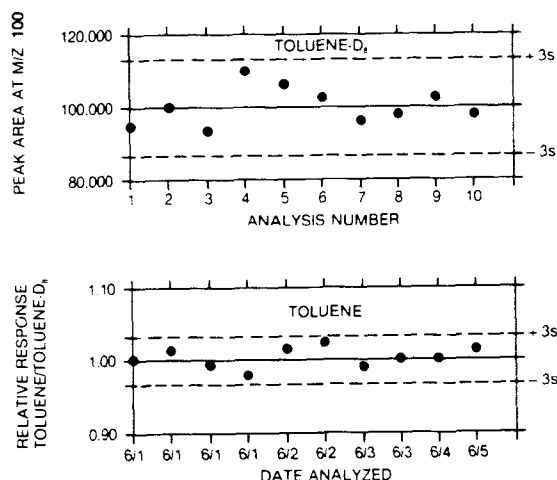


FIGURE 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d<sub>8</sub> (lower graph) Plotted as Function of Time or Analysis Number

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 7.2.3) 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 In order for the compounds for which the system has been calibrated (Table 1) to be identified, their relative retention times shall be within the retention time windows specified in Table 3.

12.1.4 The system has not been calibrated for the compounds listed in Table 2, however, the relative retention times and mass spectra of these compounds are known. Therefore, for a compound in Table 2 to be identified, its relative retention time must fall within a retention time window of  $\pm 60$  seconds or  $\pm 20$  scans (whichever is greater) of the nominal retention time of the compound 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 7.2.3) 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.

12.2.3 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 The m/z's present in the sample mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the sample 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 -- Because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography, correction for recovery of the pollutant can be made by adding a known amount of a labeled compound to every sample prior to purging. Relative response (RR) values for sample mixtures are used in conjunction with the 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--for the compounds for which the system was calibrated (Table 1) according to Section 7.5, use the response factor determined during the calibration to calculate the concentration from 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. For the compounds for which the system was not calibrated (Table 2), use the response factors in Table 5 to calculate the concentration.

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:

$$\text{Concentration in solid (ug/kg)} =$$

$$\frac{0.005 \text{ L} \times \text{aqueous conc (ug/L)}}{0.01 \times \% \text{ solids (g)}}$$

where "% solids" is from Section 10.1.3.

13.4 Dilution of samples--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 If dilution of high solids samples by greater than a factor of 100 is required, then extract the sample with methanol, as described in Section 10.6.

13.5 Dilution of samples containing high concentrations of compounds not in Table 1 -- When the EICP area of the quantitation

m/z of a compound to be identified per Section 12.3 exceeds the linear range of the GCMS system, or when any peak in the mass spectrum is saturated, dilute the sample per Sections 13.4.1-13.4.3.

- 13.6 Report results for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples to three significant figures. For samples containing less than one percent solids, the units are ug/L, and ug/kg for undiluted samples containing one percent solids or greater.

- 13.6.1 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 the GC column.
- 14.2 When the recovery of any labeled compound is outside the range given in Table 6, 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. 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, then the method does not apply to the sample being analyzed, and the result may not be reported for regulatory compliance purposes.

- 14.3 When a high level of the pollutant is present, reverse search computer programs may misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra. 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.

MASS CHROMATOGRAM DATA: UOAI01945 #1 SCANS 1 TO 1200  
 09/01/84 23:05:00 CALI: UOAI01945 #1  
 SAMPLE: UO, S, OPR, 00020, 00, U, NA: NA, NA\$  
 CONDS.: 1624B, 3.0M, 2MM, 3045, 45-24008, 150240, 20ML/MIN\$  
 RANGE: G 1, 1200 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

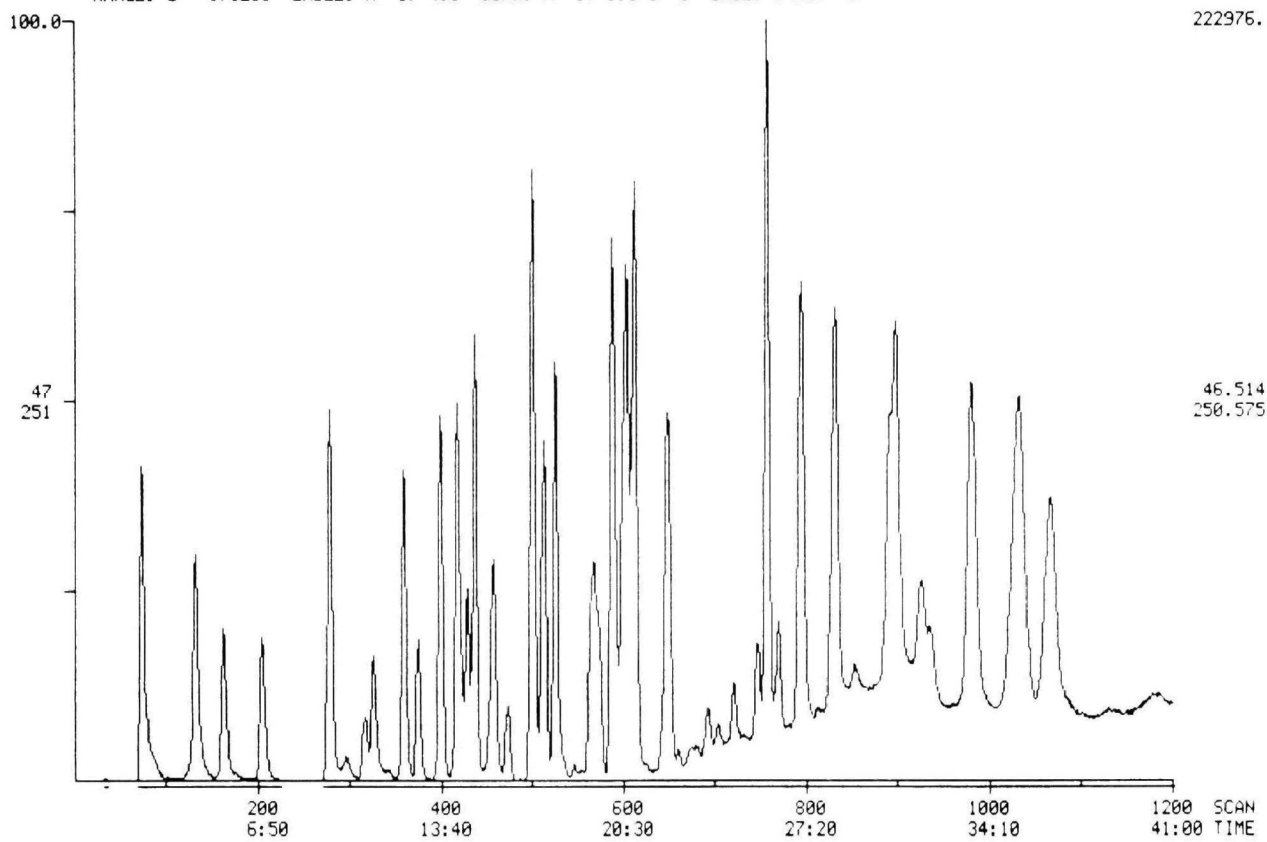


FIGURE 9 Chromatogram of Aqueous Performance Standard

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

532 allyl alcohol

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

533 carbon disulfide

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

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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

536 3-chloropropene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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)

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
79	50	80	13	81	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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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		



Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

541 1,3-dichloropropane

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

543 ethyl cyanide

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

544 ethyl methacrylate

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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)

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

546 iodomethane

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

547 isobutyl alcohol

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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				

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
42	69	43	1000	44	54	53	11	55	15	56	13
57	205	58	346	59	20	67	12	69	10	85	96
100	94										

551 1,1,1,2-tetrachloroethane

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

951 m-xylene

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

951 o- + p-xylene

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

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## Semivolatile Organic Compounds by Isotope Dilution GCMS

## 1 SCOPE AND APPLICATION

1.1 This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the semivolatile toxic organic pollutants associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); 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 the method.

1.3 The detection limits of the method are usually dependent on the level of interferences rather than instrumental limitations. The limits in Tables 5 and 6 typify the minimum quantities that can be detected with no interferences present.

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

Table 1

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

Compound	Pollutant				Labeled Compound		
	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
acenaphthene	34205	83-32-9	001 B	001 B	d <sub>10</sub>	15067-20-2	201 B
acenaphthylene	34200	208-96-8	077 B	002 B	d <sub>8</sub>	93951-97-4	277 B
anthracene	34220	120-12-7	078 B	003 B	d <sub>10</sub>	1719-06-8	278 B
benzidine	39120	92-87-5	005 B	004 B	d <sub>8</sub>	92890-63-6	205 B
benzo(a)anthracene	34526	56-55-3	072 B	005 B	d <sub>12</sub>	1718-53-2	272 B
benzo(b)fluoranthene	34230	205-99-2	074 B	007 B	d <sub>12</sub>	93951-98-5	274 B
benzo(k)fluoranthene	34242	207-08-9	075 B	009 B	d <sub>12</sub>	93952-01-3	275 B
benzo(a)pyrene	34247	50-32-8	073 B	006 B	d <sub>12</sub>	63466-71-7	273 B
benzo(ghi)perylene	34521	191-24-2	079 B	008 B	d <sub>12</sub>	93951-66-7	279 B
biphenyl (Appendix C)	81513	92-52-4	512 B		d <sub>10</sub>	1486-01-7	612 B
bis(2-chloroethyl) ether	34273	111-44-4	018 B	011 B	d <sub>8</sub>	93952-02-4	218 B
bis(2-chloroethoxy)methane	34278	111-91-1	043 B	010 B	d <sub>8</sub>	93966-78-0	243 B
bis(2-chloroisopropyl) ether	34283	108-60-1	042 B	012 B	d <sub>12</sub>	93951-67-8	242 B
bis(2-ethylhexyl) phthalate	39100	117-81-7	066 B	013 B	d <sub>4</sub>	93951-87-2	266 B
4-bromophenyl phenyl ether	34636	101-55-3	041 B	014 B	d <sub>5</sub>	93951-83-8	241 B
butyl benzyl phthalate	34292	85-68-7	067 B	015 B	d <sub>4</sub>	93951-88-3	267 B
n-C10 (Appendix C)	77427	124-18-5	517 B		d <sub>22</sub>	16416-29-8	617 B
n-C12 (Appendix C)	77588	112-40-3	506 B		d <sub>26</sub>	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 <sub>34</sub>	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 <sub>42</sub>	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 <sub>50</sub>	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 <sub>62</sub>	93952-07-9	626 B

Table 1 (continued)  
BASE/NEUTRAL EXTRACTABLE COMPOUNDS DETERMINED BY GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

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

Table 2  
ACID EXTRACTABLE COMPOUNDS DETERMINED BY GCMS USING ISOTOPE DILUTION AND INTERNAL STANDARD TECHNIQUES

Compound	Pollutant				Labeled Compound		
	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
4-chloro-3-methylphenol	34452	59-50-7	022 A	008 A	d <sub>2</sub>	93951-72-5	222 A
2-chlorophenol	34586	95-57-8	024 A	001 A	d <sub>4</sub>	93951-73-6	224 A
2,4-dichlorophenol	34601	120-83-2	031 A	002 A	d <sub>3</sub>	93951-74-7	231 A
2,4-dinitrophenol	34616	51-28-5	059 A	005 A	d <sub>3</sub>	93951-77-0	259 A
2-methyl-4,6-dinitrophenol	34657	534-52-1	060 A	004 A	d <sub>2</sub>	93951-76-9	260 A
2-nitrophenol	34591	88-75-5	057 A	006 A	d <sub>4</sub>	93951-75-1	257 A
4-nitrophenol	34646	100-02-7	058 A	007 A	d <sub>4</sub>	93951-79-2	258 A
pentachlorophenol	39032	87-86-5	064 A	009 A	<sup>13</sup> C <sub>6</sub>	85380-74-1	264 A
2,3,6-trichlorophenol (4c)	77688	933-75-5	530 A		d <sub>2</sub>	93951-81-6	630 A
2,4,5-trichlorophenol (4c)		95-95-4	531 A		d <sub>2</sub>	93951-82-7	631 A
2,4,6-trichlorophenol	34621	88-06-2	021 A	011 A	d <sub>2</sub>	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	EGD No.	Compound	CAS Registry
555	acetophenone	98-86-2	587	1,4-dinitrobenzene	100-25-4
556	4-aminobiphenyl	92-67-1	588	diphenyldisulfide	882-33-7
557	aniline	62-53-3	589	ethyl methanesulfonate	62-50-0
558	o-anisidine	90-04-0	590	ethylenethiourea	96-45-7
559	aramite	140-57-8	591	ethynylestradiol3-methyl ether	72-33-3
560	benzanthrone	82-05-3	592	hexachloropropene	1888-71-7
561	1,3-benzenediol(resorcinol)	108-46-3	593	2-isopropyl-naphthalene	2027-17-0
562	benzenethiol	108-98-5	594	isosafole	120-58-1
563	2,3-benzofluorene	243-17-4	595	longifolene	475-20-7
564	benzyl alcohol	100-51-6	596	malachite green	569-64-2
565	2-bromochlorobenzene	694-80-4	597	methapyrilene	91-80-5
566	3-bromochlorobenzene	108-37-2	598	methyl methanesulfonate	66-27-3
567	4-chloro-2-nitroaniline	89-63-4	599	2-methylbenzothiazole	120-75-2
568	5-chloro-o-toluidine	95-79-4	900	3-methylcholanthrene	56-49-5
569	4-chloroaniline	106-47-8	901	4,4'-methylene-bis(2-chloroaniline)	101-14-4
570	3-chloronitrobenzene	121-73-3	902	4,5-methylene-phenanthrene	203-64-5
571	o-cresol	95-48-7	903	1-methylfluorene	1730-37-6
572	crotoxyphos	7700-17-6	904	2-methylnaphthalene	91-57-6
573	2,6-di-tert-butyl-p-benzoquinone	719-22-2	905	1-methylphenanthrene	832-69-9
574	2,4-diaminotoluene	95-80-7	906	2-(methylthio)-benzothiazole	615-22-5
575	1,2-dibromo-3-chloropropane	96-12-8	907	1,5-naphthalenediamine	2243-62-1
576	2,6-dichloro-4-nitroaniline	99-30-9	908	1,4-naphthoquinone	130-15-4
577	1,3-dichloro-2-propanol	96-23-1	909	alpha-naphthylamine	134-32-7
578	2,3-dichloroaniline	608-27-5	910	5-nitro-o-toluidine	99-55-8
579	2,3-dichloronitro-benzene	3209-22-1	911	2-nitroaniline	88-74-4
580	1,2:3,4-diepoxybutane	1464-53-5	912	3-nitroaniline	99-09-2
581	3,3'-dimethoxybenzidine	119-90-4	913	4-nitroaniline	100-01-6
582	dimethyl sulfone	67-71-0	914	4-nitrobiphenyl	92-93-3
583	p-dimethylamino-azobenzene	60-11-7	915	N-nitrosodi-n-butylamine	924-16-3
584	7,12-dimethylbenz-(a)anthracene	57-97-6	916	N-nitrosodiethylamine	55-18-5
585	N,N-dimethylformamide	68-12-2	917	N-nitrosomethyl-ethylamine	10595-95-6
586	3,6-dimethylphenanthrene	1576-67-6	918	N-nitrosomethyl-phenylamine	614-00-6

Table 3 (continued)  
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
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	tripropyleneglycolmethyl ether	20324-33-8
942	1,3,5-trithiane	291-21-4

## 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. Each extract is dried over sodium sulfate, concentrated to a volume of five mL, cleaned up using gel permeation chromatography (GPC), if

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

necessary, and concentrated. Extracts are concentrated to one mL if GPC is not performed, and to 0.5 mL if GPC is performed. 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 (see Section 13).

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

Table 5  
GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		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 <sub>6</sub> (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 <sub>7</sub>	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 <sub>5</sub>	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 <sub>14</sub>	742	164	0.624 - 0.652	10		
713	p-cymene	755	613	1.008 - 1.023	10	426*	912*
265	phenol-d <sub>5</sub>	696	164	0.584 - 0.613	10		
365	phenol	700	265	0.995 - 1.010	10	2501*	757*
218	bis(2-chloroethyl) ether-d <sub>8</sub>	696	164	0.584 - 0.607	10		
318	bis(2-chloroethyl) ether	704	218	1.007 - 1.016	10	32	22
617	n-C10-d <sub>22</sub>	698	164	0.585 - 0.615	10		
717	n-C10	720	617	1.022 - 1.038	10	299*	1188*
226	1,3-dichlorobenzene-d <sub>4</sub>	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 <sub>4</sub>	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 <sub>4</sub>	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 <sub>12</sub>	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 <sub>14</sub> (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- <sup>13</sup> 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			

Table 5 (continued)  
GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
575	1,2-dibromo-3-chloropropane	839	164	0.721			
256	nitrobenzene-d <sub>5</sub>	845	164	0.706 - 0.727	10		
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 <sub>8</sub>	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 <sub>3</sub>	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 <sub>6</sub> (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 <sub>3</sub>	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 <sub>8</sub>	963	164	0.819 - 0.836	10		
355	naphthalene	967	255	1.001 - 1.006	10	62	42
934	thianaphene	971	164	0.835			
609	alpha-terpineol-d <sub>3</sub>	973	164	0.829 - 0.844	10		
709	alpha-terpineol	975	609	0.998 - 1.008	10	nd	nd
606	n-C12-d <sub>26</sub>	953	164	0.730 - 0.908	10		
706	n-C12	981	606	0.986 - 1.051	10	860*	3885*
629	1,2,3-trichlorobenzene-d <sub>3</sub> (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- <sup>13</sup> C <sub>4</sub>	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- <sup>13</sup> C <sub>4</sub>	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 <sub>7</sub>	1185	164	1.014 - 1.024	10		
320	2-chloronaphthalene	1200	220	0.997 - 1.007	10	80	59



Table 5 (continued)  
GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
518	n-C14	1203	164	1.034	10	256	3533
612	biphenyl-d <sub>10</sub>	1195	164	1.016 - 1.027	10		
712	biphenyl	1205	612	1.001 - 1.006	10	67	55
608	diphenyl ether-d <sub>10</sub>	1211	164	1.036 - 1.047	10		
708	diphenyl ether	1216	608	0.997 - 1.009	10	44	12
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 <sub>8</sub>	1265	164	1.080 - 1.095	10		
377	acenaphthylene	1247	277	1.000 - 1.004	10	57	18
593	2-isopropyl-naphthalene	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 <sub>4</sub>	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 <sub>3</sub>	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 <sub>10</sub>	1298	164	1.107 - 1.125	10		
301	acenaphthene	1304	201	0.999 - 1.009	10	64	55
605	dibenzofuran-d <sub>8</sub>	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 <sub>3</sub>	1359	164	1.152 - 1.181	10		
335	2,4-dinitrotoluene	1364	235	1.000 - 1.002	10	65	209*
602	beta-naphthylamine-d <sub>7</sub>	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 <sub>10</sub>	1395	164	1.185 - 1.214	10		
380	fluorene	1401	281	0.999 - 1.008	10	69	61
240	4-chlorophenyl phenyl ether-d <sub>5</sub>	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 <sub>4</sub>	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-C16-d <sub>34</sub>	1447	164	1.010 - 1.478	10		
719	n-C16	1469	619	1.013 - 1.020	10	116*	644*
237	1,2-diphenylhydrazine-d <sub>8</sub>	1433	164	1.216 - 1.248	20		
337	1,2-diphenylhydrazine (6)	1439	237	0.999 - 1.009	20	48	27
607	diphenylamine-d <sub>10</sub>	1437	164	1.213 - 1.249	20		
707	diphenylamine	1439	607	1.000 - 1.007	20	58	54
262	N-nitrosodiphenylamine-d <sub>6</sub>	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 <sub>5</sub> (5)	1495	164	1.271 - 1.307	10		
341	4-bromophenyl phenyl ether (5)	1498	241	0.990 - 1.015	10	55	17

Table 5 (continued)  
GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
925	phenacetin	1512	164	1.300			
903	1-methylfluorene	1514	164	1.302			
209	hexachlorobenzene- <sup>13</sup> C <sub>6</sub>	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 <sub>10</sub>	1578	164	1.334 - 1.380	10		
520	n-C18	1580	164	1.359	10	134*	844*
381	phenanthrene	1583	281	1.000 - 1.005	10	42	22
278	anthracene-d <sub>10</sub>	1588	164	1.342 - 1.388	10		
378	anthracene	1592	278	0.998 - 1.006	10	52	21
604	dibenzothiophene-d <sub>8</sub>	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 <sub>8</sub> (5)	1645	164	1.388 - 1.439	20		
728	carbazole (5)	1650	628	1.000 - 1.006	20	47	24
621	n-C20-d <sub>42</sub>	1655	164	1.184 - 1.662	10		
721	n-C20	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 <sub>4</sub>	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 <sub>10</sub>	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 <sub>10</sub>	1844	164	1.523 - 1.644	10		
384	pyrene	1852	284	1.001 - 1.003	10	40	48
205	benzidine-d <sub>8</sub>	1854	164	1.549 - 1.632	50		
305	benzidine	1853	205	1.000 - 1.002	50	nd	nd
522	n-C22	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-C24-d <sub>50</sub>	1997	164	1.671 - 1.764	10		
723	n-C24	2025	612	1.012 - 1.015	10	--	--
932	squalene	2039	164	1.753			
267	butylbenzyl phthalate-d <sub>4</sub> (5)	2058	164	1.715 - 1.824	10		
367	butylbenzyl phthalate (5)	2060	267	1.000 - 1.002	10	60	65
276	chrysene-d <sub>12</sub>	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 <sub>12</sub>	2082	164	1.735 - 1.846	10		

Table 5 (continued)  
GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
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 <sub>6</sub>	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 <sub>4</sub>	2123	164	1.771 - 1.880	10		
366	bis(2-ethylhexyl) phthalate	2124	266	1.000 - 1.002	10	553*	1310*
524	n-C26	2147	164	1.846	10	609*	886*
591	ethynylestradiol 3-methyl ether	2209	164	1.899			
269	di-n-octyl phthalate-d <sub>4</sub>	2239	164	1.867 - 1.982	10		
369	di-n-octyl phthalate	2240	269	1.000 - 1.002	10	72	62
525	n-C28	2272	164	1.954	10	492*	1810*
584	7,12-dimethylbenz(a)anthracene	2284	164	1.964			
274	benzo(b)fluoranthene-d <sub>12</sub>	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 <sub>12</sub>	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 <sub>12</sub>	2351	164	1.954 - 2.088	10		
373	benzo(a)pyrene	2350	273	1.000 - 1.004	10	52	15
626	n-C30-d <sub>62</sub>	2384	164	1.972 - 2.127	10		
726	n-C30	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 <sub>14</sub> (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 <sub>12</sub>	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 CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR ACID EXTRACTABLE COMPOUNDS

EGD No. (1)	Compound	Retention time			Mini- mum Level (3) (ug/mL)	Method Detection Limit (4)	
		Mean (sec)	EGD Ref	Relative (2)		low solids (ug/kg)	high solids (ug/kg)
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000 - 1.000	10		
224	2-chlorophenol-d <sub>4</sub>	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 <sub>4</sub>	898	164	0.761 - 0.783	20		
357	2-nitrophenol	900	257	0.994 - 1.009	20	39	44
231	2,4-dichlorophenol-d <sub>3</sub>	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 <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub> (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 <sub>3</sub>	1323	164	1.127 - 1.149	50		
359	2,4-dinitrophenol	1325	259	1.000 - 1.005	50	565	642
258	4-nitrophenol-d <sub>4</sub>	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 <sub>2</sub>	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- <sup>13</sup> C <sub>6</sub>	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).

(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

- 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 The quality of the analysis 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, dibenzo(a,h)anthracene, benzo(a)pyrene, 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 Cap liners are washed with detergent and water, rinsed with reagent water (see Section 6.5.1) and then solvent, and then baked for at least one hour at approximately 200 °C.
- 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. Only glass or Teflon tubing shall be used. If the sampler uses a peristaltic pump, a

- minimum length of compressible silicone rubber tubing may be used only in the pump. 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 maintaining a temperature of  $110 \pm 5$  °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, borosilicate glass beakers calibrated to one liter
      - 5.4.2.2 400 - 500 mL borosilicate glass beakers
      - 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 Concentration apparatus
    - 5.6.1 Concentrator tube--Kuderna-Danish (K-D) 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.
    - 5.6.2 Evaporation flask--Kuderna-Danish (K-D) 500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).
    - 5.6.3 Snyder column--Kuderna-Danish (K-D) three ball macro (Kontes K-503000-0232, or equivalent).
    - 5.6.4 Snyder column--Kuderna-Danish (K-D) 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 hour minimum.
    - 5.6.6 Nitrogen evaporation device--equipped with a water bath that can be maintained at 35 - 40 °C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.
  - 5.7 Water bath--heated, with concentric ring cover, capable of temperature control ( $\pm 2$  °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  $\mu$ L 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 5 aliquots of 0.5 mL each 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  $\pm 15$  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. Examine the spectrum to determine that only a single compound is present. 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 DFIPP 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 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.

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

Table 8  
CHARACTERISTIC M/Z'S AND RESPONSE FACTORS OF BASE/NEUTRAL EXTRACTABLE COMPOUNDS

Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)	Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)
acenaphthene	d <sub>10</sub>	154/164		4-chlorophenyl phenyl ether	d <sub>5</sub>	204/209	
acenaphthylene	d <sub>8</sub>	152/160		3-chloropropionitrile		54	0.42
acetophenone		105	0.79	chrysene	d <sub>12</sub>	228/240	
4-aminobiphenyl		169	0.81	o-cresol		108	0.59
aniline		93	1.04	crotoxyphos		127	0.017
o-anisidine		108	0.43	p-cymene	d <sub>14</sub>	119/130	
anthracene	d <sub>10</sub>	178/188		2,6-di-tert-butyl-p-benzoquinone		220	0.078
aramite		185	0.19	di-n-butyl phthalate	d <sub>4</sub>	149/153	
benzanthrone		230	0.15	2,4-diaminotoluene		122	0.059
1,3-benzenediol		110	0.78	dibenzo(a,h)anthracene	d <sub>14</sub>	278/292	
benzenethiol		110	0.18	dibenzofuran	d <sub>8</sub>	168/176	
benzidine	d <sub>8</sub>	184/192		dibenzothiophene	d <sub>8</sub>	184/192	
benzo(a)anthracene	d <sub>12</sub>	228/240		1,2-dibromo-3-chloropropane		157	0.22
benzo(b)fluoranthene	d <sub>12</sub>	252/264		2,6-dichloro-4-nitroaniline		124	0.019
benzo(k)fluoranthene	d <sub>12</sub>	252/264		1,3-dichloro-2-propanol		79	0.68
benzo(a)pyrene	d <sub>12</sub>	252/264		2,3-dichloroaniline		161	0.47
benzo(ghi)perylene	d <sub>12</sub>	276/288		1,2-dichlorobenzene	d <sub>4</sub>	146/152	
2,3-benzofluorene		216	0.35	1,3-dichlorobenzene	d <sub>4</sub>	146/152	
benzoic acid		105	0.16	1,4-dichlorobenzene	d <sub>4</sub>	146/152	
benzyl alcohol		79	0.47	3,3'-dichlorobenzidine	d <sub>6</sub>	252/258	
biphenyl	d <sub>10</sub>	154/164		2,2'-difluorobiphenyl (int std)		190	
bis(2-chloroethyl) ether	d <sub>8</sub>	93/101		2,3-dichloronitrobenzene		191	0.11
bis(2-chloroethoxy)methane	d <sub>6</sub>	93/99		1,2:3,4-diepoxybutane		55	0.27
bis(2-chloroisopropyl) ether	d <sub>12</sub>	121/131		diethyl phthalate	d <sub>4</sub>	149/153	
bis(2-ethylhexyl) phthalate	d <sub>4</sub>	149/153		3,3'-dimethoxybenzidine		244	0.19
2-bromochlorobenzene		111	0.33	dimethyl phthalate	d <sub>4</sub>	163/167	
3-bromochlorobenzene		192	0.40	dimethyl sulfone		79	0.40
4-bromophenyl phenyl ether	d <sub>5</sub>	248/253		p-dimethylaminoazobenzene		120	0.23
butyl benzyl phthalate	d <sub>4</sub>	149/153		7,12-dimethylbenz(a)anthracene		256	0.58
n-C10	d <sub>22</sub>	57/82		N,N-dimethylformamide		73	0.51
n-C12	d <sub>26</sub>	57/66		3,6-dimethylphenanthrene		206	0.72
n-C14		57		2,4-dimethylphenol	d <sub>3</sub>	122/125	
n-C16	d <sub>34</sub>	57/66		1,4-dinitrobenzene		168	0.24
n-C18		57		2,4-dinitrotoluene	d <sub>3</sub>	165/168	
n-C20	d <sub>42</sub>	57/66		2,6-dinitrotoluene	d <sub>3</sub>	165/167	
n-C22		57		di-n-octyl phthalate	d <sub>4</sub>	149/153	
n-C24	d <sub>50</sub>	57/66		diphenylamine	d <sub>10</sub>	169/179	
n-C26		57		diphenyl ether	d <sub>10</sub>	170/180	
n-C28		57		diphenyldisulfide		218	0.25
n-C30	d <sub>62</sub>	57/66		1,2-diphenylhydrazine (3)	d <sub>10</sub>	77/82	
carbazole	d <sub>8</sub>	167/175		ethyl methanesulfonate		109	0.28
4-chloro-2-nitroaniline		172	0.20	ethylenethiourea		102	0.22
5-chloro-o-toluidine		106	0.50				
4-chloroaniline		127	0.73				
2-chloronaphthalene	d <sub>7</sub>	162/169					
3-chloronitrobenzene		157	0.18				

Table 8  
CHARACTERISTIC M/Z'S AND RESPONSE FACTORS OF BASE/NEUTRAL EXTRACTABLE COMPOUNDS

Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)	Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)
ethynylestradiol 3-methyl ether		227	0.28	N-nitrosopiperidine		114	0.41
fluoranthene	d <sub>10</sub>	202/212		pentachlorobenzene		248	0.25
fluorene	d <sub>10</sub>	166/176		pentachloroethane		117	0.20
hexachlorobenzene	<sup>13</sup> C <sub>6</sub>	284/292		pentamethylbenzene		148	0.42
hexachlorobutadiene	<sup>13</sup> C <sub>4</sub>	225/231		perylene		252	0.30
hexachloroethane	<sup>13</sup> C <sub>2</sub>	201/204		phenacetin		108	0.38
hexachlorocyclopentadiene	<sup>13</sup> C <sub>4</sub>	237/241		phenanthrene	d <sub>10</sub>	178/188	
hexachloropropene		213	0.23	phenol	d <sub>5</sub>	94/71	
indeno(1,2,3-cd)pyrene		276		phenothiazine		199	0.15
isophorone	d <sub>8</sub>	82/88		1-phenylnaphthalene		204	0.48
2-isopropylnaphthalene		170	0.32	2-phenylnaphthalene		204	0.73
isosafrole		162	0.33	alpha-picoline	d <sub>7</sub>	93/100	
longifolene		161	0.14	pronamide		173	0.31
malachite green		330		pyrene	d <sub>10</sub>	202/212	
methapyrilene		97	0.43	pyridine		79	0.68
methyl methanesulfonate		80	0.20	safrole		162	0.45
2-methylbenzothiazole		149	0.59	squalene		69	0.042
3-methylcholanthrene		268	0.59	styrene	d <sub>5</sub>	104/109	
4,4'-methylenebis (2-chloroaniline)		231	0.21	alpha-terpineol	d <sub>3</sub>	59/62	
4,5-methylenephenanthrene		190	0.44	1,2,4,5-tetrachlorobenzene		216	0.43
1-methylfluorene		180	0.37	thianaphthene		134	1.52
2-methylnaphthalene		142	0.99	thioacetamide		75	0.28
1-methylphenanthrene		192	0.65	thioxanthone		212	0.23
2-(methylthio)benzothiazole		181	0.42	o-toluidine		106	1.04
naphthalene	d <sub>8</sub>	128/136		1,2,3-trichlorobenzene	d <sub>3</sub>	180/183	
1,5-naphthalenediamine		158	0.085	1,2,4-trichlorobenzene	d <sub>3</sub>	180/183	
1,4-naphthoquinone		158	0.021	1,2,3-trimethoxybenzene		168	0.48
alpha-naphthylamine		143	0.89	2,4,5-trimethylaniline		120	0.28
beta-naphthylamine	d <sub>7</sub>	143/150		triphenylene		228	1.32
5-nitro-o-toluidine		152	0.31	tripropylene glycol methyl ether		59	0.092
2-nitroaniline		138	0.39	1,3,5-trithiane		138	0.15
3-nitroaniline		138	0.27				
4-nitroaniline		138	0.11				
nitrobenzene	d <sub>5</sub>	123/128		(1) native/labeled			
4-nitrobiphenyl		199	0.35	(2) referenced to 2,2'-difluorobiphenyl			
N-nitrosodi-n-butylamine		84	0.47	(3) detected as azobenzene			
N-nitrosodi-n-propylamine	d <sub>14</sub>	70/78		(4) detected as diphenylamine			
N-nitrosodiethylamine		102	0.45				
N-nitrosodimethylamine	d <sub>6</sub>	74/80		NOTE: Because the composition and purity of commercially-supplied isotopically labeled standards may vary, the primary m/z of the labeled analogs given in this table should be used as guidance. The appropriate m/z of the labeled analogs should be determined prior to use for sample analysis. Deviations from the m/z's listed here must be documented by the laboratory and submitted with the data.			
N-nitrosodiphenylamine (4)	d <sub>6</sub>	169/175					
N-nitrosomethylethylamine		88	0.33				
N-nitrosomethylphenylamine		106	0.024				
N-nitrosomorpholine		56	0.49				

Table 9  
CHARACTERISTIC M/Z'S AND RESPONSE FACTORS OF ACID  
EXTRACTABLE COMPOUNDS

Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)
benzoic acid		105	0.16
4-chloro-3-methylphenol	d <sub>2</sub>	107/109	
2-chlorophenol	d <sub>4</sub>	128/132	
p-cresol		108	0.61
3,5-dibromo-4-hydroxybenzonitrile		277	0.12
2,4-dichlorophenol	d <sub>3</sub>	162/167	
2,6-dichlorophenol		162	0.42
2,4-dinitrophenol	d <sub>3</sub>	184/187	
hexanoic acid		60	0.62
2-methyl-4,6-dinitrophenol	d <sub>2</sub>	198/200	
2-nitrophenol	d <sub>4</sub>	65/109	
4-nitrophenol	d <sub>4</sub>	65/109	
pentachlorophenol	<sup>13</sup> C <sub>6</sub>	266/272	
2,3,4,6-tetrachlorophenol		232	0.17
2,3,6-trichlorophenol	d <sub>2</sub>	196/200	
2,4,5-trichlorophenol	d <sub>2</sub>	196/200	
2,4,6-trichlorophenol	d <sub>2</sub>	196/200	

(1) native/labeled

(2) referenced to 2,2'-difluorobiphenyl

NOTE: Because the composition and purity of commercially-supplied isotopically labeled standards may vary, the primary m/z of the labeled analogs given in this table should be used as guidance. The appropriate m/z of the labeled analogs should be determined prior to use for sample analysis. Deviations from the m/z's listed here must be documented by the laboratory and submitted with the data.

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

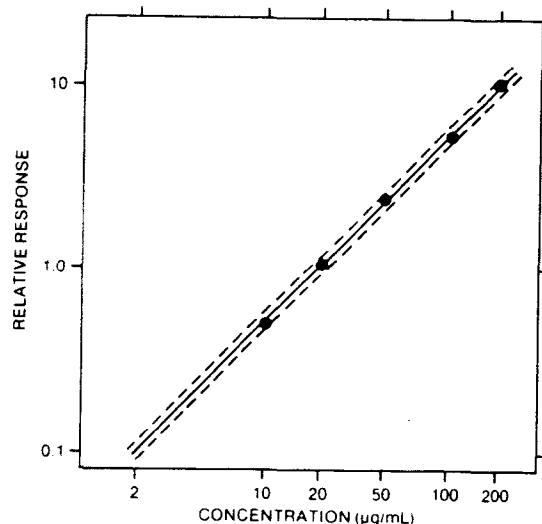


FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a  $\pm 10$  Percent Error Window.

a calibration curve for phenol using phenol-d<sub>5</sub> as the isotopic diluent. Also shown are the  $\pm 10$  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 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,

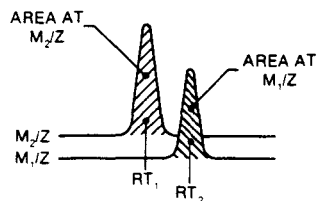


FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled ( $m_2/z$ ) and Unlabeled ( $m_1/z$ ) Pairs.

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

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

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

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

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,

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

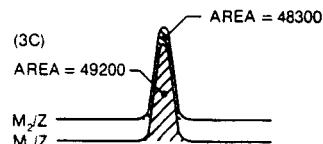
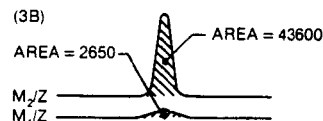
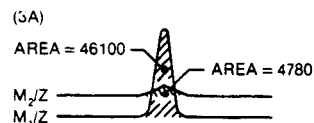


FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

$$R_y = \frac{2650}{43600} = 0.06078$$

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

$$RR = 1.115.$$

The data from these analyses are reported to three significant figures (see Section 14.6). Therefore, in order to prevent rounding errors from affecting the values to be reported, all calculations performed prior to the final determination of concentrations should be carried out using at least four significant figures.

7.4.5 To calibrate the analytical system by isotope dilution, analyze a 1.0  $\mu\text{L}$  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:

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

$A_s$  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.

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.

Table 10  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No.		Labeled and native compound initial precision and accuracy (Sec 8.2.3) (ug/L)		Labeled compound recovery (Sec 8.3 and 14.2) P (%)	Calibration verification (Sec 12.5) (ug/mL)	Labeled and native compound on-going accuracy (Sec 12.7) R (ug/L)
(1)	Compound	s	X			
301	acenaphthene	21	79 - 134		80 - 125	72 - 144
201	acenaphthene-d <sub>10</sub>	38	38 - 147	20 - 270	71 - 141	30 - 180
377	acenaphthylene	38	69 - 186		60 - 166	61 - 207
277	acenaphthylene-d <sub>8</sub>	31	39 - 146	23 - 239	66 - 152	33 - 168
378	anthracene	41	58 - 174		60 - 168	50 - 199
278	anthracene-d <sub>10</sub>	49	31 - 194	14 - 419	58 - 171	23 - 242
305	benzidine	119	16 - 518		34 - 296	11 - 672
205	benzidine-d <sub>8</sub>	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 <sub>12</sub>	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 <sub>12</sub>	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 <sub>12</sub>	114	15 - 514	ns - ns	13 - ns	ns - 685
373	benzo(a)pyrene	26	62 - 195		78 - 129	59 - 206
273	benzo(a)pyrene-d <sub>12</sub>	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 <sub>12</sub>	45	29 - 268	14 - 529	13 - ns	25 - 303
712	biphenyl (Appendix C)	41	75 - 148		58 - 171	62 - 176
612	biphenyl-d <sub>10</sub>	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 <sub>8</sub>	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 <sub>12</sub>	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 <sub>4</sub>	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 <sub>5</sub> (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 <sub>4</sub> (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 <sub>22</sub>	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 <sub>26</sub>	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
519	n-C16-d <sub>34</sub>	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 <sub>42</sub>	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 <sub>50</sub>	28	27 - 211	15 - 376	50 - 199	25 - 229
524	n-C26 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212



Table 10 (continued)  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. (1)	Compound	Labeled and native compound initial precision and accuracy (Sec 8.2.3) (ug/L)		Labeled compound recovery (Sec 8.3 and 14.2)	Calibration verification (Sec 12.5)	Labeled and native compound on-going accuracy (Sec 12.7)
		s	X	P (%)	(ug/mL)	R (ug/L)
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 <sub>62</sub>	41	27 - 242	13 - 479	24 - 423	23 - 274
728	carbazole (4c)	38	36 - 165		44 - 227	31 - 188
628	carbazole-d <sub>8</sub> (3)	31	48 - 130	29 - 215	69 - 145	40 - 156
320	2-chloronaphthalene	100	46 - 357		58 - 171	35 - 442
220	2-chloronaphthalene-d <sub>7</sub>	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 <sub>2</sub>	111	30 - 174	ns - 613	68 - 147	14 - 314
324	2-chlorophenol	13	79 - 135		78 - 129	76 - 138
224	2-chlorophenol-d <sub>4</sub>	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 <sub>5</sub>	52	40 - 161	19 - 325	57 - 175	29 - 212
376	chrysene	51	59 - 186		70 - 142	48 - 221
276	chrysene-d <sub>12</sub>	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 <sub>14</sub>	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 <sub>14</sub> (3)	45	29 - 268	14 - 529	13 - ns	25 - 303
705	dibenzofuran (Appendix C)	20	85 - 136		73 - 136	79 - 146
605	dibenzofuran-d <sub>8</sub>	31	47 - 136	28 - 220	66 - 150	39 - 160
704	dibenzothiophene (Synfuel)	31	79 - 150		72 - 140	70 - 168
604	dibenzothiophene-d <sub>8</sub>	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 <sub>4</sub>	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 <sub>4</sub>	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 <sub>4</sub>	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 <sub>4</sub>	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 <sub>6</sub>	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 <sub>3</sub>	28	38 - 164	24 - 260	64 - 157	34 - 182
370	diethyl phthalate	44	75 - 196		74 - 135	65 - 222
270	diethyl phthalate-d <sub>4</sub>	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 <sub>3</sub>	22	15 - 228	ns - 449	58 - 172	14 - 242
371	dimethyl phthalate	36	74 - 188		73 - 137	67 - 207
271	dimethyl phthalate-d <sub>4</sub>	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 <sub>3</sub>	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 <sub>3</sub>	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 <sub>3</sub>	59	44 - 184	17 - 442	36 - 278	31 - 250

Table 10 (continued)  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. (1)	Compound	Labeled and native compound initial precision and accuracy (Sec 8.2.3) (ug/L)		Labeled compound recovery (Sec 8.3 and 14.2)	Calibration verification (Sec 12.5)	Labeled and native compound on-going accuracy (Sec 12.7)
		s	X	P (%)	(ug/mL)	R (ug/L)
369	di-n-octyl phthalate	16	77 - 161		71 - 140	74 - 166
269	di-n-octyl phthalate-d <sub>4</sub>	46	12 - 383	ns - ns	21 - 467	10 - 433
707	diphenylamine (Appendix C)	45	58 - 205		57 - 176	51 - 231
607	diphenylamine-d <sub>10</sub>	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 <sub>10</sub>	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 <sub>10</sub>	35	31 - 173	17 - 316	58 - 174	26 - 200
339	fluoranthene	33	71 - 177		67 - 149	64 - 194
239	fluoranthene-d <sub>10</sub>	35	36 - 161	20 - 278	47 - 215	30 - 187
380	fluorene	29	81 - 132		74 - 135	70 - 151
280	fluorene-d <sub>10</sub>	43	51 - 131	27 - 238	61 - 164	38 - 172
309	hexachlorobenzene	16	90 - 124		78 - 128	85 - 132
209	hexachlorobenzene- <sup>13</sup> C <sub>6</sub>	81	36 - 228	13 - 595	38 - 265	23 - 321
352	hexachlorobutadiene	56	51 - 251		74 - 135	43 - 287
252	hexachlorobutadiene- <sup>13</sup> C <sub>4</sub>	63	ns - 316	ns - ns	68 - 148	ns - 413
312	hexachloroethane	227	21 - ns		71 - 141	13 - ns
212	hexachloroethane- <sup>13</sup> C	77	ns - 400	ns - ns	47 - 212	ns - 563
353	hexachlorocyclopentadiene	15	69 - 144		77 - 129	67 - 148
253	hexachlorocyclopentadiene- <sup>13</sup> C <sub>4</sub>	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 <sub>8</sub>	23	49 - 133	33 - 193	52 - 194	44 - 147
360	2-methyl-4,6-dinitrophenol	19	77 - 133		69 - 145	72 - 142
260	2-methyl-4,6-dinitrophenol-d <sub>2</sub>	64	36 - 247	16 - 527	56 - 177	28 - 307
355	naphthalene	20	80 - 139		73 - 137	75 - 149
255	naphthalene-d <sub>8</sub>	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 <sub>7</sub>	33	ns - ns	ns - ns	44 - 230	ns - ns
356	nitrobenzene	25	69 - 161		85 - 115	65 - 169
256	nitrobenzene-d <sub>5</sub>	28	18 - 265	ns - ns	46 - 219	15 - 314
357	2-nitrophenol	15	78 - 140		77 - 129	75 - 145
257	2-nitrophenol-d <sub>4</sub>	23	41 - 145	27 - 217	61 - 163	37 - 158
358	4-nitrophenol	42	62 - 146		55 - 183	51 - 175
258	4-nitrophenol-d <sub>4</sub>	188	14 - 398	ns - ns	35 - 287	ns - ns
361	N-nitrosodimethylamine	49	10 - ns		39 - 256	ns - ns
261	N-nitrosodimethylamine-d <sub>6</sub> (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 <sub>6</sub>	37	54 - 126	26 - 256	59 - 170	40 - 166
364	pentachlorophenol	21	76 - 140		77 - 130	71 - 150
264	pentachlorophenol- <sup>13</sup> C <sub>6</sub>	49	37 - 212	18 - 412	42 - 237	29 - 254
381	phenanthrene	13	93 - 119		75 - 133	87 - 126
281	phenanthrene-d <sub>10</sub>	40	45 - 130	24 - 241	67 - 149	34 - 168
365	phenol	36	77 - 127		65 - 155	62 - 154
265	phenol-d <sub>5</sub>	161	21 - 210	ns - ns	48 - 208	ns - ns

Table 10 (continued)  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. (1)	Compound	Labeled and native compound initial precision and accuracy (Sec. 8.2.3) (ug/L)		Labeled compound recovery (Sec 8.3 and 14.2)	Calibration verification (Sec 12.5) (ug/mL)	Labeled and native compound on-going accuracy (Sec 12.7) R (ug/L)
		s	X	P (%)		
703	alpha-picoline (Synfuel)	38	59 - 149		60 - 165	50 - 174
603	alpha-picoline-d <sub>7</sub>	138	11 - 380	ns - ns	31 - 324	ns - 608
384	pyrene	19	76 - 152		76 - 132	72 - 159
284	pyrene-d <sub>10</sub>	29	32 - 176	18 - 303	48 - 210	28 - 196
710	styrene (Appendix C)	42	53 - 221		65 - 153	48 - 244
610	styrene-d <sub>5</sub>	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 <sub>3</sub>	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 <sub>3</sub> (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 <sub>3</sub>	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 <sub>2</sub> (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 <sub>2</sub>	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.

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

- 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

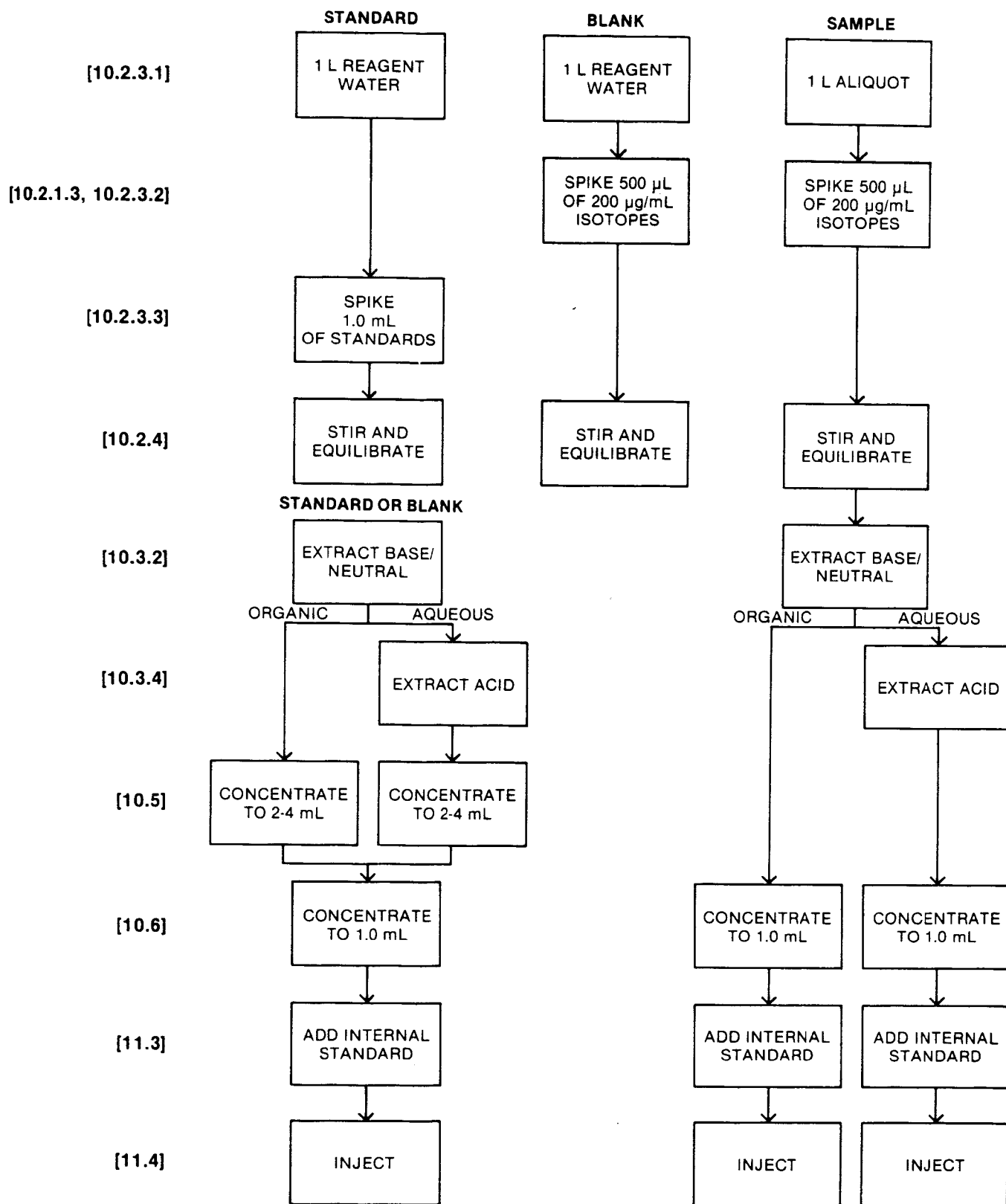


FIGURE 4 Flow Chart for Extraction/Concentration of Low Solids Precision and Recovery Standard, Blank, and Sample by Method 1625. Numbers in Brackets [ ] Refer to Section Numbers in the Method.

- 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 inch horn on the ultrasonic probe approx 1/2 inch 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  $1.0 \pm 0.1$  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 three  $1.0 \pm 0.01$  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 Discard all sticks, rocks, leaves and other foreign material prior to weighing. Weigh  $30 \pm 0.3$  grams into a clean 400 - 500 mL beaker.
- 10.2.5.3 Dilute aliquot--for samples which are expected to be difficult to extract, concentrate, or clean-up, weigh  $3 \pm 0.03$  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  $30 \pm 0.3$  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 and QC aliquots 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 QC 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  $\pm$  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 semivolatile 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 lower 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
- 10.6.1 Kuderna-Danish (K-D)--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, to 1.0 mL if it does not require clean-up, or to 0.5 mL if it has been cleaned up.

- 10.6.2 Nitrogen blowdown--Place the concentrator tube in a warm water bath (35 °C) and evaporate the solvent volume using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences. The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. Adjust the final volume to 5.0 mL if the extract is to be cleaned up by GPC, to 1.0 mL if it does not require clean-up, or to 0.5 mL if it has been cleaned 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 to 5.0 mL 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 Concentrate the extract to 0.5 mL and transfer to a screw-cap vial per Sections 10.6 and 10.7. Concentrating extracts cleaned up by GPC to 0.5 mL will place the analytes in the same part of the GCMS calibration range as in samples not subjected to GPC.

## 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  $85 - 105\%$ .

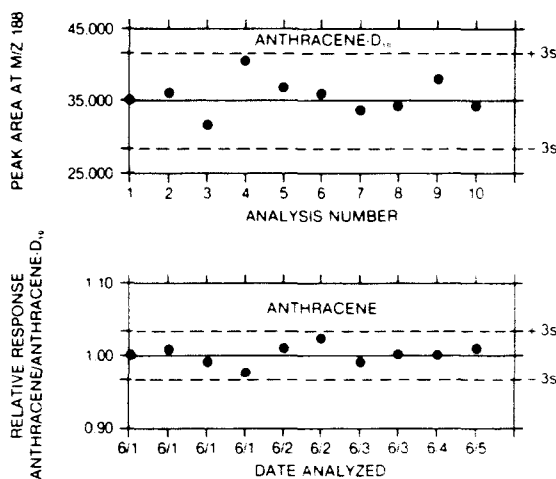


FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d<sub>10</sub> (lower graph) Plotted as a Function of Time or Analysis Number.

### 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 - 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  $\pm 15$  scans or  $\pm 15$  seconds (whichever is greater) for compounds for which no window is specified.
- 13.1.4 The system has not been calibrated for the compounds listed in Tables 3 and 4, however, the relative retention times and mass spectra of these compounds are known. Therefore, for a compound in Tables 3 or 4 to be identified, its retention time relative to the internal standard 2,2'-difluorobiphenyl must fall within a retention time window of  $\pm 30$  seconds, or  $\pm 30$  scans (whichever is greater) of the nominal retention time of the compound specified in Tables 5 or 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  $\pm 1$  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 The 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 spectrometrists (Section 1.4) is to determine the presence or absence of the compound.
- 14 QUANTITATIVE DETERMINATION
- 14.1 Isotope dilution--Because the pollutant and its labeled analog exhibit the same effects upon extraction, concentration, and gas chromatography, correction for recovery of the pollutant can be made by adding a known amount of a labeled compound to every sample prior to extraction. Relative response (RR) values for sample mixtures are used in conjunction with the 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:
- $$C_{ex} \text{ (ug/mL)} = \frac{(A_s \times C_{is})}{(A_{is} \times RF)}$$
- 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 Dilution of samples--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. For water samples, where the base/neutral and acid extracts are not combined, re-analysis is only required for the extract (B/N or A) in which the compound exceeds the calibration range. 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  $0.30 \pm 0.003$  g of sample per Section 10.2.5.
- 14.5 Dilution of samples containing high concentrations of compounds to be identified per Section 13.3 -- When the EICP area of the quantitation m/z of a compound to be identified per Section 13.3 exceeds the linear range of the GCMS system, or when any peak is saturated, dilute the sample per Section 14.4.1-14.4.3.

14.6 Results are reported to three significant figures for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples. For aqueous samples, the units are ug/L, and for samples containing one percent solids or greater (soils, sediments, filter cake, compost), the units are ug/kg, based on the dry weight of the solids.

- 14.6.1 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 loss of the internal standard 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 apply to 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.

#### REFERENCES

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- 5 "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety (1979).
- 6 "Interlaboratory Validation of U. S. Environmental Protection Agency Method 1625A, Addendum Report", SRI International, Prepared for Analysis and Evaluation Division (WH-557), USEPA, 401 M St SW, Washington DC 20460 (January 1985).
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- 10 "Inter-laboratory Validation of US Environmental Protection Agency Method 1625," USEPA, Effluent Guidelines Division, Washington, DC 20460 (June 15, 1984).
- 11 "Narrative for Episode 1036: Paragraph 4(c) Mass Spectra, Retention Times, and Response Factors", U S Testing Co, Inc, Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St SW, Washington DC 20460 (October 1985).
- 12 "Narrative for SAS 109: Analysis of Extractable Organic Pollutant Standards by Isotope Dilution GC/MS", S-CUBED Division of Maxwell Laboratories, Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St SW, Washington DC 20460 (July 1986).
- 13 Colby, Bruce N. and Ryan, Philip W., "Initial Evaluation of Methods 1634 and 1635 for the analysis of Municipal Wastewater Treatment Sludges by Isotope Dilution GC/MS", Pacific Analytical Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St SW, Washington DC 20460 (July 1986).

RIC DATA: HENID1166 #1 SCANS 1 TO 3200  
 03/13/84 5:24:00 CHL1: HENID1166 #1  
 SAMPLE: AB:G:VER:00100.00,C:NA:HA:NA\$  
 CONDS.: 1625A,30M.0,25MM,5030.30-20000.150200.30CM/S\$  
 RANGE: G 1.3200 LABEL: N 2, 3.0 QUAN: A 2, 2.0 J 0 BASE: U 20, 3

715776.

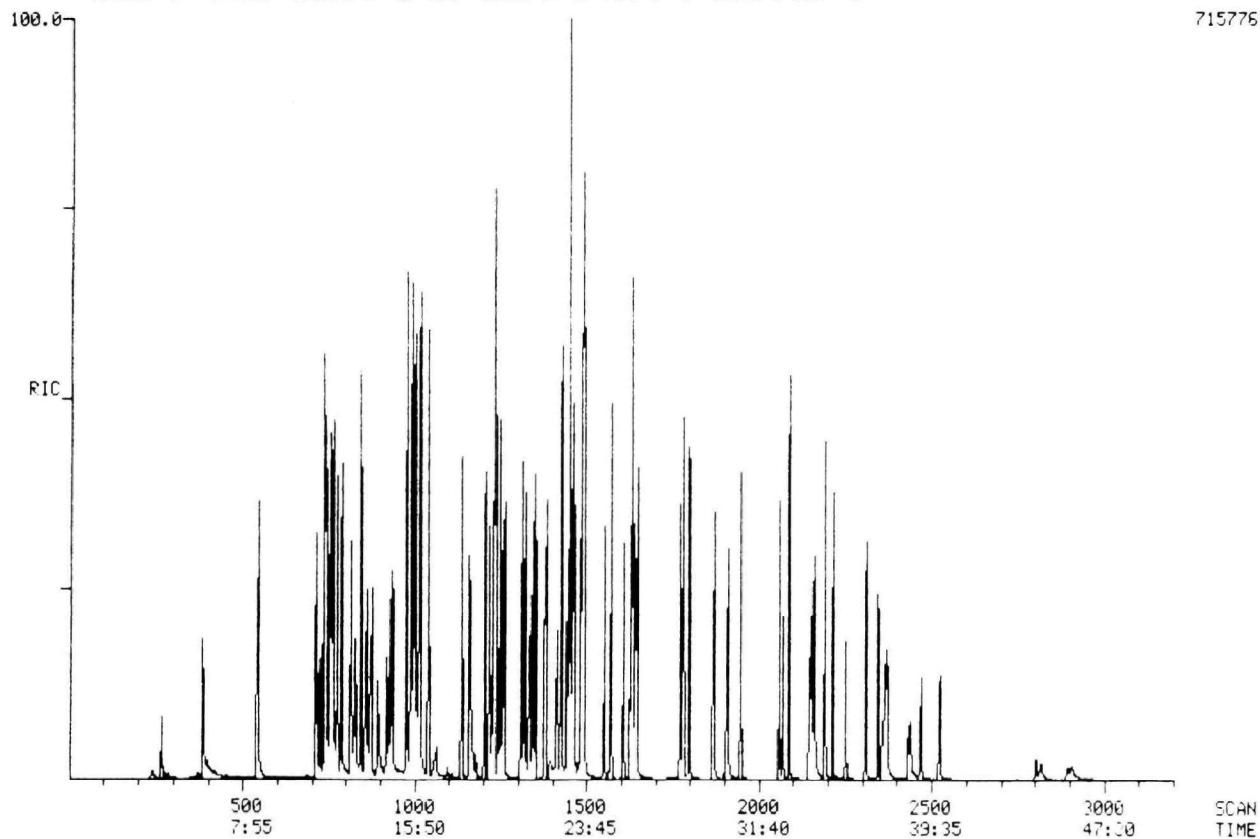


FIGURE 6 Chromatogram of Combined Acid/Base/Neutral Standard.

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

555 acetophenone

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

563 2,3-benzofluorene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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



Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

571 o-cresol

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

944 p-cresol

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

572 crotoxyphos

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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				

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

578 2,3-dichloroaniline

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

581 3,3'-dimethoxybenzidine

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

586 3,6-dimethylphenanthrene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

588 diphenyldisulfide

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

589 ethyl methanesulfonate

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

591 ethynylestradiol 3-methyl ether

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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-isopropyl-naphthalene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

595 longifolene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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-methylbenzothiazole

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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)

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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										

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

904 2-methylnaphthalene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

907 1,5-naphthalenediamine

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

911 2-nitroaniline

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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						

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

913 4-nitroaniline

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

922 pentachloroethane

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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						

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

923 pentamethylbenzene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

929 pronamide

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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										

Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

932 squalene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

936 thioxanthone

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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		



Appendix A (continued)  
Mass Spectra in the Form of Mass/Intensity Lists

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940 triphenylene

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>	<u>m/z</u>	<u>int.</u>
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

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

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**EPA METHOD 1618**

**ORGANO-HALIDE PESTICIDES, ORGANO-PHOSPHORUS  
PESTICIDES, AND PHENOXY-ACID HERBICIDES BY WIDE  
BORE CAPILLARY COLUMN GAS CHROMATOGRAPHY  
WITH SELECTIVE DETECTORS**



## Introduction

Method 1618 was developed by the Industrial Technology Division (ITD) within the United States Environmental Protection Agency's (USEPA) Office of Water Regulations and Standards (OWRS) 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.

Method 1618 is a wide bore capillary column gas chromatography method for analysis of organo-halide and organo-phosphorus pesticides, 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 method or its application should be addressed to:

W. A. Telliard  
USEPA  
Office of Water Regulations and Standards  
401 M Street SW  
Washington, DC 20460  
202/382-7131

OR

USEPA OWRS  
Sample Control Center  
P.O. Box 1407  
Alexandria, Virginia 22313  
703/557-5040

Publication date: July 1989



## Organo-halide Pesticides, Organo-phosphorus Pesticides, and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors

### 1 SCOPE AND APPLICATION

- 1.1 This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the organo-halide pesticides and polychlorinated biphenyls (PCB's), the organo-phosphorus pesticides, and the phenoxy-acid herbicides and herbicide esters, associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); 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 - 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 Section 8.6 of this method give the steps necessary to determine its 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.
- 1.4 The detection limits of this method are usually dependent on the level of

interferences rather than instrumental limitations. The limits in Tables 4 - 6 typify the minimum quantities 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

- 2.1.1 The percent solids content of a sample is determined.
- 2.1.2 Aqueous samples containing 1 - 30 percent solids -- The sample is diluted to one percent solids, if necessary. The pesticides and PCB's are extracted from a one liter sample with methylene chloride using continuous extraction techniques. For the herbicides, the pH of the sample is raised to 12 - 13 to hydrolyze esters, the sample is back-extracted to remove basic and neutral species, the pH is then reduced to less than 2, and the sample is extracted with diethyl ether using separatory funnel techniques.
- 2.1.3 Samples containing greater than 30 percent solids -- The sample is extracted with acetonitrile and then methylene chloride using ultrasonic techniques. The extract is back extracted with two percent (w/v) sodium sulfate in reagent water to remove water soluble interferences and residual acetonitrile. 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/or solid phase extraction, and then 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 dried over acidified sodium sulfate and the acids are 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 compounds, 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 (1) comparing the GC retention times of the compound on two dissimilar columns with the respective retention times of an authentic standard, and (2) comparing the concentrations of the compound determined on the primary and confirmatory GC systems. Compound identity is confirmed when the retention times and amounts agree within their respective windows.
- 2.5 Quantitative analysis is performed by using an authentic 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 The quality of the analysis 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.

- 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 - 6.



#### 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, 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 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 (Hydriion Papers, or equivalent).
  - 5.3.3 Separatory funnels -- 250, 500, 1000, and 2000 mL, with Teflon stopcocks.
  - 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 ( $\pm 2$  °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 Acrodisc-CR, 1 - 5 micron, 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 and cartridges for solid phase extraction (SPE)
- 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 50 mL volumetric flasks in the manifold.
- 5.6.2.5 Column -- Mega Bond Elut, Non-polar, C18 Octadecyl, 10 g/60 mL (Analytichem International Cat. No. 607H060, or equivalent).
- 5.6.3 Chromatographic column -- 400 mm x 22 mm i.d., with Teflon stopcock 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 caps.
- 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
- 5.7.4 Funnel, Buchner, 15 cm.
- 5.7.4.1 Flask, filter, for use with Buchner funnel
- 5.7.4.2 Filter paper, 15 cm (Whatman #41, or equivalent).
- 5.8 Derivatization apparatus -- Diazald kit
- 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 GC's 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 14.
- 5.10.1 GC columns -- Bonded phase fused silica capillary
- 5.10.1.1 Primary for organo-halide compounds -- 30 ±3 m x 0.5 ±0.05 mm i.d. DB-608, or equivalent).
- 5.10.1.2 Primary for organo-phosphate compounds -- DB-1 (or equivalent) with same dimensions as column for organo-halide compounds.
- 5.10.1.3 Confirmatory -- DB-1701, 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 ongoing (Section 14.6) 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 (Microcoulometric, Hall, 0.1., or equivalent), capable of detecting 8 pg of aldrin under the analysis conditions given in Table 4.

5.10.3.2 Flame photometric -- Capable of detecting 11 pg of malathion under the analysis conditions given in Table 5.

5.10.4 Chromatographs may be configured in one of two ways: (1) Two halide specific detectors (HSD's) in one GC; two flame photometric detectors (FPD's) 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 (0.1N) -- 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 and back extraction

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.

6.3.3 Sodium sulfate solution -- Two percent (w/v) in reagent water, pH adjusted to 8.5 - 9.0 with KOH or  $H_2SO_4$ .

6.3.4 Sodium sulfate, reagent grade, powdered anhydrous (Baker 73898, 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. NOTE: The powdered sodium sulfate is used only in ultrasonic extraction of samples containing 30 percent solids or greater, and not for drying of sample extracts. Use of granular sodium sulfate during ultrasonic extraction may lead to poor recovery of analytes.

6.4 Solvents -- Methylene chloride, hexane, ethyl ether, acetone, acetonitrile, 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.

6.5 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 °C for 16 hours minimum immediately prior to use. Alternatively, 500 mg cartridges (J.T. Baker, or equivalent) may be used.
- 6.6.2 Solid phase extraction
- 6.6.2.1 SPE cartridge calibration solution -- 2,4,6-trichlorophenol, 0.1 ug/mL in acetone.
- 6.6.2.2 SPE elution solvent -- Methylene chloride:acetonitrile:hexane (50:3:47).
- 6.6.3 Alumina, neutral, Brockman Activity I, 80 - 200 mesh (Fisher Scientific Certified, or equivalent). Heat for 16 hours at 400 - 450 °C. Seal and cool to room temperature. Add 7 percent w/w reagent water and mix for 10 - 12 hours. Keep bottle tightly sealed.
- 6.6.4 Silicic acid, 100 mesh
- 6.6.5 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 USEPA, 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 Secondary mixtures -- Using stock solutions (Section 6.10), prepare mixtures at the levels required for calibration and calibration verification (Sections 7.3 and 14.5), for initial and ongoing precision and recovery (Sections 8.2 and 14.6), and for spiking into the sample matrix (Section 8.4).
- 6.12 Surrogate spiking solutions
- 6.12.1 Chlorinated pesticides -- Prepare dibutyl chlorendate at a concentration of 2 ug/mL in acetone.
- 6.12.2 Phosphorus containing pesticides -- Prepare tributyl phosphate and triphenyl phosphate each at a concentration of 2 ug/mL in acetone.

6.12.3 Phenoxyacid herbicides -- Prepare 2,4-dichlorophenylacetic acid at a concentration of 2 ug/mL in acetone.

6.13 DDT and endrin decomposition solution -- Prepare a solution containing endrin at a concentration of 1 ug/mL and DDT at a concentration of 2 ug/mL.

6.14 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  $\pm 15$  percent of the area obtained in the initial analysis of the standard.

## 7 SETUP AND CALIBRATION

7.1 Configure the GC systems in one of the two ways given in Section 5.10.4 and establish the operating conditions in Tables 4 - 5.

7.2 Attainment of Method Detection Limit (MDL) and DDT/Endrin decomposition requirements -- Determine that each column/detector system meets the MDL's (Tables 4 - 6) and that the organohalide systems meet the DDT and Endrin decomposition test (Section 14.4).

### 7.3 Calibration

7.3.1 Calibration solutions -- Prepare calibration standards at a minimum of three concentration levels for each compound of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane or isooctane. The lowest concentration solution should be at a concentration near, but above, the MDL's (Tables 4 - 6). The highest concentration solution should be near, but below, the maximum linear range of the analytical system. The other concentration(s) should be ideally equally spaced on a logarithmic scale between the lowest and highest concentration solutions. The ratio between the highest and lowest concentration should be 100 or greater. Note: the GC retention time overlap between analytes requires that the compounds separated and analyzed as groups. Divide the single component analytes into three or four calibration groups each for the organo-halide and organo-phosphorus compounds with an approximately equal number of analytes per

group. The compound pairs specified for GC resolution (Section 14.3) shall be in the same group. PCB 1254 or 1260 and Toxaphene are calibrated separately.

7.3.2 Inject the calibration solutions 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 each column/detector system (primary and confirmatory). For the multicomponent analytes (PCB's, toxaphene), store the retention time and peak area for the five largest peaks.

7.3.3 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.

7.3.3.1 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.

7.3.3.2 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.

7.3.4 Calibration factor (ratio of area to amount injected)

7.3.4.1 Compute the coefficient of variation (relative standard deviation) of the calibration factor over the calibration range for each compound on each column/detector system.

7.3.4.2 Linearity -- If the calibration factor for any compound is constant ( $C_v < 20$  percent) over the 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 Combined QC standards -- To preclude periodic analysis of all of the individual calibration groups of compounds (Section 7.3.1), the GC systems are calibrated with combined solutions 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 factors are verified for the compounds that are resolved, and calibration factors are obtained for the unresolved peaks. These combined QC standards are prepared at the level of the mid-range calibration standard (7.3.1).

7.4.1 Analyze the combined QC standards on their respective column/detector pairs.

7.4.1.1 For those compounds that exhibit a single, resolved GC peak, the retention time shall be within  $\pm 5$  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  $\pm 20$  percent of the calibration factor in the medium level standard (Section 7.3.4).

7.4.1.2 For the peaks containing two or more compounds, compute and store the retention times at the peak maxima on both columns (primary and confirmatory), and also compute and store the calibration factors on both columns. These results will be used for calibration verification (Section 14.2 and 14.5) and for precision and recovery studies (Section 14.6).

7.5 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 matrix spike and matrix spike duplicate (MS/MSD) samples to assess accuracy and precision. 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 separations 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 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).

8.1.4 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the combined QC standard (Section 7.4) that the analysis system is in control. These procedures are described in Sections 14.1, 14.5, and 14.6.

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

8.1.6 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.
- 8.1.7 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 analysis of samples containing low solids (aqueous samples), extract, concentrate, and analyze one set of four one-liter aliquots of reagent water spiked with the combined QC standard (Section 7.4) according to the procedure in Section 10. Alternatively, sets of four replicates of the individual calibration groups (Section 7.3) may be used. For samples containing high solids, sets 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 percent recovery (X) and the coefficient of variation (Cv) of percent recovery (s) for each compound.
- 8.2.3 For each compound, compare s and X with the corresponding limits for initial precision and accuracy in Tables 7 - 9. For coeluting compounds, use the coeluted compound with the least restrictive specification (largest Cv and widest range). 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. In this case, correct the problem and repeat the test.
- 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).
- 8.3.3 The recovery of the surrogate compound shall be within the limits of 40 to 120 percent. If the recovery of any surrogate falls outside of these limits, method performance is unacceptable for 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 and precision -- The laboratory shall spike (matrix spike) at least ten percent of the samples from a given site type (e.g., influent to treatment, treated effluent, produced water, river sediment) in duplicate (MS/MSD). If only one sample from a given site type is analyzed, two aliquots of that sample shall be spiked.
- 8.4.1 The concentration of the analytes spiked into the MS/MSD 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 spiking level 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 matrix spike shall be at the concentration of the combined QC standard (Section 7.4) 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 matrix spike concentration shall be 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 7.4).
- 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 two additional sample aliquots with the



standard solution and analyze them to determine the concentrations after spiking (A) of each analyte. Calculate the percent recovery (P) of each analyte in each aliquot:

$$P = 100 (A - B) / T$$

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 7 - 9. 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 Determine the precision of the MS/MSD analyses by comparing the recoveries calculated in 8.4.2 of each spiked analyte in both aliquots. Calculate the relative percent difference (RPD) of the recoveries (not the concentrations) of each analyte with MS/MSD aliquots as:

$$RPD = \frac{P_{MS} - P_{MSD}}{(P_{MS} + P_{MSD})/2} \times 100$$

- 8.4.5 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-hour 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 - 3) or any potentially interfering compound is found in an aqueous blank at greater than 0.05 ug/L, or in a high solids reference matrix blank at greater than 1 ug/kg (assuming the same calibration factor as aldrin and diazinon for compounds not listed in Tables 1 - 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. If the analyte coelutes with an analyte in the QC standard, prepare a new QC standard without the coeluting component(s). Compute the average percent recovery (A) and the standard deviation of percent recovery (sn) 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; otherwise, the analytical problem is corrected and the test is repeated. Establish a preliminary quality control limit of  $A \pm 2sn$  for the new analyte and add the limit to Table 7, 8, or 9.

- 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 ongoing (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

Figure 1 outlines the extraction and concentration steps. Samples containing one percent solids or less are extracted directly using continuous liquid/liquid extraction techniques (Section 10.2.1). Samples containing one through 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 may be combined with the organo-chlorine extract for gas chromatography.

10.1 Determination of percent solids

10.1.1 Weigh 5 - 10 g of sample into a tared beaker. Record the weight to three significant 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:

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

### 10.2 Preparation of samples for extraction

10.2.1 Samples containing one percent solids or less -- Pesticides and PCB samples are extracted directly using continuous liquid/liquid extraction techniques; herbicides are extracted using separatory funnel techniques.

10.2.1.1 Shake the samples to ensure thorough mixing and measure 1.00 ±0.01 liter of each sample into a separate clean 1.5 - 2.0 liter beaker. Measure a separate one liter aliquot for each sample to be tested for the phenoxy-acid herbicides.

10.2.1.2 Spike 0.5 mL of the surrogate spiking solution (Section 6.12) 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 -- Samples are diluted to one percent solids and then extracted.

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 of sample as 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.

- 10.2.2.4 Bring the sample aliquot(s) to 100 - 200 mL volume with reagent water.
- 10.2.2.5 Spike 0.5 mL of the appropriate surrogate spiking solution (Section 6.12) into each sample aliquot.
- 10.2.2.6 Using a clean metal spatula, break any solid portions of the sample into small pieces.
- 10.2.2.7 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.
- 10.2.2.8 Bring the sample volume to 1.0  $\pm$  0.1 liter with reagent water.
- 10.2.3 Preparation of QC aliquots for samples containing <30 percent solids.
- 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  $\pm$  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 7.4) into a reagent water aliquot. For the herbicides, spike the herbicide standard into the remaining reagent water aliquot.
- 10.2.3.4 If a matrix spike is required, prepare an aliquot at the concentrations specified in Section 8.4.
- 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  $\pm$  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<sub>2</sub>SO<sub>4</sub> while stirring and determine and record the amount of acid required to acidify the sample to pH <2. Discard this aliquot. The volume of H<sub>2</sub>SO<sub>4</sub> will be used during the extraction of the samples in Section 10.4.6.
- 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  $\pm$  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 the combined QC standard (Section 7.4) 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 Extraction of low solids (aqueous) samples
- 10.3.1 Continuous extraction of pesticides/PCB's -- Place 100 - 150 mL methylene chloride in each continuous extractor and 200 - 300 mL in each distilling flask.

- 10.3.1.1 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.
- 10.3.1.2 Extraction -- Adjust the pH of the waters in the extractors to 5 - 9 with NaOH or  $\text{H}_2\text{SO}_4$  while monitoring with a pH meter.
- 10.3.1.3 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.
- 10.3.1.4 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 (acidified sodium sulfate for the herbicides). 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, and concentrate per Sections 10.5 through 10.7.
- 10.3.2 Hydrolysis and back-extraction of herbicides
- 10.3.2.1 Pour the sample and QC aliquots into separate 1.5 - 2 L separatory funnels. Add 250 g NaCl and shake to dissolve.
- 10.3.2.2 Add 17 mL of 6 N NaOH to each separatory funnel and shake to mix thoroughly. Check the pH of the sample and QC aliquots and adjust to >12 if required. Periodically shake the aliquots during a 1 - 2 hour hydrolysis period.
- 10.3.2.3 Rinse each beaker used for measurement of the sample and QC aliquots with 60 mL of methylene chloride, add to its respective separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. 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. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase. If the emulsion cannot be broken, continuous liquid/liquid extraction techniques may be used. Check and adjust the pH of the sample to >12 with NaOH if required.
- 10.3.2.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.
- 10.3.3 Extraction of the herbicides
- 10.3.3.1 Add 17 mL of 12 N  $\text{H}_2\text{SO}_4$  to the sample and QC aliquots. Seal and shake to mix. Caution: some samples require acidification in a hood because of the potential for generating hydrogen sulfide. Check and adjust the pH of the sample to <2 if required.
- 10.3.3.2 Add 120 mL ethyl ether to the sample and QC aliquots. Seal and extract per Section 10.3.2. Drain the aqueous phase completely into the respective beaker used for measurement of aliquot volume. Drain the ether phase into 500 mL round-bottom flask containing approx 10 g of acidified sodium sulfate making certain that the amount of water drained into the flask is minimized. Periodically, shake the round-bottom flask to mix the ether solution and the drying agent.
- 10.3.3.3 Return the aqueous phase to the separatory funnel, add a 60 mL volume of ether, and repeat the extraction a second time. Drain the aqueous phase completely into the beaker used for measurement of aliquot volume and the ether phase into the round-bottom flask.
- 10.3.3.4 Repeat the extraction a third time, combining the ether with the other extracts in the round-bottom flask. Allow the sodium sulfate to remain in contact with the ether solution for a minimum of two hours, periodically shaking the round-bottom flask to mix the ether and the

drying agent. Concentrate the extract to 5 mL per Sections 10.5 through 10.7.

- 10.4 Ultrasonic extraction of high solids aliquots
- 10.4.1 Add 60 g powdered (not granular) anhydrous sodium sulfate to the sample and the QC aliquots. Add 100 ±10 mL acetonitrile to each of the aliquots (Section 10.2.5) and mix thoroughly, to produce a free-flowing mixture.
- 10.4.2 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.
- 10.4.3 Decant the pesticide and herbicide extracts through filter paper into 1000 - 2000 mL separatory funnels.
- 10.4.4 Repeat the extraction and filtration steps (Sections 10.4.2 - 10.4.3) using a second 100 ±10 mL of acetonitrile.
- 10.4.5 Repeat the extraction step (Section 10.4.2) using 100 ±10 mL of methylene chloride. On this final extraction, swirl the sample or QC aliquot, pour into its respective filter paper, and rinse with methylene chloride. Record the total extract volume.
- 10.4.6 For each extract, prepare 1.5 - 2 liters of reagent water containing two percent sodium sulfate. For the pesticide extracts, adjust the pH of the water to 6.0 - 9.0 with NaOH or H<sub>2</sub>SO<sub>4</sub>. For the herbicide extracts, adjust the pH of the water to <2.
- 10.4.7 Back extract each extract three times sequentially with 500 mL of the aqueous sodium sulfate solution, returning the bottom (organic) layer to the separatory funnel the first two times while discarding the top (aqueous) layer. On the final back extraction, filter each pesticide extract through a prerinsed drying column containing 7 to 10 cm anhydrous sodium sulfate into a 500 - 1000

mL graduated cylinder. Filter the herbicide extracts similarly using acidified sodium sulfate. Record the final extract volume.

- 10.4.8 Filter the extracts through Whatman #41 paper into 500 mL K-D evaporator flasks equipped with 10 mL concentrator tubes. Rinse the graduated cylinder or centrifuge tube with 30 - 50 mL of methylene chloride and pour through the filter to complete the transfer. Concentrate the extracts per Sections 10.5 through 10.7.
- 10.5 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 Florisil or silica gel 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 Florisil, silica gel, and/or sulfur removal procedures in Section 11.

10.7 Herbicide extracts -- These extracts are concentrated to 5 - 10 mL and the herbicides are derivatized per Section 12.

## 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 shall first repeat the tests in Section 8.2 to demonstrate that the requirements of Section 8.2 can be met using the cleanup procedure(s) as an integral part of the method. Figure 1 outlines the cleanup steps.

11.1.1 Gel permeation chromatography (Section 11.2) removes many high molecular weight interferences 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 solid phase extraction cartridge (Section 11.3) removes polar organic compounds such as phenols. It is used for cleanup of organo-chlorine and organo-phosphate extracts.

11.1.3 The Florisil column (Section 11.4) allows for selected fractionation of the organo-chlorine compounds and will also eliminate polar interferences.

11.1.4 Alumina column cleanup (Section 11.5) may also be used for cleanup of the organo-chlorine compounds.

11.1.5 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides and herbicides, is

removed using GPC, mercury, or activated copper. Sulfur removal (Section 11.6) from extracts containing organo-chlorine is required when sulfur is known or suspected to be present. Mercury and copper should not be used for sulfur removal from extracts expected to contain the organo-phosphorus pesticides because some of these analytes are also removed (Reference 8).

## 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

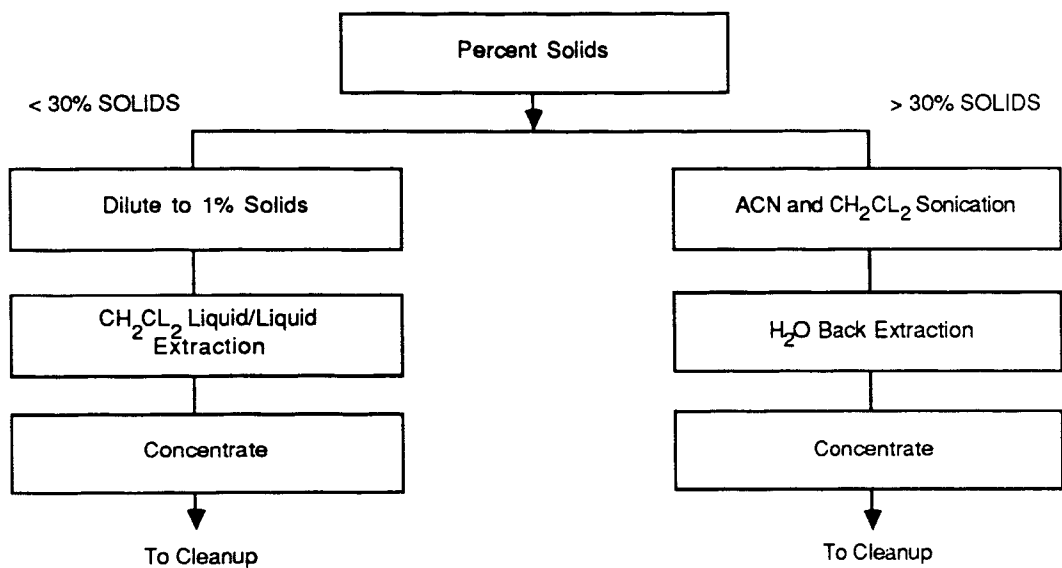
11.2.2.1 Load 5 mL of the calibration solution (Section 6.5) into the sample loop.

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.

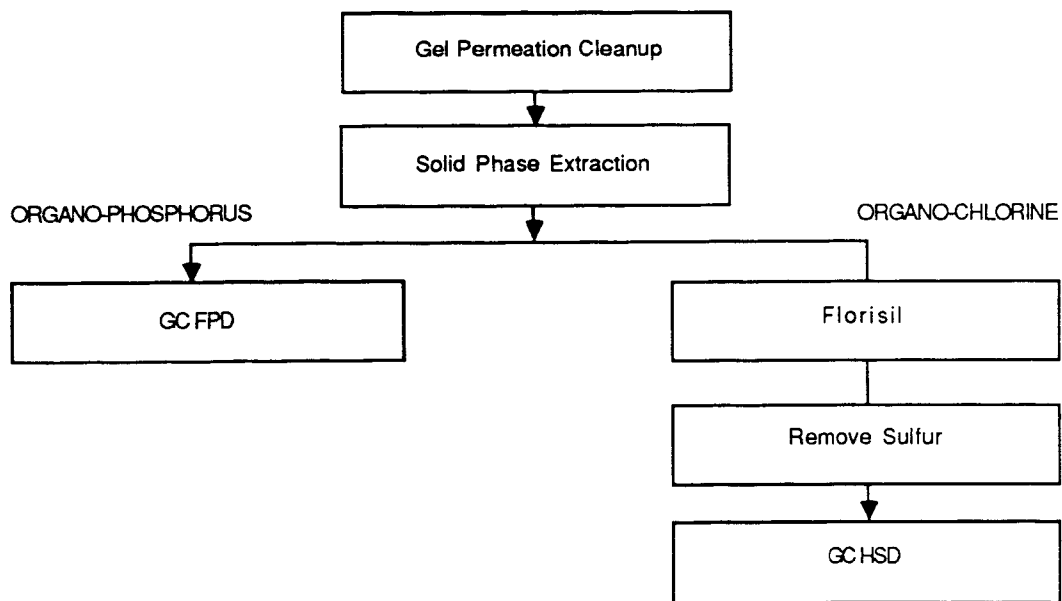
11.2.2.3 Set the "dump time" to allow >85 percent removal of the corn oil and >85 percent collection of the phthalate.

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



Method 1618 - Extraction and Concentration Steps



Method 1618 - Cleanup and Analysis Steps

FIGURE 1 Method 1618 - Extraction, Cleanup, and Analysis

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 gravimetricly by evaporating the solvent from a 50 µL 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 Section 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 extracts per Sections 10.5 - 10.7.

### 11.3 Solid phase extraction (SPE)

#### 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 SPE 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 sequentially with 10 mL portions each of hexane, methanol, and water using vacuum for 30 seconds after each eluant. Follow this pre-elution with 1 mL methylene chloride and three 10 mL portions of the elution solvent (6.6.2.2) using vacuum for five minutes after each eluant. Tap the

cartridge lightly while under vacuum to dry between eluants. The three portions of elution solvent may be collected and used as a blank if desired. Finally, elute the cartridge with 10 mL each of methanol and water, using the vacuum for 30 seconds after each eluant.

- 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 test mixture, add the trichlorophenol solution (Section 6.6.2.1) to the combined calibration standard (Section 7.4). Elute the mixture using the procedure in 11.3.4.

- 11.3.3.2 Concentrate the eluant to 1.0 mL and inject 1.0 µL of the concentrated eluant into the GC using the procedure in Section 13. The recovery of all organo-chlorine or organo-phosphorus analytes (including the unresolved GC peaks) shall be within the ranges for recovery specified in Tables 7 - 8, and the peak for trichlorophenol shall not be detectable; otherwise the SPE cartridge is not performing properly and the cartridge lot shall be 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 50 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 the SPE cartridge. Apply vacuum for five minutes to dry the cartridge. Tap gently to aid in drying.
- 11.3.4.3 Elute each cartridge into its volumetric flask sequentially with three 10 mL portions of the elutions solvent (6.6.2.2), using vacuum for five minutes after each portion. Collect the eluants in the 50 mL volumetric flasks.
- 11.3.4.4 Release the vacuum and remove the 50 mL volumetric flasks.
- 11.3.4.5 Concentrate the eluted extracts to 1.0 mL using the nitrogen blow-down apparatus. 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 7.5) 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 percent 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).

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 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.

11.6.4 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 ESTERIFICATION OF PHENOXY-ACID HERBICIDES

12.1 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.

- 12.2 Esterification -- Observe the safety precautions regarding diazomethane in Section 4.
- 12.2.1 Set up the diazomethane generation apparatus as given in the instructions in the Diazald kit.
- 12.2.2 Transfer one mL of the isooctane solution (Section 12.1) 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 to account for the loss.
- 12.2.3 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.
- 12.2.4 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 11.3 for SPE 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 through 6 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 confirmatory columns are shown in Figures 2 through 6.
- 13.1 Calibrate the system as described in Section 7.
- 13.2 Combining pesticide and herbicide extracts
- 13.2.1 Pesticide extracts cleaned up by solid phase extraction -- Combine the 1.0 mL final organo-chlorine pesticide extract (Section 11.3.4.5 or 11.5.4) with the 1.0 mL final herbicide extract (Section 11.3.4.5 or 11.5.4 if the herbicide extract required cleanup; Section 12.2.4 if it did not).
- 13.2.2 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 11.5.4 if the herbicide extract required cleanup; Section 12.2.4 if it did not).
- 13.3 Set the injection volume on the autosampler to inject 1.0  $\mu$ L of all standards and extracts of blanks and samples.
- 13.4 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 after the last analyte is expected to elute 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 (Section 7.4) 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 -- The absolute retention times of the peak maxima shall be within  $\pm 10$  seconds of the retention times in the initial calibration (Section 7.4.1).
- 14.3 GC resolution -- Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 10 percent of the taller of the two peaks.

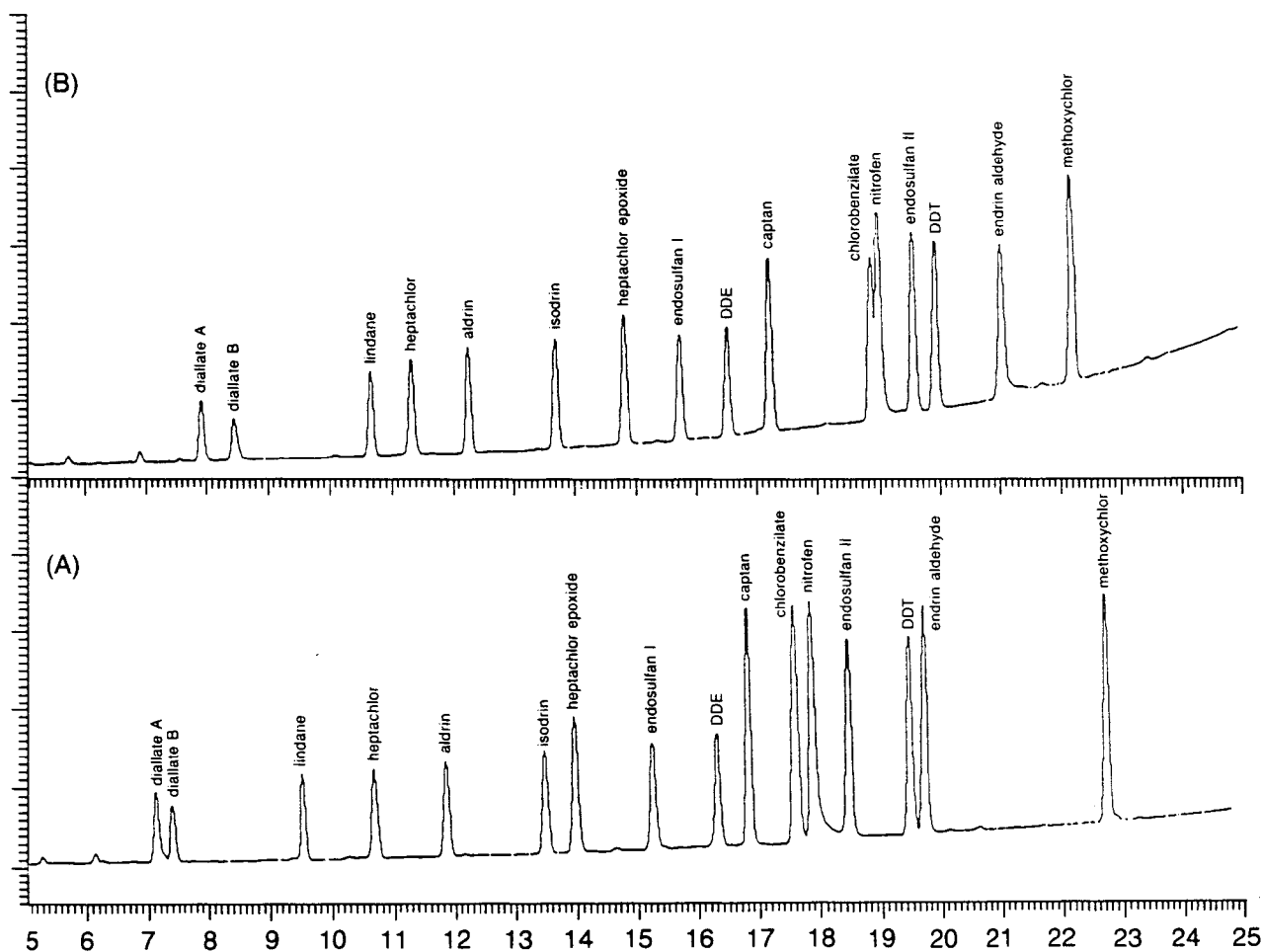


FIGURE 2 Organochlorine Mix A [(A) DDB-608 and (B) DB-1701].

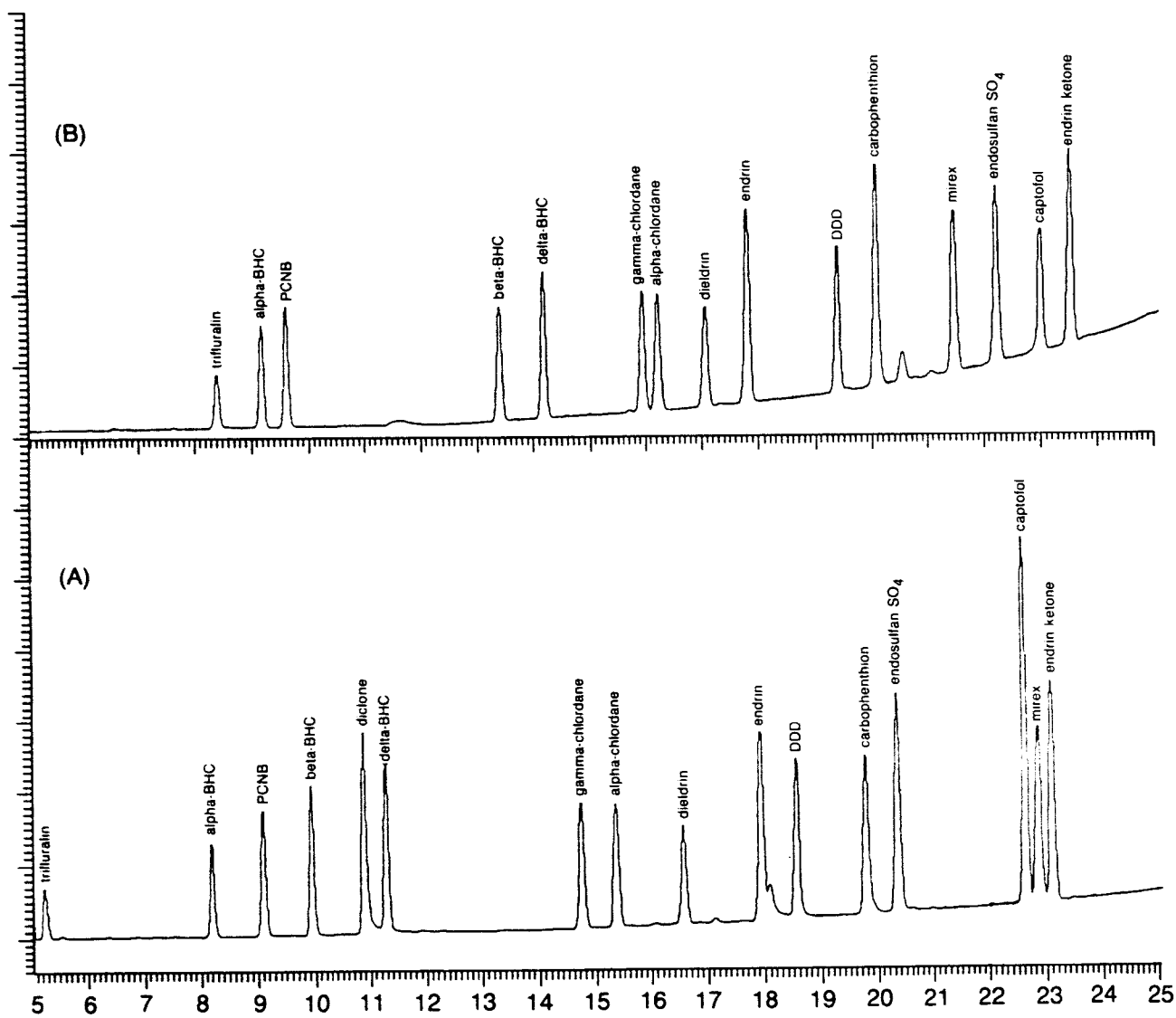


FIGURE 3 Organochlorine Mix B [(A) DB-608 and (B) DB-1701].

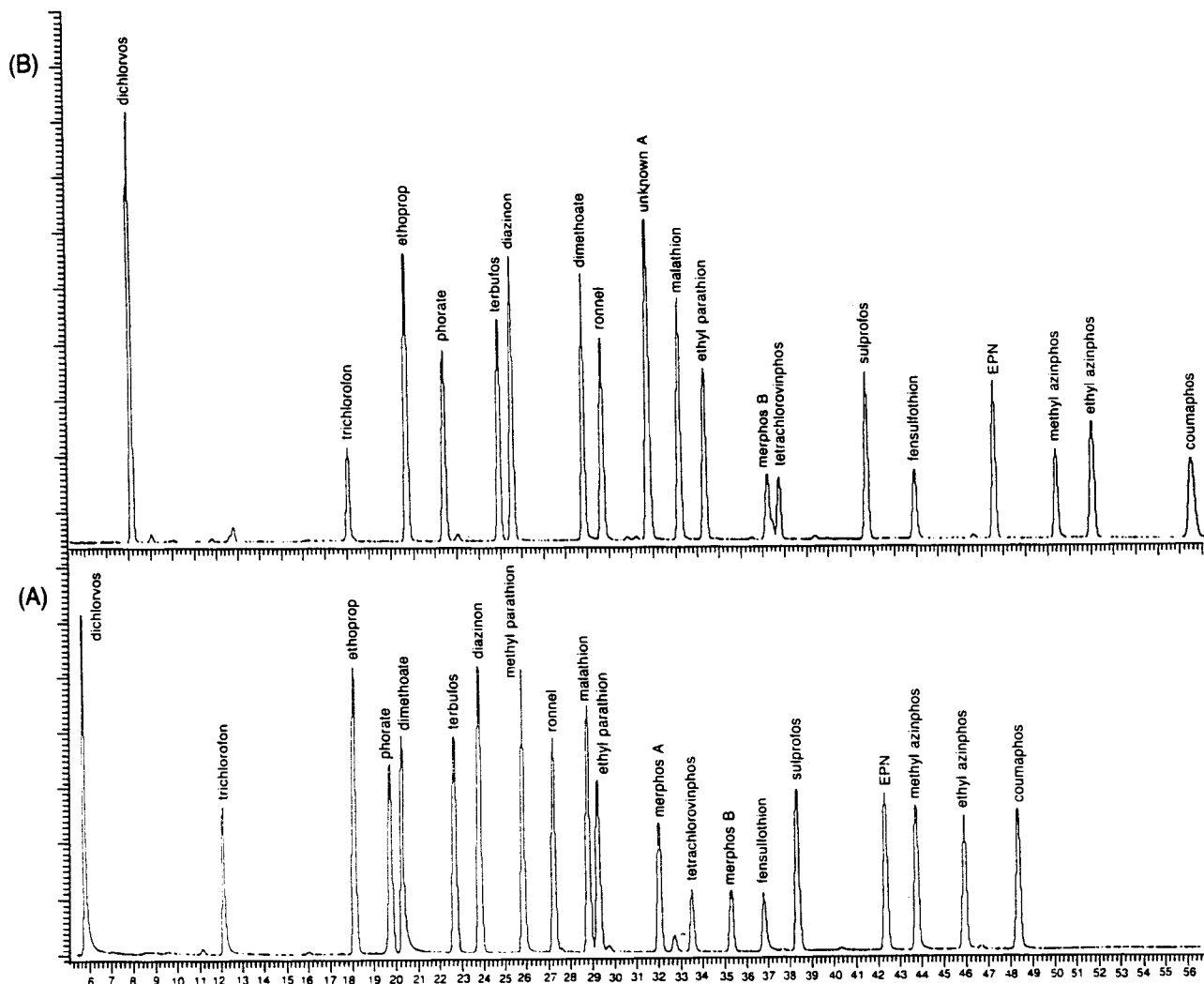


FIGURE 4 Organophosphate Mix A [(A) DB-1 and (B) DB-1701].

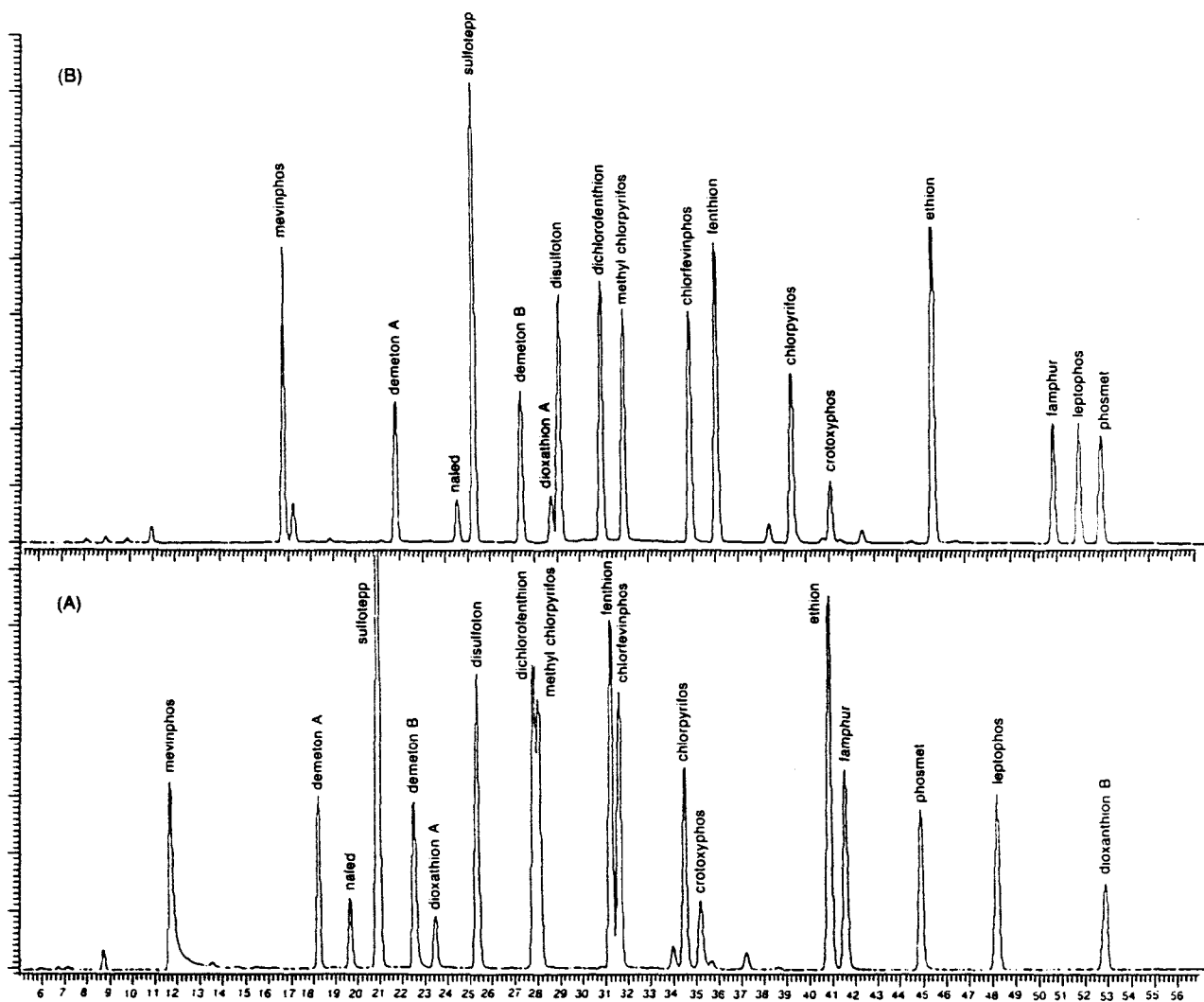


FIGURE 5 Organophosphate Mix B [(A) DB-1 and (B) DB-1701].

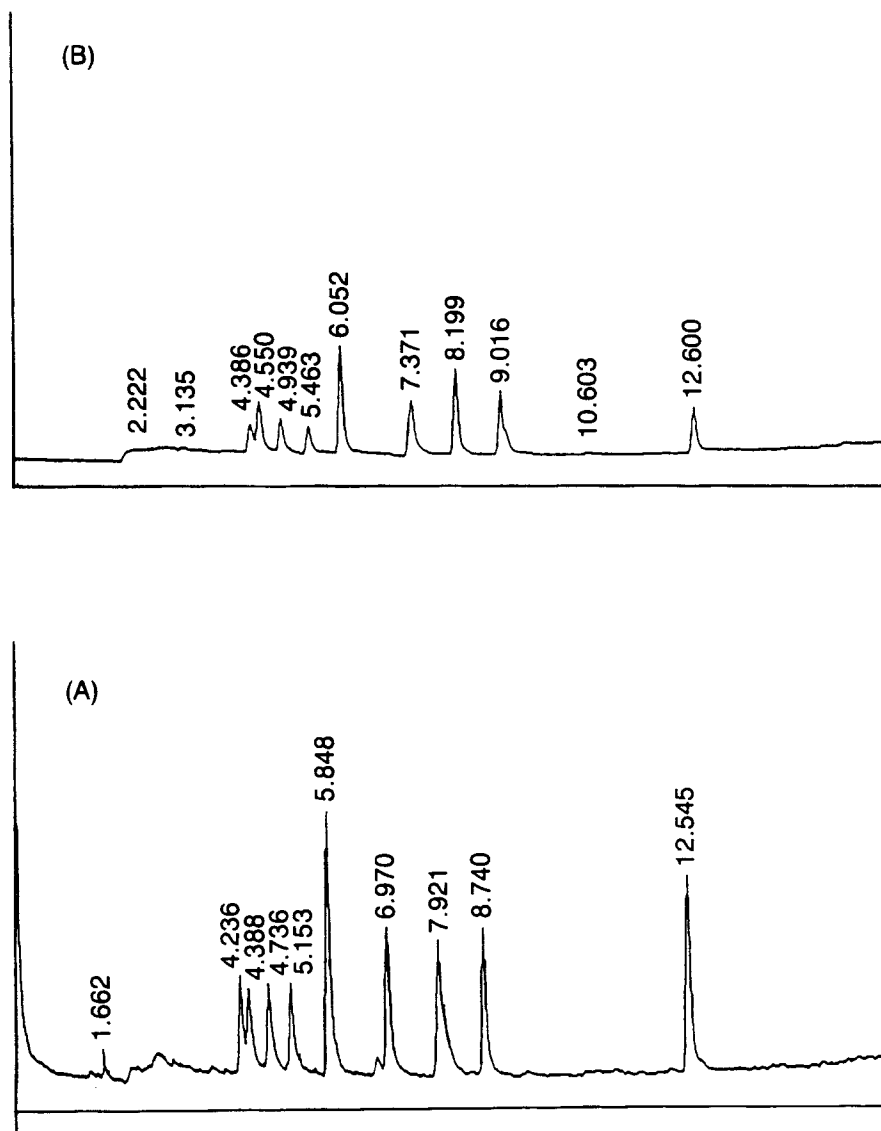


FIGURE 6 Phenoxy-acid Herbicides [(A) DB-608 and (B) DB-1701]

- 14.3.1 Organo-halide compounds
  - 14.3.1.1 Primary column (DB-608) -- DDT and endrin aldehyde.
  - 14.3.1.2 Confirmatory column (DB-1701) -- Alpha and gamma chlordane.
- 14.3.2 Organo-phosphorus compounds
  - 14.3.2.1 Primary column (DB-1) -- Malathion and ethyl parathion.
  - 14.3.2.2 Confirmatory column (DB-1701) -- Terbufos and diazinon.
- 14.4 Decomposition of DDT and endrin
  - 14.4.1 Analyze a total of 2 ng DDT and 1 ng endrin on each organo-chlorine column using the analytical conditions specified in Table 4.
  - 14.4.2 Measure the total area of all peaks in the chromatogram.
  - 14.4.3 The area of peaks other than the sum of the areas of the DDT and endrin peaks shall be less than 20 percent the sum of the areas of these two peaks. If the area is greater than this sum, the system is not performing acceptably for DDT and endrin. In this case, the GC system that failed shall be repaired and the performance tests (Sections 14.1 - 14.4) shall be repeated until the specification is met. Note: DDT and endrin decomposition are usually caused by accumulations of particulates in the injector and in the front end of the column. Cleaning and silanizing the injection port liner, and breaking off a short Section of the front end of the column will usually eliminate the decomposition problem.
- 14.5 Calibration verification -- Calibration is verified for the combined QC standard only.
  - 14.5.1 Inject the combined QC standard (Section 7.4)
  - 14.5.2 Compute the percent recovery of each compound or coeluting compounds, based on the calibration data (Section 7.4).
  - 14.5.3 For each compound or coeluted compounds, compare this calibration verification recovery with the corresponding limits for ongoing accuracy in Tables 7 - 9. For

coeluting compounds, use the coeluted compound with the least restrictive specification (the widest range). If the recoveries for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any recovery falls outside the calibration verification range, system performance is unacceptable for that compound. In this case, correct the problem and repeat the test, or recalibrate (Section 7). If verification requirements are met, the calibration is assumed to be valid for the multicomponent analytes (PCB's and toxaphene).

- 14.6 Ongoing precision and recovery
  - 14.6.1 Analyze the extract of the precision and recovery standard extracted with each sample lot (Sections 10.2.3.3 and 10.2.5.7).
  - 14.6.2 Compute the percent recovery of each analyte and coeluting compounds.
  - 14.6.3 For each compound or coeluted compounds, compare the percent recovery with the limits for ongoing recovery in Tables 7 - 9. For coeluted compounds, use the coeluted compound with the least restrictive specification (widest range). 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 ongoing precision and recovery test.
  - 14.6.4 Add results which pass the specifications in Section 14.6.3 to initial and previous ongoing 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 14.2), and with data stored in the retention time and calibration libraries (Section 7.3.3 and 7.3.4.1). Identification is confirmed when retention time and amounts agree per the criteria below.
- 15.2 For each compound on each column/detector system, establish a retention time window  $\pm 20$  seconds on either side of the retention time in the calibration data (Section 7.3.3). For compounds that have a retention time curve (Section 7.3.3.2), 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 7.3.3).
- 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  $\pm 30$  seconds of the retention times for the computed amounts (Section 16), as determined by the retention time calibration curve (Section 7.3.3.2), and (2) the computed amounts (Section 16) on each system (primary and confirmatory) agree within a factor of three.

## 16 QUANTITATIVE DETERMINATION

- 16.1 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).
- 16.2 Liquid samples -- Compute the concentration in the sample using the following equation:
- $$C_s = \frac{10 (C_{ex})}{(V_s)}$$
- where,
- $C_s$  = the concentration in the sample in ug/L.
- 10 = extract total volume in mL.
- $C_{ex}$  = concentration in the extract in ug/mL.
- $V_s$  = volume of sample extracted in liters.
- 16.3 Solid samples -- Compute the concentration in the solid phase of the sample using the following equation:
- $$C_s = \frac{10 (C_{ex})}{1000 (W_s) (\% \text{ solids})}$$
- where,
- $C_s$  = concentration in the sample in ug/kg.
- 10 = extract total volume in mL.
- $C_{ex}$  = concentration in the extract in ug/mL.
- 1000 = used to convert grams to kilograms.
- $W_s$  = sample weight in grams.
- % solids = percent solids as determined in Section 10.1.3.
- 16.4 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 uL aliquot of the diluted extract is analyzed.
- 16.5 Two or more PCB's in a given sample are quantitated and reported as total PCB.
- 16.6 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 ng/L) of the compounds 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 11.2), and the SPE cartridge (Section 11.3), and samples for the organo-halide compounds by florisil (Section 11.4) or alumina (11.5), and sulfur removal (Section 11.6). If these techniques do not remove the interfering compounds, the extract is diluted by a factor of 10 and reanalyzed (Section 16.4).
- 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 specified in Section 8.3, the sample shall be reextracted and reanalyzed. If the surrogate recovery is still outside this range, the sample is diluted by a factor of 10 and reanalyzed (Section 16.4).
- 17.4 Recovery of matrix spikes -- In most samples, matrix spike recoveries will be similar to those from reagent water or from the high solids reference matrix. If the matrix spike recovery is outside the range specified in Tables 7 - 9, the sample shall be diluted by a factor of 10, respiked, and reanalyzed. If the matrix spike recovery is still outside the range, the method does not apply to 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.

## REFERENCES

- 1 "Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206, (August 1977).
- 2 "OSHA Safety and Health Standards, General Industry" OSHA 2206, 29 CFR 1910 (January 1976).
- 3 "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety (1979).
- 4 Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and Its Use in Standardizing Florisil Columns," J. Assoc. Off. Analytical Chemists, 51, 29 (1968).
- 5 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-79-019 (March 1979).
- 6 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, Philadelphia, PA, 76 (1980).
- 7 "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL, Cincinnati, OH 45268, EPA 600/4-70-020 (March 1979).
- 8 "Method Development and Validation, EPA Method 1618, Cleanup Procedures", Colorado State University, Department of Environmental Health, Colorado Pesticide Center, November 1988 and January 1989.
- 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).

Table 1

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

EGD No.	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 (pentachloronitrobenzene)	82-68-8
113	Toxaphene	8001-35-2
442	Trifluralin	1582-09-8

NON-ITD ORGANO-HALIDE COMPOUNDS THAT CAN BE  
ANALYZED BY THIS METHOD

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

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

EGD No.	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 ORGANO-PHOSPHATE COMPOUNDS THAT CAN BE  
ANALYZED BY THIS METHOD

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	953-17-3
Ronnel	299-84-3
Sulprofos	35400-43-2
Tokuthion	34643-46-4
Trichloronate	327-98-0

Table 3  
PHENOXYACID HERBICIDES DETERMINED BY WIDE BORE,  
FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY  
WITH HALIDE SPECIFIC DETECTOR

EGD No.	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 THAT CAN BE  
ANALYZED BY THIS METHOD

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

Table 4  
GAS CHROMATOGRAPHY OF ORGANO-HALIDE PESTICIDES

EGD No.	Compound	Retention Time (1)		MDL (2) (ng/L)	EGD No.	Compound	Retention Time (1)		MDL (2) (ng/L)
		DB-608	DB-1701				DB-608	DB-1701	
442	Trifluralin	5.16	8.58	50 est	430	Methoxychlor	22.80	22.34	30
432	Diallate-A	7.15	8.05	45	435	Endrin ketone	23.00	23.71	8
	Diallate-B	7.42	8.58	32	106	PCB-1242			
102	alpha-BHC	8.14	9.45	6	109	PCB-1232			
440	PCNB	9.03	9.91	6	112	PCB-1016			
104	gamma-BHC (Lindane)	9.52	10.84	11	108	PCB-1221			
103	beta-BHC	9.86	13.58	7	110	PCB-1248			
100	Heptachlor	10.66	11.56	5	107	PCB-1254			
478	Dichlorone	10.80	(3)	(4)	111	PCB-1260	15.44	14.64	140
105	delta-BHC	11.20	14.39	5			15.73	15.36	
089	Aldrin	11.84	12.50	8			16.94	16.53	
437	Isodrin	13.47	13.93	13			17.28	18.70	
101	Heptachlor epoxide	13.97	15.03	12			19.17	19.92	
	gamma-Chlordane	14.63	16.20	9	113	Toxaphene	16.60	16.60	910
091	alpha-Chlordane	15.24	16.48	8			17.37	17.52	
095	Endosulfan I	15.25	15.96	11			18.11	17.92	
093	4,4'-DDE	16.34	16.76	10			19.46	18.73	
090	Dieldrin	16.41	17.32	6			19.69	19.00	
433	Captan	16.83	17.32	(4)					
431	Chlorobenzilate	17.58	18.97	25	(1)	Columns: 30 m x 0.53 mm i.d.; DB-608: 0.83 micron; DB-1701: 1.0 micron.			
098	Endrin	17.80	18.06	4		Conditions: 150 °C for 0.5 min, 150 - 270 @ 5 °C per minute, 270 °C until endrin ketone elutes.			
436	Nitrofen (TOK)	17.86	19.14	13		Carrier gas flow rate: approximately 7 mL/min.			
439	Kepone	17.92	25.03	(4)	(2)	40 CFR Part 136, Appendix B (49 FR 43234). Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.			
094	4,4'-DDD	18.43	19.56	5	(3)	Does not elute from DB-1701 column at level tested.			
096	Endosulfan II	18.45	19.72	8	(4)	Not recovered from water at levels tested.			
092	4,4'-DDT	19.48	20.10	12					
441	Carbophenothion	19.65	20.21	50					
099	Endrin aldehyde	19.72	21.18	11					
097	Endosulfan sulfate	20.21	22.36	7					
434	Captafol	22.51	23.11	(4)					
438	Mirex	22.75	21.82	4					

Table 5  
GAS CHROMATOGRAPHY OF ORGANO-PHOSPHORUS PESTICIDES

EGD No.	Compound	Retention Time (1)		MDL (2) (ng/L)	EGD No.	Compound	Retention Time (1)		MDL (2) (ng/L)
		DB-608	DB-1701				DB-608	DB-1701	
450	Dichlorvos	6.56	9.22	4	461	Chlorfevinphos	32.05	36.08	2
444	Mevinphos	11.85	16.20	74	479	Crotoxyphos	32.65	37.58	81
445	Trichlorofon	12.69	18.85	150 (3)		Tokuthion	33.30	37.17	2
471	Demeton-A	17.70	20.57	19	466	Tetrachlorvinphos	33.40	37.85	12
	Ethoprop	18.49	21.43	7		Merphos-B	35.16	37.37	18
459	Naled	18.92	23.00	18	454	Fensulfothion	36.58	43.86	104
455	Dicrotophos	19.33	26.30	81		Methyl trithion	36.62	40.52	10
470	Monocrotophos	19.62	29.24	85	463	Ethion	37.61	41.67	13
477	Sulfotepp	20.04	23.68	6		Sulprofos (Bolstar)	38.10	41.74	6
457	Phorate	20.12	23.08	10	446	Famphur	38.24	46.37	27
449	Dimethoate	20.59	29.29	27	465	Phosmet	41.24	48.22	14
	Demeton-B	21.40	25.52	21	467	EPN	41.94	47.52	9
452	Dioxathion	22.24	26.70	121	453	Azinphos methyl	43.33	50.26	9
472	Terbufos	22.97	24.55	26	474	Leptophos	44.32	47.36	14
473	Phosphamidon-E	23.70	29.89	28	468	Azinphos ethyl	45.55	51.88	22
458	Disulfoton	23.89	27.01	32		Triphenyl phosphate	47.68	40.43	-
460	Diazinon	24.03	26.10	38		(surr)			
	Tributyl phosphate	24.50	17.20	-	443	Coumaphos	48.02	56.44	24
	(surr)								
	Phosphamidon-Z	25.88	32.62	116	(1) Columns: 30 m x 0.53 mm i.d.; DB-1: 1.5 micron; DB-1701: 1.0 micron. Conditions: 110 °C for 0.5 min, 110 - 250 at 3 °C per minute, 250 °C until coumaphos elutes. Carrier gas flow rate: approximately 7 mL/min.				
456	Methyl parathion	25.98	32.12	18					
	Dichlorofenthion	26.11	28.66	6					
	Methyl chlorpyrifos	26.29	29.53	13					
	Ronnel	27.33	30.09	11					
475	Malathion	28.87	33.49	11	(2) 40 CFR Part 136, Appendix B (49 FR 43234).				
447	Fenthion	29.14	32.16	22	(3) Estimated: Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.				
448	Parathion (ethyl)	29.29	34.61	10					
469	Chlorpyrifos	29.48	32.15	4					
	Trichloronate	30.44	32.12	14					

Table 6  
GAS CHROMATOGRAPHY OF PHENOXY-ACID  
HERBICIDES

EGD No.	Compound	Retention Time (1)		MDL (2) (ng/L)
		DB-608	DB-1701	
481	2,4-D	5.85	6.05	100
480	Dinoseb			100 est
482	2,4,5-T	7.92	8.20	50
483	2,4,5-TP (Silvex)	6.97	7.37	40
	Dalapon			1000 est
	2,4-DB (Butoxon)	8.74	9.02	50
	Dicamba	4.39	4.39	110
	Dichlorprop	5.15	5.46	40
	MCPA	4.74	4.94	90
	MCPP	4.24	4.55	56

- (1) Columns: Same as for the organo-chlorine pesticides. See Table 4.  
Conditions: 175 °C for 0.5 min, 175 - 270 @ 5 °C per minute.  
Carrier gas flow rate: approximately 7 mL/min.
- (2) 40 CFR Part 136, Appendix B (49 FR 43234).  
Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.

Table 7  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR ORGANO-HALIDE COMPOUNDS

EGD No. (1)	Compound	Spike level (ng/L)	Acceptance Criteria			
			Initial precision and accuracy Sec 8.2 (%)		Calibration verification Sec 14.5 (ug/mL)	Recovery Sec 8.4 Ongoing accuracy Sec 14.6 R (%)
			s	X		
089	Aldrin	100	12	82 - 108	79 - 113	76 - 114
102	alpha-BHC	100	10	57 - 135	69 - 108	38 - 154
103	beta-BHC	100	10	66 - 130	85 - 102	50 - 146
105	delta-BHC	100	24	60 - 122	79 - 103	45 - 136
104	gamma-BHC (Lindane)	100	10	66 - 112	75 - 119	55 - 123
434	Captafol (2)				70 - 107	
433	Captan (2)				49 - 114	
441	Carbophenothion	1000	10	63 - 141	79 - 102	43 - 161
091	Chlordane-alpha	100	10	79 - 122	73 - 102	69 - 133
	Chlordane-gamma	100	13	32 - 140	79 - 113	4 - 169
431	Chlorobenzilate	500	19	58 - 118	54 - 129	43 - 133
094	4,4'-DDD	100	12	69 - 117	77 - 109	57 - 129
093	4,4'-DDE	200	13	66 - 114	81 - 121	54 - 126
092	4,4'-DDT	200	19	86 - 112	77 - 118	79 - 119
432	Diallate	250	16	44 - 120	70 - 124	24 - 139
478	Dichlone (2)			79 - 110		
090	Dieldrin	100	11	66 - 140	48 - 115	48 - 158
095	Endosulfan I	200	14	41 - 133	78 - 119	18 - 156
096	Endosulfan II	200	19	78 - 142	76 - 119	62 - 158
097	Endosulfan sulfate	100	17	50 - 130	70 - 109	31 - 149
098	Endrin	100	13	17 - 149	5 - 117	0 - 182
099	Endrin aldehyde	200	13	0 - 149	86 - 117	0 - 190
435	Endrin ketone	100	25	36 - 126	68 - 135	14 - 148
100	Heptachlor	100	12	78 - 104	80 - 114	71 - 111
101	Heptachlor epoxide	100	13	63 - 117	79 - 117	49 - 131
437	Isodrin	100	15	69 - 113	71 - 126	45 - 127
439	Kepone (2)				47 - 134	
430	Methoxychlor	200	19	50 - 136	47 - 128	28 - 158
438	Mirex	100	23	25 - 155	78 - 114	0 - 188
436	Nitrofen (TOK)	200	22	15 - 139	59 - 142	0 - 170
112	PCB-1016					
108	PCB-1221					
109	PCB-1232					
106	PCB-1242					
110	PCB-1248					
107	PCB-1254					
111	PCB-1260	1000	20	82 - 112	79 - 126	75 - 119
440	PCNB	100	11	49 - 129	78 - 101	29 - 149
113	Toxaphene	5000	20	82 - 112	68 - 134	76 - 122
442	Trifluralin	200	12	32 - 148	47 - 134	3 - 177

- (1) Reference numbers beginning with 0 or 1 indicate a pollutant quantified by the internal standard method.  
(2) Not recovered.



Table 8  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR ORGANO-PHOSPHORUS COMPOUNDS

EGD No.	Compound	Spike level (ng/L)	Acceptance Criteria			
			Initial precision and accuracy		Calibration verification	Recovery
			Sec 8.2 (%)		Sec 14.5 (ug/mL)	Sec 8.4 Ongoing accuracy Sec 14.6 R (%)
			s	X		
468	Azinphos ethyl	100	10	71 - 117	77 - 127	59 - 129
453	Azinphos methyl	100	10	52 - 112	83 - 119	37 - 127
461	Chlorfevinphos	50	11	56 - 132	83 - 114	37 - 151
469	Chlorpyrifos	50	10	61 - 112	80 - 119	48 - 125
443	Coumaphos	50	10	78 - 104	82 - 120	72 - 110
479	Crotoxyphos	200	46	28 - 116	68 - 136	6 - 138
471	Demeton-S	200	23	33 - 101	64 - 123	16 - 118
460	Diazinon	100	10	70 - 110	86 - 114	60 - 120
450	Dichlorvos	50	18	52 - 106	77 - 103	39 - 119
455	Dicrotophos (1)					78 - 122
449	Dimethoate	100	89	27 - 100	73 - 127	22 - 100
452	Dioxathion	600	22	59 - 101	79 - 121	49 - 111
458	Disulfoton	100	30	46 - 98	70 - 118	33 - 111
467	EPN	100	13	74 - 124	81 - 108	62 - 136
463	Ethion	100	11	72 - 134	70 - 118	47 - 149
446	Famphur	200	12	81 - 101	81 - 113	76 - 106
454	Fensulfothion	200	65	13 - 115	42 - 139	0 - 141
447	Fenthion	100	13	69 - 101	73 - 137	61 - 109
464	Hexamethylphosphoramide (1)					70 - 130
474	Leptophos	100	10	85 - 105	85 - 112	80 - 110
475	Malathion	100	10	75 - 109	82 - 108	66 - 118
456	Methyl parathion	100	15	72 - 112	89 - 114	61 - 123
444	Mevinphos	100	23	24 - 100	73 - 135	7 - 107
470	Monocrotophos (1)					19 - 206
459	Naled	100	10	0 - 148	77 - 114	0 - 176
448	Parathion	100	10	71 - 111	79 - 110	61 - 121
457	Phorate	100	19	54 - 100	70 - 118	43 - 109
465	Phosmet	200	39	44 - 119	61 - 159	25 - 138
473	Phosphamidon-Z	330	45	0 - 100	81 - 102	0 - 100
477	Sulfotepp	50	10	70 - 120	75 - 115	58 - 132
476	TEPP (1)					70 - 130
472	Terbufos	100	23	60 - 110	82 - 111	47 - 123
466	Tetrachlorvinphos	100	11	48 - 110	73 - 119	32 - 126
445	Trichlorofon (1)					70 - 130
451	Tricresylphosphate	300	10	81 - 101	70 - 130	74 - 114
462	Trimethylphosphate (1)					70 - 130
	Dichlorofenthion	100	10	75 - 115	80 - 110	65 - 125
	Ethoprop	100	14	79 - 103	84 - 108	73 - 109
	Merphos-B	200	10	68 - 102	72 - 118	59 - 111
	Methyl chlorpyrifos	100	10	88 - 108	81 - 114	83 - 113
	Methyl trithion	100	20	21 - 137	78 - 122	0 - 166
	Ronnel	100	10	79 - 111	78 - 113	71 - 119
	Sulprofos (Bolstar)	50	10	75 - 100	81 - 118	70 - 100
	Tokuthion	100	17	73 - 105	70 - 130	65 - 113
	Trichloronate	100	10	82 - 102	80 - 113	77 - 107

(1) Not recovered.

Table 9  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR PHENOXY-ACID COMPOUNDS

EGD No.	Compound	Spike level (ng/L)	Acceptance Criteria			
			Initial precision and accuracy <u>Sec 8.2 (%)</u>		Calibration verification <u>Sec 14.5</u> (ug/mL)	Recovery Sec 8.4 Ongoing accuracy <u>Sec 14.6</u> R (%)
			s	X		
481	2,4-D	200	16	41 - 107	70 - 130	23 - 131
480	Dinoseb					
482	2,4,5-T	100	17	30 - 132	70 - 130	5 - 158
483	2,4,5-TP (Silvex)	100	14	36 - 120	70 - 130	15 - 141
	Dalapon					
	2,4-DB (Butoxon)	100	16	22 - 118	70 - 130	0 - 142
	Dicamba	200	18	37 - 145	70 - 130	10 - 172
	Dichlorprop	100	14	49 - 133	70 - 130	28 - 154
	MCPA	200	14	46 - 130	70 - 130	25 - 151
	MCPP	400	14	65 - 149	70 - 130	42 - 170

**EPA METHOD 1613**  
**TETRA- THROUGH OCTA- CHLORINATED DIOXINS**  
**AND FURANS BY ISOTOPE DILUTION HRGC/HRMS**



## Introduction

Method 1613 was developed by the Industrial Technology Division (ITD) within the United States Environmental Protection Agency's (USEPA) Office of Water Regulations and Standards (OWRS) 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.

Method 1613 is a high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) method for analysis of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) using isotope dilution. Specificity is provided for determination of the 2,3,7,8- substituted isomers of tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and tetrachlorodibenzofuran (2,3,7,8-TCDF).

Questions concerning the method or its application should be addressed to:

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Office of Water Regulations and Standards  
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OR

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703/557-5040

Publication date: July 1989



## Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

### 1 SCOPE AND APPLICATION

- 1.1 This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the tetra-through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); and the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); and other dioxin and furan compounds amenable to high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS). Specificity is provided for determination of the 2,3,7,8- substituted isomers of tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and tetrachlorodibenzofuran (2,3,7,8-TCDF).
- 1.2 The method is based on EPA, industry, commercial laboratory, and academic methods (References 1 - 6).
- 1.3 The compounds listed in Table 1 may be determined in waters, soils, sludges, and other matrices by this method.
- 1.4 The detection limits of the method are usually dependent on the level of interferences rather than instrumental limitations. The levels in Table 2 typify the minimum quantities that can be detected with no interferences present.
- 1.5 The GCMS portions of the method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. 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 Stable isotopically labeled analogs of 16 of the PCDDs and PCDFs are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are filtered and then extracted with methylene chloride using separatory funnel

procedures; the particulates from the water samples, soils, and other finely divided solids are extracted using a combined Soxhlet extraction/Dean-Stark azeotropic distillation (Reference 7). Prior to cleanup and analysis, the extracts of the filtered water and the particulates are combined.

- 2.2 After extraction,  $^{37}\text{Cl}_4$ -labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Samples cleanup may include back extraction with acid and/or base, and gel permeation, alumina, silica gel, and activated carbon chromatography. High performance liquid chromatography (HPLC) can be used for further isolation of the 2,3,7,8- isomers or other specific isomers or congeners.
- 2.3 After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, two internal standards are added to each extract, and a 1  $\mu\text{L}$  aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution ( $\geq 10,000$ ) mass spectrometer. The labeled compounds serve to correct for the variability of the analytical technique.
- 2.4 Dioxins and furans are identified by comparing GC retention time ranges and the ion abundance ratios of the  $m/z$ 's with the corresponding retention time ranges of authentic standards and the theoretical ion abundance ratios of the exact  $m/z$ 's. Isomers and congeners are identified when the retention time ranges and  $m/z$  abundance ratios agree within pre-defined limits. By using a GC column or columns capable of resolving the 2,3,7,8-substituted isomers from all other tetra-isomers, the 2,3,7,8-substituted isomers are identified when the retention time and  $m/z$  abundance ratios agree within pre-defined limits of the retention times and exact  $m/z$  ratios of authentic standards.
- 2.5 Quantitative analysis is performed by GCMS using selected ion current profile (SICP) areas, in one of two ways: 1) For the

16 2,3,7,8-substituted isomers for which labeled analogs are available (see Table 1), the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique; 2) For non-2,3,7,8-substituted isomers and the total concentrations of all isomers within a level of chlorination (i.e., total TCDD), concentrations are determined assuming response factors from the calibration of labeled analogs at the same level of chlorination. Although a labeled analog of the octachlorinated dibenzofuran (OCDF) is available, using high resolution mass spectrometry, it produces an m/z that may interfere with the identification and quantitation of the native octachlorinated dibenzo-p-dioxin (OCDD). Therefore, this labeled analog has not been included in the calibration standards, and the native OCDF is quantitated against the labeled OCDD.

- 2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, 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 (References 8 - 9). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.
- 3.2 Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples, but may also remove the analytes of interest by adsorption on the glass surface.
- 3.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 s may aid in cleaning.
- 3.2.2 After detergent washing, glassware should be immediately rinsed first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, and then acetone, and methylene chloride.

- 3.2.3 Do not bake reusable glassware in an oven. Repeated baking of glassware may cause active sites on the glass surface that will irreversibly adsorb PCDDs/PCDFs.

- 3.2.4 Immediately prior to use, Soxhlet extraction glassware should be pre-extracted with toluene for approximately 3 hours. See Section 11.1.2.3. Separatory funnels should be shaken with methylene chloride for 2 minutes.

- 3.3 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix blanks initially and with each sample set (samples started through the extraction process on a given 12-hour shift, to a maximum of 20). The reference matrix blank must simulate, as closely as possible, the sample matrix under test. Reagent water (Section 6.6.1) is used to simulate water samples; playground sand (Section 6.6.2) or white quartz sand (Section 6.5.4) can be used to simulate soils; filter paper (Section 6.6.3) is used to simulate papers and similar materials; other materials (Section 6.6.4) can be used to simulate other matrices.

- 3.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCDDs and PCDFs. The most frequently encountered interferences are chlorinated-biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCDDs and PCDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 12 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCDDs and PCDFs at the levels shown in Table 2.

### 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.



- 4.1.1 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. It is soluble in water to approximately 200 parts-per-trillion and in organic solvents to 0.14 percent. On the basis of the available toxicological and physical properties of 2,3,7,8-TCDD, all of the PCDDs and PCDFs should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures, and who understand the associated risks.
- 4.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this method. However, if primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator shall be worn when high concentrations are handled.
- 4.2 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 10 - 13. The references and bibliography at the end of Reference 13 are particularly comprehensive in dealing with the general subject of laboratory safety.
- 4.3 The PCDDs and PCDFs and samples suspected to contain these compounds are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory 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 PCDDs and PCDFs are extremely toxic to laboratory animals. However, they have been handled for years without injury in analytical and biological laboratories. Each laboratory must develop a strict safety program for handling the PCDDs and PCDFs. The following laboratory practices are recommended (References 2 and 14):
- 4.3.1 Facility -- When finely divided samples (dusts, soils, dry chemicals) are handled, all operations, including removal of samples from sample containers, weighing, transferring and mixing should be performed in a glove box demonstrated to be leak tight or fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.
- 4.3.2 Protective equipment -- Throwaway plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the PCDDs or PCDFs, an additional set of gloves can also be worn beneath the latex gloves.
- 4.3.3 Training -- Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.
- 4.3.4 Personal hygiene -- Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).
- 4.3.5 Confinement -- Isolated work area, posted with signs, segregated glassware and tools, plastic absorbent paper on bench tops.
- 4.3.6 Effluent vapors -- The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.
- 4.3.7 Waste
- 4.3.7.1 Handling -- Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

- 4.3.7.2 Disposal
- 4.3.7.2.1 The PCDDs and PCDFs decompose above 800 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling extremely toxic wastes.
- 4.3.7.2.2 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength greater than 290 nm for several days. (Use F 40 BL lamps or equivalent.) Analyze liquid wastes and dispose of the solutions when the PCDDs and PCDFs can no longer be detected.
- 4.3.8 Decontamination
- 4.3.8.1 Personal decontamination -- Use any mild soap with plenty of scrubbing action.
- 4.3.8.2 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. If glassware is first rinsed with solvent, then the dish water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.
- 4.3.9 Laundry -- Clothing known to be contaminated 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 of the potential problem. The washer should be run through a cycle before being used again for other clothing.
- 4.3.10 Wipe tests -- A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by GC can achieve a limit of detection of 0.1 ug per wipe. Less than 0.1 ug per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 ug on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed in the past.
- 4.3.11 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.
- 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, paper pulps, 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 before use.
- 5.1.1.5.2 Liners are detergent water washed, then rinsed with reagent water (Section 6.6.1) and then solvent, and baked at approximately 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. 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.

## 129

- 5.5.2 Glass funnel -- 125 - 250 mL
- 5.5.3 Glass fiber filter paper (Whatman GF/D, or equivalent)
- 5.5.4 Drying column -- 15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.
- 5.5.5 Buchner funnel, 15 cm.
- 5.5.6 Glass fiber filter paper for above.
- 5.5.7 Pressure filtration apparatus -- Millipore YT30 142 HW, or equivalent.
- 5.6 Centrifuge apparatus
  - 5.6.1 Centrifuge -- Capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5,000 rpm minimum
  - 5.6.2 Centrifuge bottles -- 500 mL, with screw caps, to fit centrifuge
  - 5.6.3 Centrifuge tubes -- 12-15 mL, with screw caps, to fit centrifuge
- 5.7 Cleanup apparatus
  - 5.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).
    - 5.7.1.1 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).
    - 5.7.1.2 Syringe, 10 mL, with Luer fitting.
    - 5.7.1.3 Syringe filter holder, stainless steel, and glass fiber or Teflon filters (Gelman 4310, or equivalent).
    - 5.7.1.4 UV detectors -- 254-nm, 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).
  - 5.7.2 Reverse phase high performance liquid chromatograph
    - 5.7.2.1 Column oven and detector -- Perkin-Elmer Model LC-65T (or equivalent) operated at 0.02 AUFS at 235 nm.
    - 5.7.2.2 Injector -- Rheodyne 7120 (or equivalent) with 50 uL sample loop.
    - 5.7.2.3 Column -- Two 6.2 x 250 mm Zorbax-ODS columns in series (DuPont Instruments Division, Wilmington, DE, or equivalent), operated at 50 °C with 2.0 mL/min methanol isocratic effluent.
    - 5.7.2.4 Pump -- Altex 110A (or equivalent).
  - 5.7.3 Pipets
    - 5.7.3.1 Disposable, Pasteur, 150 mm x 5 mm i.d. (Fisher Scientific 13-678-6A, or equivalent).
    - 5.7.3.2 Disposable, serological, 10 mL (6 mm i.d.).
  - 5.7.4 Chromatographic columns
    - 5.7.4.1 150 mm x 8 mm i.d., (Kontes K-420155, or equivalent) with coarse glass frit or glass wool plug and 250 mL reservoir.
    - 5.7.4.2 200 mm x 15 mm i.d., with coarse glass frit or glass wool plug and 250 mL reservoir.
  - 5.7.5 Oven -- For storage of adsorbents, capable of maintaining a temperature of 130 ±5 °C.
- 5.8 Concentration apparatus
  - 5.8.1 Rotary evaporator -- Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.
    - 5.8.1.1 A vacuum source is required for use of the rotary evaporator. It must be equipped with a shutoff valve at the evaporator, and preferably, have a vacuum gauge.
    - 5.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.
    - 5.8.1.3 Round bottom flask -- 500 mL or larger, with ground glass fitting compatible with the rotary evaporator.
  - 5.8.2 Nitrogen blowdown apparatus -- Equipped with water bath controlled at 35 - 40 °C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.

- 5.8.3 Sample vials -- Amber glass, 2 - 5 mL with Teflon-lined screw cap.
- 5.9 Gas chromatograph -- Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 14.
- 5.9.1 GC Column for PCDDs and PCDFs and for isomer specificity for 2,3,7,8-TCDD -- 60  $\pm$  5 m x 0.32  $\pm$  0.02 mm i.d.; 0.25  $\mu$ m 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase fused silica capillary column (J & W DB-5, or equivalent).
- 5.9.2 GC Column for isomer specificity for 2,3,7,8-TCDF -- 30  $\pm$  5 m x 0.32  $\pm$  0.02 mm i.d.; 0.25  $\mu$ m bonded phase fused silica capillary column (J & W DB-225, or equivalent).
- 5.10 Mass spectrometer -- 28 - 40 eV electron impact ionization, shall repetitively selectively monitor 11 exact m/z's minimum at high resolution ( $\geq$ 10,000) during a period of approximately 1 second.
- 5.10.1 The groups of m/z's to be monitored are shown in Table 3. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all PCDDs and PCDFs are detected. The theoretical abundance ratios for the m/z's are given in Table 3A, along with the control limits of each ratio.
- 5.10.2 The mass spectrometer shall be operated in a mass drift correction mode, using perfluorokerosene (PFK) to provide lock masses. The lock mass for each group of m/z's is shown in Table 3. Each lock mass shall be monitored and shall not vary by more than  $\pm$ 10 percent throughout its respective retention time window. Variations of the lock mass by more than 10 percent indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Re-injection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.
- 5.11 GC/MS interface -- The mass spectrometer shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm 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.

- 5.12 Data system -- Shall collect and record and store MS data.
- 5.12.1 Data acquisition -- The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.
- 5.12.2 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. Computations of relative standard deviation (coefficient of variation) are used to test calibration linearity. Statistics on initial (Section 8.2) and ongoing (Section 14.5) performance shall be computed and maintained.

## 6 REAGENTS AND STANDARDS

- 6.1 pH adjustment and back extraction
- 6.1.1 Potassium hydroxide -- Dissolve 20 g reagent grade KOH in 100 mL reagent water.
- 6.1.2 Sulfuric acid -- Reagent grade (specific gravity 1.84).
- 6.1.3 Sodium chloride -- Reagent grade, prepare a five percent (w/v) solution in reagent water.
- 6.2 Solution drying and evaporation
- 6.2.1 Solution drying -- Sodium sulfate, reagent grade, granular anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.
- 6.2.2 Prepurified nitrogen
- 6.3 Solvents -- Acetone, toluene, cyclohexane, hexane, nonane, methanol, methylene chloride, and nonane: distilled-in-glass, pesticide quality, lot certified to be free of interferences.

- 6.4 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
- 6.5 Adsorbents for sample cleanup
  - 6.5.1 Silica gel
    - 6.5.1.1 Activated silica gel -- Bio-Sil A, 100 - 200 mesh (Bio-Rad 131-1340, or equivalent), rinsed with methylene chloride, baked at 250 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.
    - 6.5.1.2 Acid silica gel (30 percent w/w) -- Thoroughly mix 4.4 g of concentrated sulfuric acid with 10.0 g activated silica gel. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with Teflon-lined cap.
    - 6.5.1.3 Basic silica gel -- Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with Teflon-lined cap.
  - 6.5.2 Alumina
    - 6.5.2.1 Neutral alumina -- Bio-Rad Laboratories 132-1140 Neutral Alumina Ag 7 (or equivalent). Heat to 600 °C for 24 hours minimum. Store at 130 °C in a covered flask. Use within five days of baking at 600 °C.
    - 6.5.2.2 Acid alumina -- Bio-Rad Laboratories 132-1340 Acid Alumina AG 4 (or equivalent). Activate by heating to 130 °C for 12 hours minimum.
    - 6.5.2.3 Basic alumina -- Bio-Rad Laboratories 132-1240 Basic Alumina AG 10 (or equivalent). Activate by heating to 600 °C for 24 hours minimum. Alternatively, activate by heating alumina in a tube furnace at 650 - 700 °C under an air flow of approximately 400 cc/min. To avoid melting the alumina, do not heat over 700 °C. Store at 130 °C in a covered flask. Use within five days of baking.
  - 6.5.3 AX-21/Celite
    - 6.5.3.1 Activated carbon -- AX-21 (Anderson Development Company, Adrian, MI, or equivalent). Prewash with methanol and dry in vacuo at 110 °C.
    - 6.5.3.2 Celite 545 -- (Supelco 2-0199, or equivalent).
    - 6.5.3.3 Thoroughly mix 5.35 g AX-21 and 62.0 g Celite 545 to produce a 7.9% w/w mixture. Activate the mixture at 130 °C for six hours minimum. Store in a dessicator.
  - 6.5.4 White quartz sand, 60/70 mesh -- For Soxhlet/Dean-Stark extraction, (Aldrich Chemical Co, Milwaukee WI Cat No. 27,437-9, or equivalent). Bake at 450 °C for four hours minimum.
- 6.6 Reference matrices
  - 6.6.1 Reagent water -- Water in which the PCDDs and PCDFs and interfering compounds are not detected by this method.
  - 6.6.2 High solids reference matrix -- Playground sand or similar material in which the PCDDs and PCDFs and interfering compounds are not detected by this method. May be prepared by extraction with methylene chloride and/or baking at 450 °C for four hours minimum.
  - 6.6.3 Filter paper -- Gelman type A (or equivalent) glass fiber filter paper in which the PCDDs and PCDFs and interfering compounds are not detected by this method. Cut the paper to simulate the surface area of the paper sample being tested.
  - 6.6.4 Other matrices -- This method may be verified on any matrix by performing the tests given in Section 8.2. Ideally, the matrix should be free of the PCDDs and PCDFs, but in no case shall the background level of the PCDDs and PCDFs in the reference matrix exceed three times the minimum levels given in Table 2. If low background levels of the PCDDs and PCDFs are present in the reference matrix, the spike level of the analytes used in Section 8.2 should be increased to provide a spike-to-background ratio in the range of 1/1 to 5/1 (Reference 15).
- 6.7 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 98 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 room temperature in screw-capped vials with Teflon-lined caps. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. If solvent loss has occurred, the solution should be replaced.

#### 6.8 Stock solutions

6.8.1 Preparation -- Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent). Observe the safety precautions in Section 4, and the recommendation in Section 4.1.2.

6.8.2 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 - 2 mg of 2,3,7,8-TCDD to three significant figures in a 10 mL ground glass stoppered volumetric flask and fill to the mark with nonane. After the TCDD is completely dissolved, transfer the solution to a clean 15 mL vial with Teflon-lined cap.

6.8.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories.

6.9 Secondary standard -- Using stock solutions (Section 6.8), prepare secondary standard solutions containing the compounds and concentrations shown in Table 4 in nonane.

6.10 Labeled compound spiking standard -- From stock standard solutions prepared as above, or from purchased mixtures, prepare this standard to contain the labeled compounds at the concentrations shown in Table 4 in nonane. This solution is diluted with acetone prior to use (Section 10.3.2).

6.11 Cleanup standard - Prepare  $^{37}\text{Cl}_4$ -2,3,7,8-TCDD at the concentration shown in Table 4 in nonane.

6.12 Internal standard -- Prepare at the concentration shown in Table 4 in nonane.

6.13 Calibration standards (CS1 through CS5) -- Combine the solutions in Sections 6.9, 6.10, 6.11, and 6.12 to produce the five calibration solutions shown in Table 4 in nonane. These solutions permit the relative response (labeled to unlabeled) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER).

6.14 Precision and recovery standard (PAR) -- Used for determination of initial (Section 8.2) and ongoing (Section 14.5) precision and recovery. This solution contains the analytes and labeled compounds at the concentrations listed in Table 4 in nonane. This solution is diluted with acetone prior to use (Section 10.3.4).

6.15 GC retention time window defining solutions -- Used to define the beginning and ending retention times for the dioxin and furan isomers.

6.15.1 DB-5 column window defining standard -- Cambridge Isotope Laboratories ED-1732-A, or equivalent, containing the compounds listed in Table 5.

6.16 Isomer specificity test standards -- Used to demonstrate isomer specificity for the 2,3,7,8-tetra- isomers of dioxin and furan.

6.16.1 Standards for the DB-5 column -- Cambridge Isotope Laboratories ED-908, ED-908-C, or ED-935, or equivalent, containing the compounds listed in Table 5.

6.16.2 Standards for the DB-225 column -- Cambridge Isotope Laboratories EF-937 or EF-938, or equivalent, containing the compounds listed in Table 5.

6.17 Stability of solutions -- Standard solutions used for quantitative purposes (Sections 6.9 - 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 m/z remains within  $\pm 15$  percent of the area obtained in the initial analysis of the standard. Any standards failing to meet this criterion should be assayed against reference standards, as in Section 6.8.3., before further use.

## 7 CALIBRATION

7.1 Assemble the GCMS and establish the operating conditions necessary to meet the relative retention time specifications in Table 2.

7.1.1 The following GC operating conditions may be used for guidance and adjusted as needed to meet the relative retention time specifications in Table 2:

Injector temp: 270 °C  
Interface temp: 290 °C  
Initial temp and time: 200 °C, 2 min  
Temp Program: 200-220 °C at 5 °C/min  
                  220 °C for 16 min  
                  220-235 °C at 5 °C/min  
                  235 °C for 7 min  
                  235-330 °C at 5 °C/min

7.1.2 Obtain a selected ion current profile of each analyte in Table 4 at the exact masses specified in Table 3 and at  $\geq 10,000$  resolving power by injecting an authentic standard of the PCDDs and PCDFs either singly or as part of a mixture in which there is no interference between closely eluted components, using the procedure in Section 13.

7.2 The ion abundance ratios, minimum levels, and absolute retention times -- Inject the CS1 calibration solution (Table 4) per the procedure in Section 13 and the conditions in Table 2.

7.2.1 Measure the selected ion current profile (SICP) areas for each analyte and compute the ion abundance ratios specified in Table 3. Compare the computed ratio to the theoretical ratio given in Table 3.

7.2.2 All PCDDs and PCDFs shall be within their respective ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 7.1) prior to repeat of the test.

7.2.3 Verify that the HRGC/HRMS instrument meets the minimum levels in Table 2; otherwise, the mass spectrometer shall be adjusted and this test repeated until the minimum levels in Table 2 are met.

7.2.4 The retention times of  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD (the internal

standards, Section 6.12) shall exceed 27 and 38 minutes, respectively, on the DB-5 column, and the retention time of  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD shall exceed 17 minutes on the DB-225 column; otherwise, the GC temperature program shall be adjusted and this test repeated until the minimum retention time criteria are met.

7.3 Retention time windows -- Analyze the window defining mixtures (Section 6.15) using the procedure in Section 13 (Figures 2A - 2D).

7.4 Isomer specificity

7.4.1 Analyze the isomer specificity test standards (Section 6.16) using the procedure in Section 13.

7.4.2 Compute the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers, on their respective columns, per Figure 3.

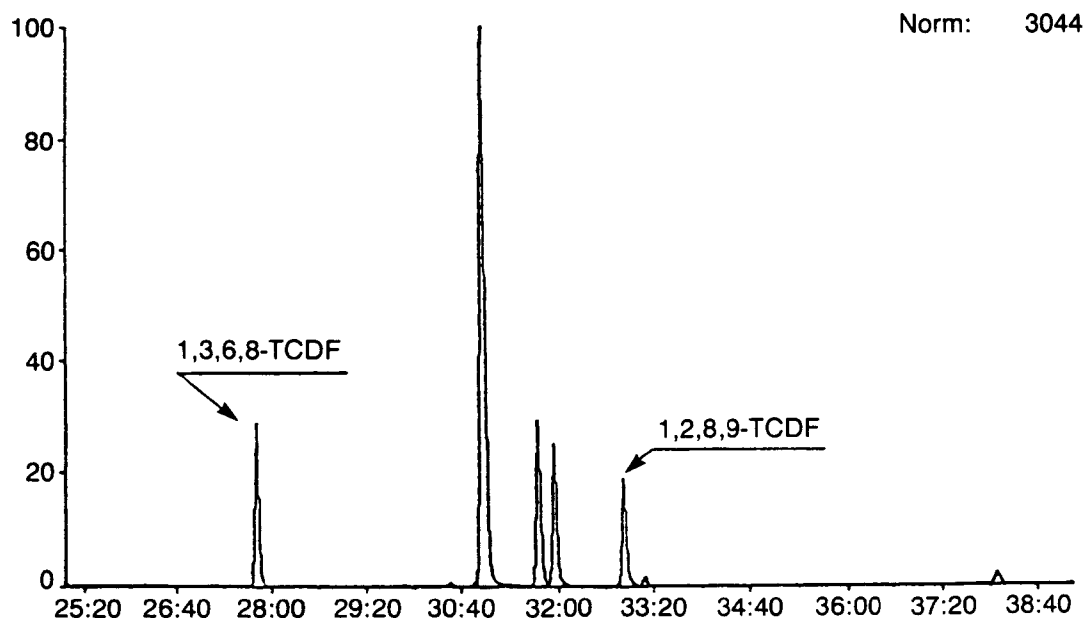
7.4.3 Verify that the height of the valley between the most closely eluted isomers and the 2,3,7,8- isomers is less than 25 percent (computed as  $100 \times y/y$  in Figure 3). If the valley exceeds 25 percent, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate (Section 7.2 through 7.4).

7.5 Calibration with isotope dilution -- Isotope dilution is used when 1) labeled compounds are available, 2) interferences do not preclude its use, and 3) the SICP area for the analyte at the exact m/z (Table 3) is in the calibration range for the analyte. The reference compound for each native and labeled compound is shown in Table 6. 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 7.6) is used.

7.5.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (native to labeled) vs concentration in standard solutions is plotted or computed using a linear regression. Relative response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
 Sample 1 Injection 1 Group 2 Mass 303.9016



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
 Sample 1 Injection 1 Group 2 Mass 319.8965

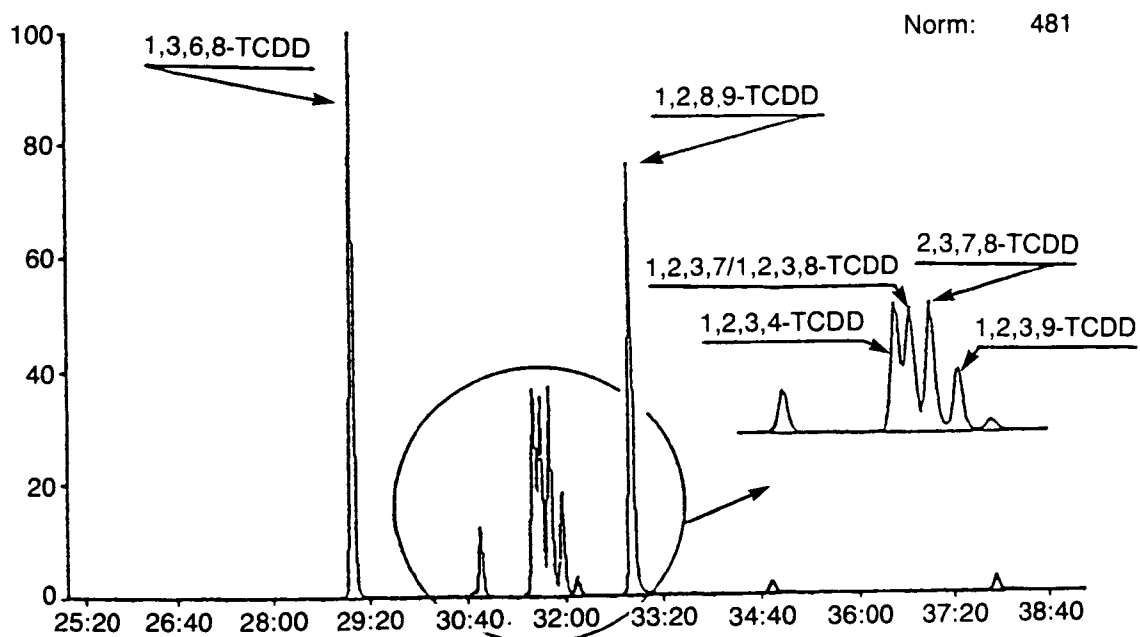
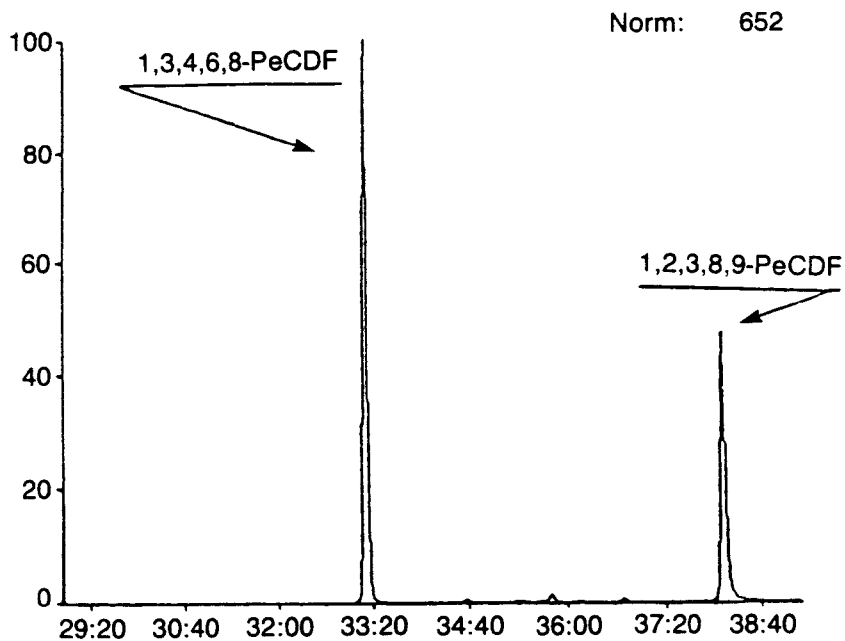


FIGURE 2A First and Last Eluted Tetra- Dioxin and Furan Isomers

6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 2 Mass 339.8597



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 2 Mass 355.8546

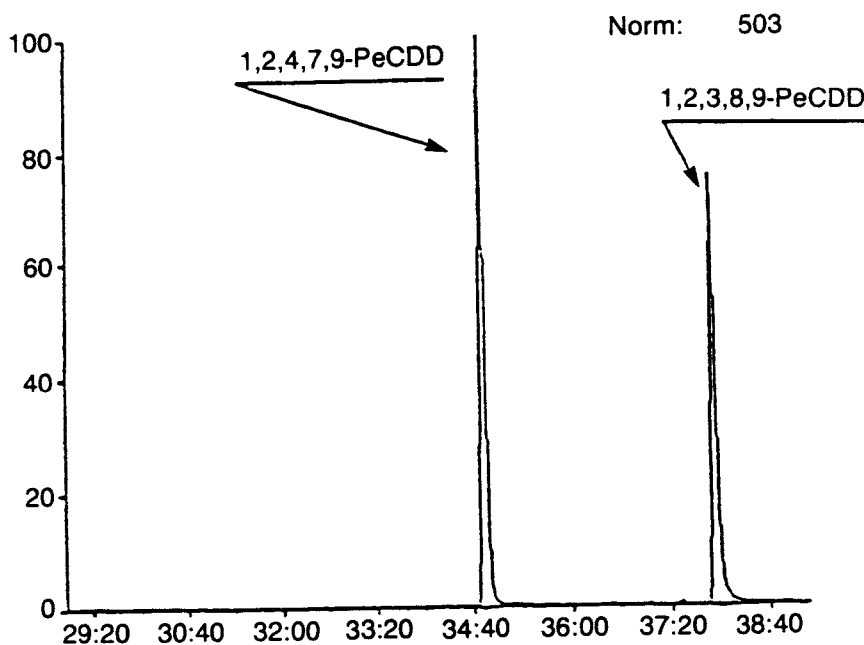
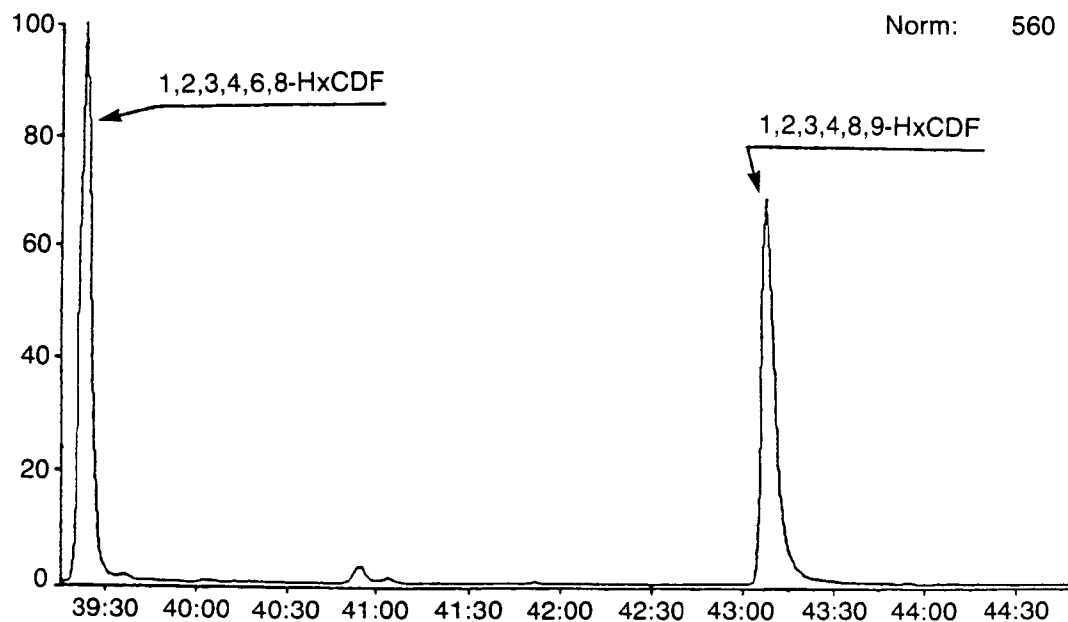


FIGURE 2B First and Last Eluted Penta- Dioxin and Furan Isomers

6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 3 Mass 373.8208



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 3 Mass 389.8156

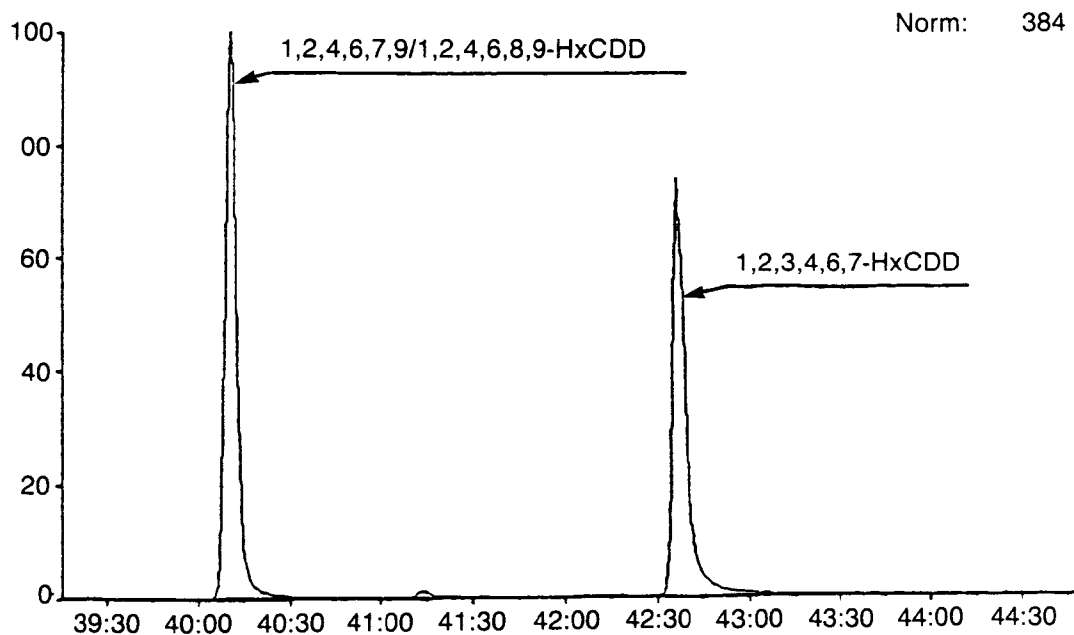
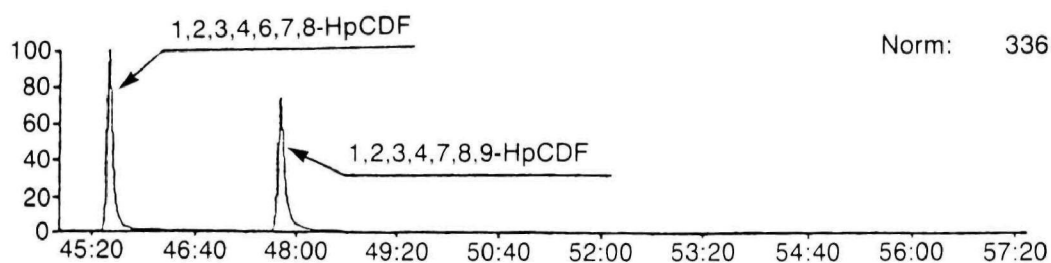
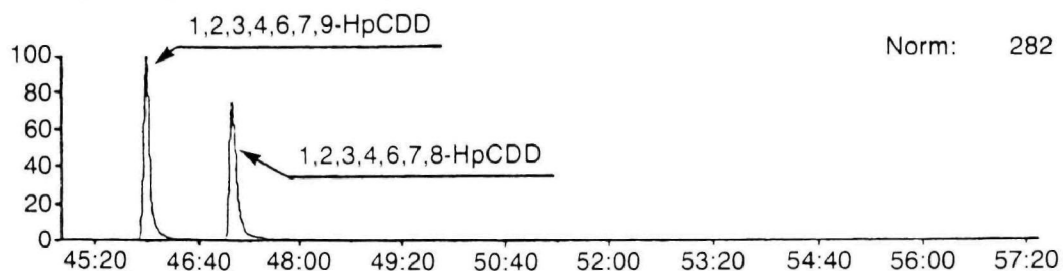


FIGURE 2C First and Last Eluted Hexa- Dioxin and Furan Isomers

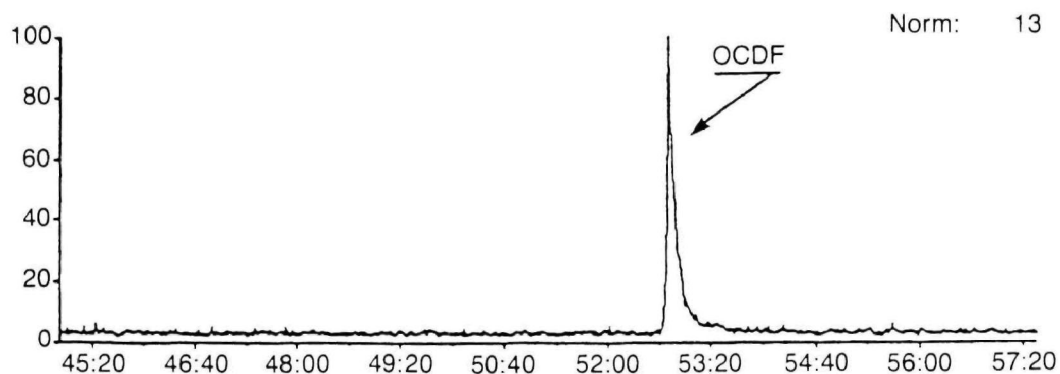
6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 4 Mass 407.7818



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 4 Mass 423.7766



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 4 Mass 441.7428



6-MAY-88 Sir: Voltage 705 Sys: DB5US  
Sample 1 Injection 1 Group 4 Mass 457.7377

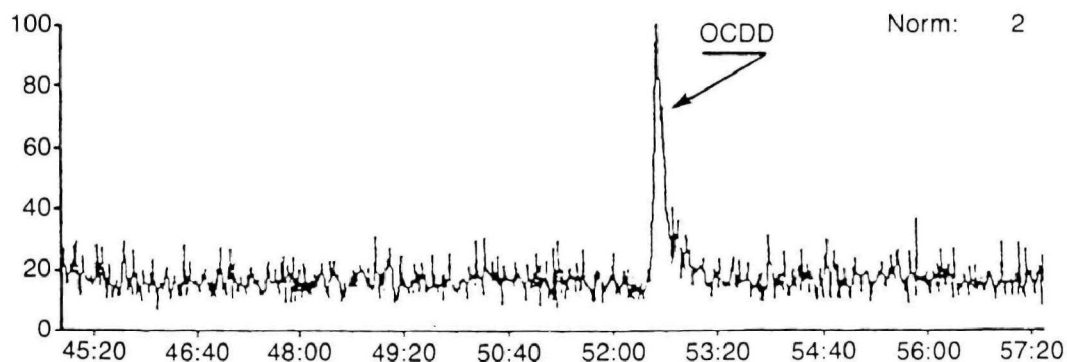
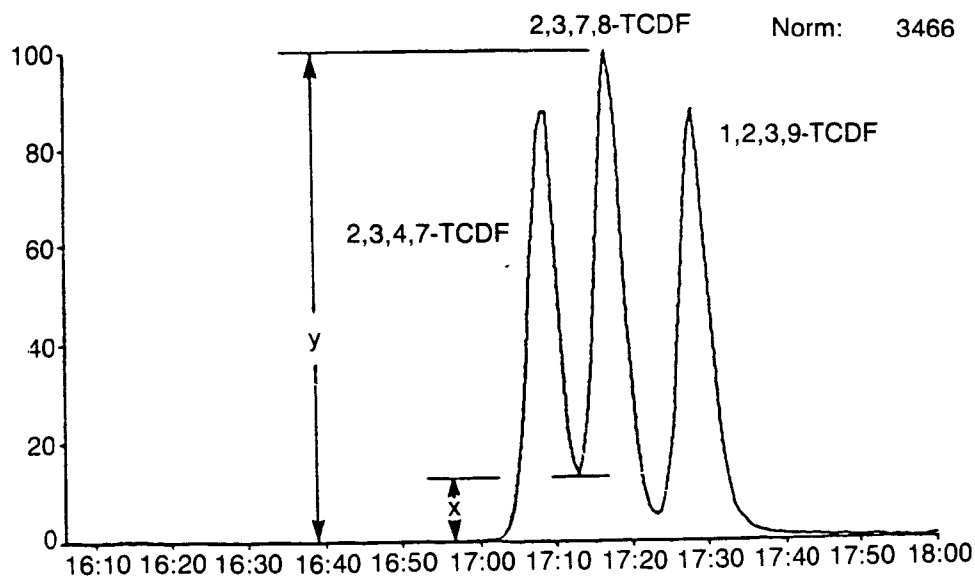


FIGURE 2D First and Last Eluted Hepta- Dioxin and Furan Isomers

3A DB225 Column

21-APR-88 Sir: Voltage 705 Sys: DB225  
Sample 1 Injection 1 Group 1 Mass 305.8987  
Text: COLUMN PERFORMANCE



3B DB5 Column

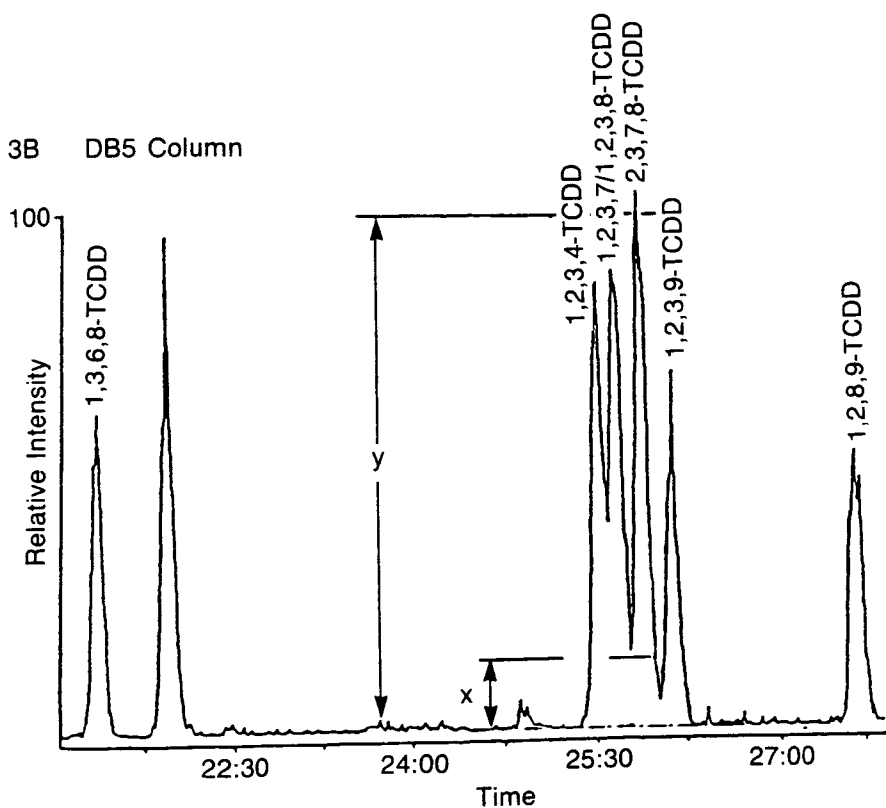


FIGURE 3 Valley between 2,3,7,8- Tetra Dioxin and Furan Isomers and Other Closely Eluted Isomers

7.5.2 The relative response of a PCDD or PCDF to its labeled analog is determined from isotope ratio values computed from acquired data. Three isotope ratios are used in this process:

R<sub>x</sub> = the isotope ratio measured for the pure pollutant.

R<sub>y</sub> = the isotope ratio measured for the labeled compound.

R<sub>m</sub> = the isotope ratio of an analytical mixture of pollutant and labeled compounds.

The m/z's are selected such that R<sub>x</sub> > R<sub>y</sub>. If R<sub>m</sub> is not between 2R<sub>y</sub> and 0.5R<sub>x</sub>, the method does not apply and the sample is analyzed by the internal standard method.

7.5.3 When there is no overlap between the GC peaks or the quantitation m/z's, as occurs with nearly all of the PCDDs and PCDFs and their respective labeled analogs, the RR is calculated per the following:

$$R_x = \frac{[\text{area } m_1/z]}{1}$$

at the retention time of the native compound.

$$R_y = \frac{1}{[\text{area } m_2/z]}$$

at the retention time of the labeled compound (RT<sub>2</sub>).

$$R_m = \frac{[\text{area at } m_1/z \text{ (at RT}_2\text{)}]}{[\text{area at } m_2/z \text{ (at RT}_1\text{)}]}$$

as measured in the mixture of the native and labeled compounds (Figure 4) (RT<sub>1</sub>).

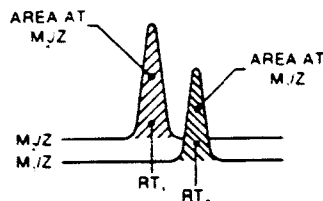


FIGURE 4 Selected Ion Current Profiles for Chromatographically Resolved Labeled (m<sub>2</sub>/z) and Unlabeled (m<sub>1</sub>/z) Pairs.

7.5.4 To calibrate the analytical system by isotope dilution, inject a 1.0 uL aliquot of calibration standards CS1 through CS5 (Section 6.13 and Table 4) using the procedure in Section 13 and the conditions in Table 2. Compute the RR at each concentration.

7.5.5 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.

7.6 Calibration by internal standard -- The internal standard method is applied to determination of compounds having no labeled analog, and to measurement of labeled compounds for intra-laboratory statistics (Sections 8.4 and 14.5.4).

7.6.1 Response factors -- Calibration requires the determination of response factors (RF) defined by the following equation:

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

where,

A<sub>s</sub> is the area of the exact m/z for the compound in the calibration standard.

A<sub>is</sub> is the area of the exact m/z for the internal standard.

C<sub>is</sub> is the concentration of the GCMS internal standard (Section 6.12 and Table 4) in pg/uL.

C<sub>s</sub> is the concentration of the compound in the calibration standard in pg/uL.

7.6.1.1 The response factor is determined for at least five concentrations appropriate to the response of each compound (Section 6.13); nominally, 0.5, 2, 10, 40, and 200 ng/mL. The amount of internal standard added to each calibration solution and extract is the same (100 ng/mL) so that C<sub>is</sub> remains constant. The RF is plotted vs concentration for each compound in the standard (C<sub>s</sub>) to produce a calibration curve.

7.6.1.2 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.

- 7.7 Combined calibration -- By using calibration solutions (Section 6.13 and Table 4) containing the unlabeled and labeled compounds, and the internal standards, 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 14.3) by analyzing the calibration verification standard (VER, Table 4). Recalibration is required if calibration verification criteria (Section 14.3.4) 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 16). 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) or to an alternate matrix, the high solids reference matrix (Section 6.6.2) or the alternate matrix (Section 6.6.4) is substituted for the reagent water matrix (Section 6.6.1) in all performance 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 procedures in Sections 7.2 through 7.4 and Section 8.2 to demonstrate method performance.
- 8.1.3 Analyses of blanks are required to demonstrate freedom from contamination (Section 3.2). 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. Procedures for dilutions are given in Section 16.4.
- 8.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the precision and recovery standard that the analytical system is in control. These procedures are described in Sections 14.1 through 14.5.
- 8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in 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 four 1-liter aliquots of reagent water spiked with the diluted precision and recovery standard (PAR) (Sections 6.14 and 10.3.4) according to the procedures in Sections 10 through 13. For an alternate sample matrix, four aliquots of the alternate matrix are used. All sample processing steps, including preparation (Section 10), extraction (Section 11), and cleanup (Section 12) that are to be used for processing samples shall be included in this test.
- 8.2.2 Using results of the set of four analyses, compute the average recovery (X) in ng/mL and the standard deviation of the recovery (s) in ng/mL for each compound, by isotope dilution for PCDDs and PCDFs with a labeled analog, and by internal standard for labeled compounds and PCDDs and PCDFs 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 7. 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. Correct the problem and repeat the test (Section 8.2).

8.3 The laboratory shall spike all samples and QC aliquots with the diluted labeled compound spiking standard (Sections 6.10 and 10.3.2) to assess method performance on the sample matrix.

8.3.1 Analyze each sample according to the procedures in Sections 10 through 13.

8.3.2 Compute the percent recovery ( $P$ ) of the labeled compounds in the labeled compound spiking standard and the cleanup standard using the internal standard method (Section 7.6).

8.3.3 Compare the labeled compound recovery for each compound with the corresponding limits in Table 7. If the recovery of any compound falls outside its limit, method performance is unacceptable for that compound in that sample. To overcome such difficulties, water samples are diluted and smaller amounts of soils, sludges, sediments and other matrices are reanalyzed per Section 17.

8.4 Method accuracy for samples shall be assessed and records shall be maintained.

8.4.1 After the analysis of five samples of a given matrix type (water, soil, sludge, pulp, etc) for which the labeled compound spiking standards pass the tests in Section 8.3, compute the average percent recovery ( $P$ ) and the standard deviation of the percent recovery ( $sp$ ) for the labeled compounds only. 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 pulp, the accuracy interval is expressed as 70 - 110%.

8.4.2 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 -- Reference matrix blanks are analyzed to demonstrate freedom from contamination (Section 3.2).

8.5.1 Extract and concentrate a 1-liter reagent water blank (Section 6.6.1), high solids reference matrix blank (Section 6.6.2), paper matrix blank (Section 6.6.3) or alternate reference matrix blank (Section 6.6.4) with each sample set (samples started through the extraction process on the same 12-hour shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the precision and recovery standard (Section 14.5) to demonstrate freedom from contamination.

8.5.2 If any of the PCDDs or PCDFs (Table 1) or any potentially interfering compound is found in blank at greater than the minimum level (Table 2), assuming a response factor of 1 relative to the  $^{13}C_{12-1,2,3,4}$ -TCDD internal standard for compounds not listed in Table 1, 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 and then maintained in a calibrated state. The standards used for calibration (Section 7), calibration verification (Section 14.3), and for initial (Section 8.2) and ongoing (Section 14.5) precision and recovery should be identical, so that the most precise results will be obtained. A GCMS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCDDs and PCDFs 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 17). 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 18).

- 9.3 Begin sample extraction within one year of collection, and analyze all extracts within 40 days of extraction.

## 10 SAMPLE PREPARATION

The sample preparation process involves modifying the physical form of the sample so that the PCDDs and PCDFs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 8 lists the phase(s) and quantity extracted for various sample matrices. Samples containing a solid phase and samples containing particle sizes larger than 1 mm require preparation prior to extraction. Because PCDDs/PCDFs are strongly associated with particulates, the preparation of aqueous samples is dependent on the solids content of the sample. Aqueous samples containing less than one percent solids are extracted in a separatory funnel. A smaller sample aliquot is used for aqueous samples containing one percent solids or more. For samples expected or known to contain high levels of the PCDDs and/or PCDFs, the smallest sample size representative of the entire sample should be used, and the sample extract should be diluted, if necessary, per Section 16.4.

- 10.1 Determine percent solids
- 10.1.1 Weigh 5 - 10 g of sample (to three significant figures) into a tared beaker. NOTE: This aliquot is used only for determining the solids content of the sample, not for analysis of PCDDs/PCDFs.
- 10.1.2 Dry overnight (12 hours minimum) at 110 ± 5 °C, and cool in a dessicator.
- 10.1.3 Calculate percent solids as follows:

% solids =

$$\frac{\text{weight of sample after drying}}{\text{weight of sample before drying}} \times 100$$

## 10.2 Determine particle size

- 10.2.1 Spread the dried sample from Section 10.1.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

- 10.2.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction.

- 10.3 Preparation of aqueous samples containing less than one percent solids -- The extraction procedure for aqueous samples containing less than one percent solids involves filtering the sample, extracting the particulate phase and the filtrate separately, and combining the extracts for analysis. The aqueous portion is extracted by shaking with methylene chloride in a separatory funnel. The particulate material is extracted using the SDS procedure.

- 10.3.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample in the bottle on a top loading balance to ±1 g.

- 10.3.2 Dilute a sufficient volume of the labeled compound spiking standard by a factor of 50 with acetone. 1.0 mL of the diluted solution is required for each sample, but no more solution should be prepared than can be used in one day. Spike 1.0 mL of the diluted solution into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for 1 - 2 hours, with occasional shaking.

- 10.3.3 For each sample or sample set (to a maximum of 20) to be extracted during the same 12-hour shift, place two 1.0 liter aliquots of reagent water in clean 2 liter separatory flasks.

- 10.3.4 Spike 1.0 mL of the diluted labeled compound spiking standard (Section 6.10) into one reagent water aliquot. This aliquot will serve as the blank. Dilute 20 uL of the precision and recovery standard (Section 6.14) to 1.0 mL with acetone. Spike 1.0 mL of the diluted precision and recovery standard into the

- remaining reagent water aliquot. This aliquot will serve as the PAR (Section 14.5).
- 10.3.5 Assemble a Buchner funnel on top of a clean 1 L filtration flask. Apply a vacuum to the flask, and pour the entire contents of the sample bottle through a glass fiber filter (Section 5.5.4) in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulates.
- 10.3.6 Rinse the sample bottle twice with 5 mL of reagent water to transfer any remaining particulates onto the filter.
- 10.3.7 Rinse the any particulates off the sides of the Buchner funnel with small quantities of reagent water.
- 10.3.8 Weigh the empty sample bottle on a top-loading balance to  $\pm 1$  g. Determine the weight of the sample by difference. Do not discard the bottle at this point.
- 10.3.9 Extract the filtrates using the procedures in Section 11.
- 10.3.10 Extract the particulates using the procedures in Section 11.
- 10.4 Preparation of samples containing greater than one percent solids
- 10.4.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in 10.1.3) into a clean beaker or glass jar.
- 10.4.2 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 10.3.2) into the sample aliquot(s).
- 10.4.3 For each sample or sample set (to a maximum of 20) to be extracted during the same 12-hour shift, weigh two 10 g aliquots of the appropriate reference matrix (Section 6.6) into clean beakers or glass jars.
- 10.4.4 Spike 1.0 mL of the diluted labeled compound spiking solution into one reference matrix aliquot. This aliquot will serve as the blank. Spike 1.0 mL of the diluted precision and recovery standard (Section 10.3.4) into the remaining reference matrix aliquot. This aliquot will serve as the PAR (Section 14.5).
- 10.4.5 Stir or tumble and equilibrate the aliquots for 1 - 2 hours.
- 10.4.6 Extract the aliquots using the procedures in Section 11.
- 10.5 Multi-phase samples
- 10.5.1 Pressure filter the sample, blank, and PAR aliquots through Whatman GF/D glass fiber filter paper. If necessary, centrifuge these aliquots for 30 minutes at greater than 5000 rpm prior to filtration.
- 10.5.2 Discard any aqueous phase (if present). Remove any non-aqueous liquid (if present) and reserve for recombination with the extract of the solid phase (Section 11.1.2.5). Prepare the filter papers of the sample and QC aliquots for particle size reduction and blending (Section 10.6).
- 10.6 Sample grinding, homogenization, or blending -- Samples with particle sizes greater than 1 mm (as determined by Section 10.2.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or by blending.
- 10.6.1 Each size reducing preparation procedure on each matrix shall be verified by running the tests in Section 8.2 before the procedure is employed routinely.
- 10.6.2 The grinding, homogenization, or blending procedures shall be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.
- 10.6.3 Grinding -- Tissue samples, certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Section 10.4.5 or 10.5.2 in a clean grinder. Do not allow the sample temperature to exceed 50 °C. Grind the blank and reference matrix aliquots using a clean grinder.

- 10.6.4 Homogenization or blending -- Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the sample, blank, and PAR aliquots from Section 10.4.5, 10.5.2, or 10.6.3.
- 10.6.5 Extract the aliquots using the procedures in Section 11.
- 11 EXTRACTION AND CONCENTRATION
- 11.1 Extraction
- 11.1.1 Extraction of filtrates -- extract the aqueous samples, blanks, and PAR aliquots according to the following procedures.
- 11.1.1.1 Pour filtered aqueous sample into a 2-L separatory funnel. Add 60 mL methylene chloride to the sample bottle, seal, and shake 60 seconds to rinse the inner surface.
- 11.1.1.2 Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 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, employ mechanical techniques to complete the phase separation (e.g. a glass stirring rod). Drain the methylene chloride extract into a 500-mL KD concentrator.
- 11.1.1.3 Extract the water sample two more times using 60 mL of fresh methylene chloride each time. Drain each extract into the KD concentrator. After the third extraction, rinse the separatory funnel with at least 30 mL of fresh methylene chloride.
- 11.1.2 Soxhlet/Dean-Stark extraction of solids -- Extract the solid samples, particulates, blanks, and PAR aliquots using the following procedure.
- 11.1.2.1 Charge a clean extraction thimble with 5.0 g of 100/200 mesh silica (Section 6.5.1.1) and 100 g of quartz sand (Section 6.5.4). NOTE: Do not disturb the silica layer throughout the extraction process.
- 11.1.2.2 Place the thimble in a clean extractor. Place 30 - 40 mL of toluene in the receiver and 200 - 250 mL in the flask.
- 11.1.2.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1 - 2 drops of toluene per second will fall from the condensor tip into the receiver. Extract the apparatus for 3 hours minimum.
- 11.1.2.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.
- 11.1.2.5 Load the wet sample from Section 10.4.6, 10.5.2, 10.6.3, or 10.6.4, and any non-aqueous liquid from Section 10.5.2 into the thimble and manually mix into the sand layer with a clean metal spatula carefully breaking up any large lumps of sample.
- 11.1.2.6 Reassemble the pre-extracted SDS apparatus and add a fresh charge of toluene to the receiver and reflux flask.
- 11.1.2.7 Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Check the apparatus for foaming frequently during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.
- 11.1.2.8 Drain the water from the receiver at 1 - 2 hours and 8 - 9 hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16 - 24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.
- 11.1.2.9 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the extract from the receiver and flask into a 500 mL separatory funnel. Rinse the receiver and flask with toluene and add to the separatory funnel. Proceed with back extraction per Section 11.1.3.
- 11.1.3 Back extraction with base and acid
- 11.1.3.1 Spike 1.0 mL of the cleanup standard (Section 6.11) into the separatory funnels containing the sample and QC extracts (Section 11.1.1.3 or 11.1.2.9).

- 11.1.3.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 6.1.1). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the PCDDs and PCDFs.
- 11.1.3.3 Partition the extract against 50 mL of sodium chloride solution (Section 6.1.3) in the same way as with base. Discard the aqueous layer.
- 11.1.3.4 Partition the extract against 50 mL of sulfuric acid (Section 6.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.
- 11.1.3.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.
- 11.1.3.6 Pour each extract through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the separatory funnel with 30 - 50 mL of toluene and pour through the drying column. Collect each extract in a 500 mL round bottom flask. Concentrate and clean up the samples and QC aliquots per Sections 11.2 and 12.
- 11.2 Concentration
- 11.2.1 Macro-concentration -- Concentrate the extracts in separate 500 mL round bottom flasks on a rotary evaporator.
- 11.2.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45 °C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for contamination check if necessary. Between samples, three 2 - 3 mL aliquots of toluene should be rinsed down the feed tube into a waste beaker.
- 11.2.1.2 Attach the round bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.
- 11.2.1.3 Lower the flask into the water bath and adjust the speed of rotation and the temperature as required to complete the concentration in 15 - 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur. NOTE: If the rate of concentration is too fast, analyte loss may occur.
- 11.2.1.4 When the liquid in the concentration flask has reached an apparent volume of 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully, admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of hexane.
- 11.2.1.5 Transfer the extract to a vial using three 2 - 3 mL rinses of hexane. Proceed with micro-concentration and solvent exchange.
- 11.2.1.6 The extracts of the filtered aqueous sample and its particulates must be combined prior to cleanup and analysis. Transfer the concentrated extract of the aqueous sample to the flask containing the concentrated particulate extract. Rinse the flask twice with 5 mL toluene, and add these rinses to the flask with the combined extracts. Reattach the flask to the rotary evaporator and continue to concentrate the combined extract until the volume is approximately 2 mL. Proceed with micro-concentration and solvent exchange.
- 11.2.2 Micro-concentration and solvent exchange
- 11.2.2.1 Toluene extracts to be subjected to GPC cleanup are exchanged into methylene chloride. Extracts that are to be cleaned up using silica gel, alumina, and/or AX-21/Celite are exchanged into hexane. Extracts to be subjected to HPLC are exchanged into nonane.
- 11.2.2.2 Transfer the vial containing the sample extract to a nitrogen evaporation device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. NOTE: A large vortex in the solvent may cause analyte loss.
- 11.2.2.3 Lower the vial into a 45 °C water bath and continue concentrating.

- 11.2.2.4 When the volume of the liquid is approximately 100  $\mu$ L, add 2 - 3 mL of the desired solvent (methylene chloride or hexane) and continue concentration to approximately 100  $\mu$ L. Repeat the addition of solvent and concentrate once more.
- 11.2.2.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. Proceed with GPC cleanup (Section 12.2).
- 11.2.2.6 If the extract is to be cleaned up by column chromatography (alumina, silica gel, AX-21/Celite), bring the final volume to 1.0 mL with hexane. Proceed with column cleanups (Sections 12.3 - 12.5).
- 11.2.2.7 For extracts to be concentrated for injection into the HPLC or GCMS -- add 10  $\mu$ L of nonane to the vial. Evaporate the solvent to the level of the nonane. Evaporate the hexane in the vial to the level of the nonane.
- 11.2.2.8 Seal the vial and label with the sample number. Store in the dark at room temperature until ready for HPLC or GCMS.

## 12 EXTRACT CLEANUP

- 12.1 Cleanup may not be necessary for relatively clean samples (e.g., 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. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 8.2 can be met using the cleanup procedure.
- 12.1.1 Gel permeation chromatography (Section 12.2) removes many high molecular weight interferences that cause GC column performance to degrade. It may be 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).
- 12.1.2 Acid, neutral, and basic silica gel, and alumina (Sections 12.3 and 12.4) are used to remove nonpolar and polar interferences.
- 12.1.3 AX-21/Celite (Section 12.5) is used to remove nonpolar interferences.

12.1.4 HPLC (Section 12.6) is used to provide specificity for the 2,3,7,8-substituted and other PCDD and PCDF isomers.

## 12.2 Gel permeation chromatography (GPC)

### 12.2.1 Column packing

12.2.1.1 Place 70 - 75 g of SX-3 Bio-beads in a 400 - 500 mL beaker.

12.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (12 hours minimum).

12.2.1.3 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.

12.2.1.4 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.

### 12.2.2 Column calibration

12.2.2.1 Load 5 mL of the calibration solution (Section 6.4) into the sample loop.

12.2.2.2 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.

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

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

12.2.2.5 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.

12.2.3 Extract cleanup -- GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5 mL

extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into aliquots for GPC and the aliquots are combined after elution from the column. The solids content of the extract may be obtained gravimetrically by evaporating the solvent from a 50 µL aliquot.

12.2.3.1 Filter the extract or load through the filter holder to remove particulates. Load the 5.0 mL extract onto the column.

12.2.3.2 Elute the extract using the calibration data determined in Section 12.2.2. Collect the eluate in a clean 400 - 500 mL beaker.

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

12.2.3.4 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.

12.2.3.5 Concentrate the eluate per Section 11.2.1, 11.2.2, and 11.3.1 or 11.3.2 for further cleanup or for injection into the GCMS.

### 12.3 Silica gel cleanup

12.3.1 Place a glass wool plug in a 15 mm i.d. chromatography column. Pack the column in the following order (bottom to top): 1 g silica gel (Section 6.5.1.1), four g basic silica gel (Section 6.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 6.5.1.2), 2 g silica gel, 1 g sodium sulfate (Section 6.2.1). Tap the column to settle the adsorbents.

12.3.2 Pre-rinse the column with 50 - 100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

12.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

12.3.4 Rinse the receiver twice with 1 mL portions of hexane and apply separately to the column. Elute the PCDDs/PCDFs with 100 mL hexane and collect the eluate.

12.3.5 Concentrate the eluate per Section 11.2.1 or 11.2.2 for further cleanup or for injection into the HPLC or GCMS.

### 12.4 Alumina cleanup

12.4.1 Place a glass wool plug in a 15 mm i.d. chromatography column.

12.4.2 Pack the column in the following order (bottom to top): 1 g neutral alumina (Section 6.5.2.1), 3 g basic alumina (Section 6.5.2.2), 1 g neutral alumina, 6 g acid alumina (Section 6.5.2.3), 2 g neutral alumina, 1 g sodium sulfate (Section 6.2.1). Tap the column to settle the adsorbents.

12.4.3 Pre-rinse the column with 50 - 100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate.

12.4.4 Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

12.4.5 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

12.4.6 Rinse the receiver twice with 1 mL portions of hexane and apply separately to the column. Elute the interfering compounds with 100 mL hexane and discard the eluate.

12.4.7 Elute the PCDDs and PCDFs with 20 mL of methylene chloride:hexane (1:1 v/v).

12.4.8 Concentrate the eluate per Section 11.2.1 or 11.2.2 for further cleanup or for injection into the HPLC or GCMS.

### 12.5 AX-21/Celite

12.5.1 Cut both ends from a 10 mL disposable serological pipet to produce a 10 cm column. Fire polish both ends and flare both ends if desired. Insert a glass wool plug at one end, then pack the column with 1 g of the activated AX-21/Celite to form a 2 cm long adsorbent bed. Insert a glass wool plug on top of the bed to hold the adsorbent in place.

12.5.2 Pre-rinse the column with five mL of toluene followed by 2 mL methylene chloride:methanol:toluene (15:4:1 v/v), 1 mL methylene chloride:cyclohexane (1:1

- v/v), and five mL hexane. If the flow rate of eluate exceeds 0.5 mL per min, discard the column.
- 12.5.3 When the solvent is within 1 mm of the column packing, apply the sample extract to the column. Rinse the sample container twice with 1 mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.
- 12.5.4 Elute the interfering compounds with 2 mL of hexane, 2 mL of methylene chloride:cyclohexane (1:1 v/v), and 2 mL of methylene chloride:methanol:toluene (15:4:1 v/v). Discard the eluate.
- 12.5.5 Invert the column and elute the PCDDs and PCDFs with 20 mL of toluene. If carbon particles are present in the eluate, filter through glass fiber filter paper.
- 12.5.6 Concentrate the eluate per Section 11.2.1 or 11.2.2 for further cleanup or for injection into the HPLC or GCMS.
- 12.6 HPLC (Reference 6)
- 12.6.1 Column calibration
- 12.6.1.1 Prepare a calibration standard containing the 2,3,7,8- isomers and/or other isomers of interest at a concentration of approximately 500 pg/uL in chloroform.
- 12.6.1.2 Inject 30 uL of the calibration solution into the HPLC and record the signal from the detector. Collect the eluant for re-use. The elution order will be the tetra-through octa-isomers.
- 12.6.1.3 Establish the collect time for the tetra-isomers and for the other isomers of interest. Following calibration, flush the injection system with copious quantities of chloroform, including a minimum of five 50-uL injections while the detector is monitored, to ensure that residual PCDDs and PCDFs are removed from the system.
- 12.6.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the PCDDs and PCDFs from the calibration standard (Section 12.6.1.1) is 75 - 125 percent compared to the calibration (Section 12.6.1.2). 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 system.
- 12.6.2 Extract cleanup -- HPLC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 30 uL of extract. If the extract cannot be concentrated to less than 30 uL, it is split into fractions and the fractions are combined after elution from the column.
- 12.6.2.1 Rinse the sides of the vial twice with 30 uL of chloroform and reduce to the level of the nonane with the blowdown apparatus. Rinse the sides of the vial with 20 uL of chloroform to bring the extract volume to 30 uL.
- 12.6.2.2 Inject the 30 uL extract into the HPLC.
- 12.6.2.3 Elute the extract using the calibration data determined in 12.6.1. Collect the fraction(s) in a clean 20 mL concentrator tube containing 5 mL of hexane:acetone (1:1 v/v).
- 12.6.2.4 If an extract containing greater than 100 ng/mL of total PCDD or PCDF is encountered, a 30 uL chloroform blank shall be run through the system to check for carry-over.
- 12.6.2.5 Concentrate the eluate per Section 11.2.2 for injection into the GCMS.
- 13 HRGC/HRMS ANALYSIS
- 13.1 Establish the operating conditions given in Section 7.1.
- 13.2 Add 10 uL of the internal standard solution (Section 6.12) to the sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume (e.g., 19 uL) with pure nonane only.
- 13.3 Inject 1.0 uL of the concentrated extract containing the internal standard solution, using on-column or splitless injection. Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the octachloro-

dioxin and furan have eluted. Return the column to the initial temperature for analysis of the next extract or standard.

#### 14 SYSTEM AND LABORATORY PERFORMANCE

14.1 At the beginning of each 12-hour shift during which analyses are performed, GCMS system performance and calibration are verified for all native and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 6.13 and Table 4) and the isomer specificity test standards (Sections 6.16 and Table 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 Mass spectrometer resolution -- A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour shift. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

14.2.1 The analysis time for PCDDs and PCDFs may exceed 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 instrument performance. Therefore, a mass-drift correction is mandatory. A lock-mass ion from the reference compound (PFK) is used for tuning the mass spectrometer. The lock-mass ion is dependent on the masses of the ions monitored within each descriptor, as shown in Table 3. 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 time lost in cleaning the source.

14.2.2 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 PFK reference peak, verify that the exact mass of  $m/z$  380.9760 (PFK) is within 5 ppm of the required value.

#### 14.3 Calibration verification

14.3.1 Inject the VER standard using the procedure in Section 13.

14.3.2 The  $m/z$  abundance ratios for all PCDDs and PCDFs shall be within the limits in Table 3A; otherwise, the mass spectrometer shall be adjusted until the  $m/z$  abundance ratios fall within the limits specified, and the verification test (Section 14.3.1) repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 14.2) prior to repeat of the verification test.

14.3.3 Compute the concentration of each native compound by isotope dilution (Section 7.5) for those compounds that have labeled analogs (Table 1). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the averaged relative response and averaged response factor from the calibration data in Section 7.

14.3.4 For each compound, compare the concentration with the calibration verification limit in Table 7. If all compounds meet the acceptance criteria, calibration has been verified. 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 resolution (Section 14.2) and verification (Section 14.3.1) tests, or recalibrate (Section 7).

#### 14.4 Retention times and GC resolution

14.4.1 Retention times



- 14.4.1.1 Absolute -- The absolute retention times of the  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD GCMS internal standards shall be within  $\pm 15$  seconds of the retention times obtained during calibration (Section 7.2.4).
- 14.4.1.2 Relative -- The relative retention times of native and labeled PCDDs and PCDFs shall be within the limits given in Table 2.
- 14.4.2 GC resolution
- 14.4.2.1 Inject the isomer specificity standards (Section 6.16) on their respective columns.
- 14.4.2.2 The valley height between 2,3,7,8-TCDD and the other tetra- dioxin isomers at m/z 319.8965, and between 2,3,7,8-TCDF and the other tetra- furan isomers at m/z 303.9016 shall not exceed 25 percent on their respective columns (Figure 3).
- 14.4.3 If the absolute or relative retention time of any compound is not within the limits specified or the 2,3,7,8- isomers are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 14.3.1) or recalibrate (Section 7).
- 14.5 Ongoing precision and accuracy
- 14.5.1 Analyze the extract of the precision and recovery standard (PAR) (Section 10.3.4 or 10.4.4) prior to analysis of samples from the same set.
- 14.5.2 Compute the concentration of each PCDD or PCDF by isotope dilution (Section 7.5) for those compounds that have labeled analogs. Compute the concentration of the labeled compounds by the internal standard method.
- 14.5.3 For each compound, compare the concentration with the limits for ongoing accuracy in Table 7. 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, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-extract the sample set (Section 10) and repeat the ongoing precision and recovery test (Section 14.5).
- 14.5.4 Add results which pass the specifications in Section 14.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each PCDD and PCDF in each matrix type 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
- Identification is accomplished by comparison of data from analysis of a sample or blank with data for authentic standards. For compounds for which the relative retention times are known, identification is confirmed per Sections 15.1 and 15.2.
- 15.1 Labeled compounds and native PCDDs and PCDFs having no labeled analog
- 15.1.1 The signals for the exact m/z's being monitored (Table 3A) shall be present and shall maximize within the same two consecutive scans.
- 15.1.2 Either (1) the ratio of the background corrected exact SICP areas, or (2) the corrected relative intensities of the exact m/z's at the GC peak maximum shall be within the limits in Table 3A.
- 15.1.3 For the individual labeled compounds and individual PCDDs and PCDFs, the relative retention time shall be within the limits specified in Table 2.
- 15.2 PCDDs and PCDFs having a labeled analog
- 15.2.1 The signals for the exact m/z's being monitored (Table 3) shall be present and shall maximize within the same two consecutive scans.
- 15.2.2 The ratio of the ion abundances of the exact m/z's at the GC peak maximum shall agree within the limits in Table 3.

15.2.3 The relative retention time between the native compound and its labeled analog shall be within the windows specified in Table 2.

15.3 If identification is ambiguous, an experienced spectrometrists (Section 1.5) is to determine the presence or absence of the compound.

## 16 QUANTITATIVE DETERMINATION

16.1 Isotope dilution -- By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the native compound can be made because the native compound 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 data described in Section 7.5 to determine concentrations directly, so long as labeled compound spiking levels are constant.

16.1.1 Because of a potential interference, the labeled analog of OCDF is not added to the sample. Therefore, this native analyte is quantitated against the labeled OCDD.

16.1.2 Because the labeled analog of 1,2,3,7,8,9-HxCDD is used as an internal standard (i.e., not added before extraction of the sample), it cannot be used to quantitate the native compound. Therefore, the native 1,2,3,7,8,9-HxCDD is quantitated using the average of the responses of the labeled analogs of the other two 2,3,7,8-substituted HxCDD's, 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD.

16.1.3 Any peaks representing non-2,3,7,8-substituted dioxins or furans are quantitated using an average of the response factors from all the labeled 2,3,7,8- isomers in the same level of chlorination.

16.2 Internal standard -- Compute the concentrations of the labeled analogs and the cleanup standard in the extract using the response factors determined from calibration data (Section 7.6) and the following equation:

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

where  $C_{ex}$  is the concentration of the compound in the extract and the other terms are as defined in Section 7.6.1.

16.3 The concentration of the native compound in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 10), as follows:

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

where,

$V_{ex}$  is the extract volume in mL.

$W_s$  is the sample weight in Kg.

16.4 If the SICP area at the quantitation m/z for any compound exceeds the calibration range of the system, a smaller sample aliquot is extracted.

16.4.1 For aqueous samples containing one percent solids or less, dilute 100 mL, 10 mL, etc., of sample to 1 liter with reagent water and extract per Section 11.

16.4.2 For samples containing greater than one percent solids, extract an amount of sample equal to 1/10, 1/100, etc of the amount determined in 10.1.3. Extract per Section 10.4.

16.4.3 If a smaller sample size will not be representative of the entire sample, dilute the sample extract by a factor of 10, adjust the concentration of the instrument internal standard to 100 pg/uL in the extract, and analyze an aliquot of this diluted extract by the internal standard method.

16.5 Results are reported to three significant figures for the native and labeled isomers found in all standards, blanks, and samples. For aqueous samples, the units are ng/L; for samples containing one percent or greater solids (soils, sediments, filter, cake, compost), the units are ng/kg, based on the dry weight of the sample.

16.5.1 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 16.4).

16.5.2 For native 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 16.4) and the labeled compound recovery is within the normal range for the method (Section 17.4).

16.5.3 Additionally, the total concentrations of all isomers in an individual level of chlorination (i.e. total TCDD, total PeCDD, etc.) are reported to three significant figures in units of ng/L, for both dioxins and furans. The total or ng/kg concentration in each level of chlorination is the sum of the concentrations of all isomers identified in that level, including any non-2,3,7,8-substituted isomers.

#### 17 ANALYSIS OF COMPLEX SAMPLES

17.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts will not concentrate to 10 uL (Section 11); others may overload the GC column and/or mass spectrometer.

17.2 Analyze a smaller aliquot of the sample (Section 16.4) when the extract will not concentrate to 20 uL after all cleanup procedures have been exhausted.

17.3 Interferences at the primary m/z -- If an interference occurs at the primary quantitation m/z (Table 3) for any native or labeled compound, the alternate m/z is used for quantitation.

17.4 Recovery of labeled compound spiking standards -- In most samples, recoveries of the labeled compound spiking standards will be similar to those from reagent water or from the alternate matrix (Section 6.6). If recovery is outside of the limits given in Table 7, a diluted sample (Section 16.4) is analyzed. If the recoveries of the labeled compound spiking standards in the diluted sample are outside of the limits (per the criteria above), then the verification standard (Section 14.3) shall be analyzed and calibration verified (Section 14.3.4). If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed. If the calibration is verified and the diluted sample does not meet the limits

for labeled compound recovery, then the method does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes.

#### 18 METHOD PERFORMANCE

EPA is in the process of developing performance data for this draft method. When these tests are complete, the specifications in this method will be modified based on these data, and the supporting documents will be referenced in this section.

#### REFERENCES

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- 10 "Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206, (Aug 1977).
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- 17 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, Philadelphia, PA, 76 (1980).
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Table 1  
POLYCHLORINATED DIBENZODIOXINS AND FURANS DETERMINED BY ISOTOPE DILUTION AND INTERNAL STANDARD  
HIGH RESOLUTION GAS CHROMATOGRAPHY (HRGC)/HIGH RESOLUTION MASS SPECTROMETRY (HRMS)

PCDDs/PCDFs (1) Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD	76523-40-5
		$^{37}\text{Cl}_4$ -2,3,7,8-TCDD	85508-50-5
Total-TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}\text{C}_{12}$ -2,3,7,8-TCDF	89059-46-1
Total-TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD	109719-79-1
Total-PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF	116843-02-8
Total-PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD(2)	109719-82-6
Total-HxCDD	34465-4608		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}\text{C}_{12}$ -2,3,4,6,7,8-HxCDF	116843-05-1
Total-HxCDF			
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD	109719-83-7
Total-HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF	109719-94-0
Total-HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}\text{C}_{12}$ -OCDD	114423-97-1
OCDF	39001-02-0		

(1) Polychlorinated dioxins and furans

TCDD = Tetrachlorodibenzo-p-dioxin  
 PeCDD = Pentachlorodibenzo-p-dioxin  
 HxCDD = Hexachlorodibenzo-p-dioxin  
 HpCDD = Heptachlorodibenzo-p-dioxin  
 OCDD = Octachlorodibenzo-p-dioxin

TCDF = Tetrachlorodibenzofuran  
 PeCDF = Pentachlorodibenzofuran  
 HxCDF = Hexachlorodibenzofuran  
 HpCDF = Heptachlorodibenzofuran  
 OCDF = Octachlorodibenzofuran

(2) Labeled analog is used as an internal standard and therefore cannot be used for quantitation by isotope dilution.

Table 2  
RETENTION TIMES AND MINIMUM LEVELS FOR PCDDs AND PCDFs

Compound	Absolute	Retention Time Reference	Relative Retention Time (1)	Minimum Level (2)		
	Retention Time (Minutes)			Water pg/L ppq	Solid ng/kg ppt	Extract pg/uL ppb
Compounds using <sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD as internal standard						
Native Compounds						
2,3,7,8-TCDF	26.35	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	0.999 - 1.001	10	1	0.5
2,3,7,8-TCDD	27.24	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	0.999 - 1.001	10	1	0.5
1,2,3,7,8-PeCDF	31.16	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	0.999 - 1.001	50	5	2.5
2,3,4,7,8-PeCDF	32.16	<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	0.999 - 1.001	50	5	2.5
1,2,3,7,8-PeCDD	32.45	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	0.999 - 1.001	50	5	2.5
Labeled Compounds						
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	26.35	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	0.970 - 0.980			
<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	27.03	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	1.000 - 1.000			
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	27.22	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	1.002 - 1.012			
<sup>37</sup> Cl <sub>4</sub> -2,3,7,8-TCDD	27.23	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	1.002 - 1.013			
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	31.16	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDF	1.147 - 1.159			
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	32.15	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	1.183 - 1.196			
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	32.44	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	1.194 - 1.206			
Compounds using <sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD as internal standard						
Native Compounds						
1,2,3,4,7,8-HxCDF	36.19	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	0.999 - 1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	36.29	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	0.999 - 1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	37.19	<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-HxCDF	0.999 - 1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	37.30	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	0.999 - 1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	37.36	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	0.999 - 1.001	50	5	2.5
1,2,3,7,8,9-HxCDD	38.07	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	0.999 - 1.001	50	5	2.5
1,2,3,7,8,9-HxCDF	38.23	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	0.999 - 1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDF	40.55	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	0.999 - 1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	42.27	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	0.999 - 1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	43.01	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	0.999 - 1.001	50	5	2.5
OCDD	46.56	<sup>13</sup> C <sub>12</sub> -OCDD	0.999 - 1.001	100	10	5.0
OCDF	47.05	<sup>13</sup> C <sub>12</sub> -OCDD	1.007 - 1.013	100	10	5.0
Labeled Compounds						
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	36.18	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	0.946 - 0.956			
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	36.27	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	0.948 - 0.958			
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	37.29	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	0.975 - 0.985			
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	37.38	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	0.977 - 0.987			
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	38.06	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.000 - 1.000			
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	38.23	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	0.999 - 1.010			
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	40.54	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.060 - 1.071			
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	42.27	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.105 - 1.116			
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	43.01	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.124 - 1.136			
<sup>13</sup> C <sub>12</sub> -OCDD	46.55	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.217 - 1.230			
<sup>13</sup> C <sub>12</sub> -OCDF	47.04	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	1.229 - 1.242			

- (1) Initial specifications are estimated based on isotope dilution and internal standard data from Method 1625. These specifications may be revised when further data have been collected by EPA using Method 1613.
- (2) Level at which the analytical system will give acceptable SICP and calibration.

Table 3  
DESCRIPTORS, MASSES, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs (1)

Descriptor Number	Accurate m/z (2)	m/z Type	Elemental Composition	Compound (3)	Primary m/z?
1	292.9825	Lock	C <sub>7</sub> F <sub>11</sub>	PFK	
	303.9016	M	C <sub>12</sub> H <sub>4</sub> <sup>37</sup> Cl <sub>4</sub> O	TCDF	Yes
	305.8987	M+2	C <sub>12</sub> H <sub>4</sub> <sup>37</sup> Cl <sub>4</sub> O	TCDF	
	315.9419	M	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O	TCDF(4)	Yes
	317.9389	M+2	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl O	TCDF(4)	
	319.8965	M	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O <sub>2</sub>	TCDD	Yes
	321.8936	M+2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl O <sub>2</sub>	TCDD	
	327.8847	M	C <sub>12</sub> H <sub>4</sub> <sup>37</sup> Cl <sub>4</sub> O <sub>2</sub>	TCDD(4)	
	330.9792	QC	C <sub>7</sub> F <sub>13</sub>	PFK	
	331.9368	M	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O <sub>2</sub>	TCDD(4)	Yes
	333.9339	M+2	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl O <sub>2</sub>	TCDD(4)	
	375.8364	M+2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl O	HxCDFE	
2	339.8597	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl O	PeCDF	Yes
	341.8567	M+4	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF	
	351.9000	M+2	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl O	PeCDF(4)	Yes
	353.8970	M+4	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF(4)	
	354.9792	Lock	C <sub>9</sub> F <sub>13</sub>	PFK	
	355.8546	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl O <sub>2</sub>	PeCDD	Yes
	357.8516	M+4	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	PeCDD	
	367.8949	M+2	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl O <sub>2</sub>	PeCDD(4)	Yes
	369.8919	M+4	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	PeCDD(4)	
	409.7974	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl O	HpCDPE	
3	373.8208	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl O	HxCDF	Yes
	375.8178	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDF	
	383.8639	M	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> O	HxCDF(4)	Yes
	385.8610	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl O	HxCDF(4)	
	389.8157	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl O <sub>2</sub>	HxCDD	Yes
	391.8127	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HxCDD	
	392.9760	Lock	C <sub>9</sub> F <sub>15</sub>	PFK	
	401.8559	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl O <sub>2</sub>	HxCDD(4)	Yes
	403.8529	M+4	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HxCDD(4)	
	430.9729	QC	C <sub>9</sub> F <sub>13</sub>	PFK	
	445.7555	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDFE	

Table 3 (continued)  
DESCRIPTORS, MASSES, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs (1)

Descriptor Number	Accurate m/z (2)	m/z Type	Elemental Composition	Compound (3)	Primary m/z?
4	407.7818	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl O	HpCDF	Yes
	409.7789	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O	HpCDF	
	417.8253	M	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> O	HpCDF(4)	Yes
	419.8220	M+2	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl O	HpCDF(4)	
	423.7766	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl O <sub>2</sub>	HpCDD	Yes
	425.7737	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD	
	430.9729	Lock	C <sub>9</sub> F <sub>17</sub>	PFK	
	435.8169	M+2	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl O <sub>2</sub>	HpCDD(4)	Yes
	437.8140	M+4	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD(4)	
	479.7165	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> O	NCDPE	
5	441.7428	M+2	C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl O	OCDF	Yes
	442.9728	Lock	C <sub>10</sub> F <sub>17</sub>	PFK	
	443.7399	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDF	
	457.7377	M+2	C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl O <sub>2</sub>	OCDD	Yes
	459.7348	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	OCDD	
	469.7779	M+2	<sup>13</sup> C <sub>12</sub> <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl O <sub>2</sub>	OCDD(4)	Yes
	471.7750	M+4	<sup>13</sup> C <sub>12</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	OCDD(4)	
	513.6775	M+4	C <sub>12</sub> <sup>35</sup> Cl <sub>8</sub> <sup>37</sup> Cl <sub>2</sub> O	DCDPE	

(1) From Reference 5

(2) Nuclidic masses used:

H = 1.007825      C = 12.00000      <sup>13</sup>C = 13.003355      F = 18.9984  
O = 15.994915      <sup>35</sup>Cl = 34.968853      <sup>37</sup>Cl = 36.965903

(3) Compound abbreviations:

Chlorinated dibenzo-p-dioxins

TCDD = Tetrachlorodibenzo-p-dioxin  
PeCDD = Pentachlorodibenzo-p-dioxin  
HxCDD = Hexachlorodibenzo-p-dioxin  
HpCDD = Heptachlorodibenzo-p-dioxin  
OCDD = Octachlorodibenzo-p-dioxin

Chlorinated diphenyl ethers

HxCDE = Hexachlorodiphenyl ether  
HpCDE = Heptachlorodiphenyl ether  
OCDE = Octachlorodiphenyl ether  
NCDPE = Nonachlorodiphenyl ether  
DCDPE = Decachlorodiphenyl ether

Chlorinated dibenzofurans

TCDF = Tetrachlorodibenzofuran  
PeCDF = Pentachlorodibenzofuran  
HxCDF = Hexachlorodibenzofuran  
HpCDF = Heptachlorodibenzofuran

Lock mass and QC compound

PFK = Perfluorokerosene

(4) Labeled compound



Table 3A  
THEORETICAL M/Z RATIOS AND CONTROL LIMITS

No. of Chlorine Atoms	m/z's Forming Ratio	Theoretical Ratio	Control Limits(1)	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 (2)	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.05	0.88	1.20
7 (3)	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

(1) Represent  $\pm 15\%$  windows around the theoretical ion abundance ratios.

(2) Used for  $^{13}\text{C}$ -HxCDF only.

(3) Used for  $^{13}\text{C}$ -HpCDF only.

Table 4  
CONCENTRATIONS OF SOLUTIONS CONTAINING LABELED AND UNLABELED CDDs AND CDFs

Compound	Stock Solution (1) ng/mL	Spike Solutions (2) ng/mL	Calibration and Verification Solutions					
			CS1	CS2	ng/mL			PAR(4) ng/mL
					VER(3) CS3	CS4	CS5	
Native CDDs and CDFs								
2,3,7,8-TCDD	-	-	0.5	2	10	40	200	40
2,3,7,8-TCDF	-	-	0.5	2	10	40	200	40
1,2,3,7,8-PeCDD	-	-	2.5	10	50	200	1000	200
1,2,3,7,8-PeCDF	-	-	2.5	10	50	200	1000	200
2,3,4,7,8-PeCDF	-	-	2.5	10	50	200	1000	200
1,2,3,4,7,8-HxCDD	-	-	2.5	10	50	200	1000	200
1,2,3,6,7,8-HxCDD	-	-	2.5	10	50	200	1000	200
1,2,3,7,8,9-HxCDD	-	-	2.5	10	50	200	1000	200
1,2,3,4,7,8-HxCDF	-	-	2.5	10	50	200	1000	200
1,2,3,6,7,8-HxCDF	-	-	2.5	10	50	200	1000	200
1,2,3,7,8,9-HxCDF	-	-	2.5	10	50	200	1000	200
2,3,4,6,7,8-HxCDF	-	-	2.5	10	50	200	1000	200
1,2,3,4,6,7,8-HpCDD	-	-	2.5	10	50	200	1000	200
1,2,3,4,6,7,8-HpCDF	-	-	2.5	10	50	200	1000	200
1,2,3,4,7,8,9-HpCDF	-	-	2.5	10	50	200	1000	200
OCDD	-	-	5.0	20	100	400	2000	400
OCDF	-	-	5.0	20	100	400	2000	400
Labeled Compound Spiking Standards								
<sup>13</sup> C <sup>12</sup> -2,3,7,8-TCDD	100	2	100	100	100	100	100	-
<sup>13</sup> C <sup>12</sup> -2,3,7,8-TCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-HxCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	100	2	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -OCDD	200	4	200	200	200	200	200	-
Cleanup Standard								
<sup>37</sup> Cl <sub>4</sub> -2,3,7,8-TCDD	-	0.8	0.5	2	10	40	200	-
Internal Standards								
<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	-	200	100	100	100	100	100	-
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	-	200	100	100	100	100	100	-

- (1) Stock solution (Section 6.10) - Prepared in nonane, and diluted daily with acetone to prepare the spiking solution (Section 10.3.2).
- (2) Spiking solutions (Sections 6.11, 6.12, 8.3, 10.3.2, and 10.4.2).
- (3) Calibration verification solution (Section 14.3).
- (4) Precision and recovery standard (Section 6.14) - Prepared in nonane, and diluted daily with acetone to prepare the spiking solution (Section 10.3.4).

Table 5

GC RETENTION TIME WINDOW DEFINING MIXTURES AND ISOMER  
SPECIFICITY TEST MIXTURESDB-5 Column GC Retention Time Window Defining Standard  
(Section 6.15)

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 TCDD Isomer Specificity Test Standard  
(Section 6.16.1)

1,2,3,4-TCDD	1,2,3,7-TCDD
1,2,7,8-TCDD	1,2,3,8-TCDD
1,4,7,8-TCDD	2,3,7,8-TCDD

DB-225 Column TCDF Isomer Specificity Test Standard  
(Section 6.16.2)

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 6  
REFERENCE COMPOUNDS FOR NATIVE AND LABELED PCDDs AND PCDFs

Native PCDDs and PCDFs	Reference Compound	Labeled PCDDs and PCDFs	Reference Compound
2,3,7,8-TCDD	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD
2,3,7,8-TCDF	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD
1,2,3,7,8-PeCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD
1,2,3,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD
2,3,4,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD
1,2,3,4,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,6,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,7,8,9-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,4,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,7,8,9-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
2,3,4,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-HxCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
1,2,3,4,7,8,9-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
OCDD	<sup>13</sup> C <sub>12</sub> -OCDD	<sup>13</sup> C <sub>12</sub> -OCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD
OCDF	<sup>13</sup> C <sub>12</sub> -OCDD	<sup>37</sup> Cl <sub>4</sub> -2,3,7,8-TCDD	<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD

Table 7  
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS (1)

Compound	Test Concen- tration (ng/mL)	Initial Precision and Accuracy <u>Sec 8.2.3</u> s                      X		Labeled Compound Recovery Sec 8.3 <u>and 16.2</u> P (%)	Calibration Verification <u>Sec 14.5</u> (ug/mL)	Ongoing Accuracy <u>Sec 14.6</u> R (%)
PCDDs/PCDFs by internal standard						
<sup>13</sup> C-tetra-hepta CDD and CDF	100	32	60 - 145	25 - 150	65 - 140	55 - 150
<sup>37</sup> Cl-tetra CDD	40	13	24 - 58	25 - 150	26 - 56	22 - 60
<sup>13</sup> C-octa CDD	200	64	120 - 290	25 - 150	130 - 280	110 - 300
PCDDs/PCDFs by isotope dilution						
tetra CDD and CDF	40	9	30 - 52	25 - 150	30 - 52	28 - 56
penta - hepta CDD and CDF	200	45	150 - 260	25 - 150	150 - 260	140 - 280
octa CDD and CDF	400	90	300 - 520	25 - 150	300 - 520	280 - 560

(1) Based on data from Method 1625.

Table 8  
SAMPLE PHASE AND QUANTITY EXTRACTED FOR VARIOUS MATRICES

Sample Matrix (1)	Example	Percent Solids	Phase	Quantity Extracted
<b>SINGLE PHASE</b>				
Aqueous	Drinking water Groundwater Treated wastewater	<1	(2)	1000 mL
Solid	Dry soil Compost Ash	>20	Solid	10 g
Organic	Waste solvent Waste oil Organic polymer	<1	Organic	10 g
<b>MULTIPHASE</b>				
Liquid/Solid				
Aqueous/solid	Wet soil Untreated effluent Digested municipal sludge Filter cake Paper pulp Tissue	1-30	Solid	10 g
Organic/solid	Industrial sludge Oily waste	1-100	Both	10 g
Liquid/Liquid				
Aqueous/organic	In-process effluent Untreated effluent Drum waste	<1	Organic	10 g
Aqueous/organic/ solid	Untreated effluent Drum waste	>1	Organic & solid	10 g

- (1) The exact matrix may be vague for some samples. In general, when the CDDs and CDFs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase, because of their low solubility in water.
- (2) Aqueous samples are filtered after spiking with labeled analogs. The filtrate and the material trapped on the filter are extracted separately, and then the extracts are combined for analysis.



**EPA METHOD 1620**

**METALS BY INDUCTIVELY COUPLED  
PLASMA ATOMIC EMISSION SPECTROSCOPY  
AND ATOMIC ABSORPTION SPECTROSCOPY**





## Introduction

Method 1620 was developed by the Industrial Technology Division (ITD) within the United States Environmental Protection Agency's (USEPA) Office of Water Regulations and Standards (OWRS) 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.

Method 1620 includes inductively coupled plasma atomic emission (ICP) spectroscopy, graphite furnace atomic absorption (GFAA) spectroscopy, and cold vapor atomic absorption (CVAA) spectroscopy techniques for analysis of 27 specified metals. The method also includes an ICP technique for use as a semiquantitative screen for 42 specified elements.

Questions concerning the method or its application should be addressed to:

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

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Alexandria, Virginia 22313  
703/557-5040

Publication date: September 1989 DRAFT



## Metals by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption Spectroscopy

### 1 SCOPE AND APPLICATION

- 1.1 This method is designed to meet the survey requirements of the USEPA ITD. It is used to determine specified elements associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); and the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); and other elements amenable to analysis by inductively coupled plasma (ICP) atomic emission spectroscopy, graphite furnace atomic absorption (GFAA) spectroscopy, and cold vapor atomic absorption (CVAA) spectroscopy.
- 1.2 The method is a consolidation of USEPA Methods 200.7 (ICP for trace elements), 204.2 (Sb), 206.2 (As), 239.2 (Pb), 270.2 (Se), 279.2 (Tl), 245.5 (Hg), 245.1 (Hg), and 245.2 (Hg). The method is used for analysis of trace elements by ICP atomic emission spectroscopy and GFAA spectroscopy, for analysis of mercury by CVAA spectroscopy, and as a semi-quantitative ICP screen for specified elements.
- 1.3 The elements listed in Tables 1, 2 and 4 may be determined in waters, soils, sediments, and sludges by this method.
- 1.4 The recommended wavelengths and instrument detection limits of this method are shown in Tables 1-2. Actual sample detection limits are dependent on the sample matrix rather than instrumental limitations. The levels given typify the minimum quantities that can be detected with no interferences present. Table 2 also lists the optimum concentration range.
- 1.5 Table 4 lists the wavelengths and lower threshold limits (LTL) for the 42 elements for semiquantitative ICP screen.
- 1.6 The ICP and AA portions of this method are for use only by analysts experienced with the instrumentation or under the close supervision of such qualified persons. 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 ICP-Atomic Emission Spectrometric Method for Analysis of Water and Soil/Sediment Samples
  - 2.1.1 The method describes a technique for the simultaneous or sequential multi-element 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.
  - 2.1.2 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 during sample 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 Section 3.1.1 (and tests for their presence as described in Section 3.1.2) should also be recognized and appropriate corrections made.
  - 2.1.3 Dissolved elements (those which will pass through a 0.45  $\mu$ m membrane filter) are determined in samples that have been filtered and acidified. Appropriate steps

must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 3.1.)

- 2.1.4 Total elements (total concentration in an unfiltered sample) 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 the effects of potential interferences. (See Section 3.1.)
- 2.1.5 Table 1 lists elements that may be analyzed by this method 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. Instruments with ultrasonic nebulization may be able to achieve lower instrumental detection limits.
- 2.1.6 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.
- 2.1.7 The semiquantitative screening procedure requires a sequential ICP instrument (2 channel minimum) interfaced with a computerized data system capable of the short sampling times and the narrow survey windows necessary to perform a semiquantitative ICP screen.
- 2.1.7.1 Table 4 lists the wavelengths to be used in the semiquantitative ICP screen for each analyte, and the lower threshold limits (LTL). The LTL for each analyte is highly dependent upon sample matrix and subject to change on a sample-by-sample basis.
- 2.1.8 Sludge samples having less than 1% solids are treated as water samples. Those having between 1% to 30% solids should be diluted to less than 1% solids, and then treated as water samples. Sludge samples having greater than 30% solids should be treated as soil samples.

## 2.2 GFAA Spectroscopy for Analysis of Water and Soil/Sediment Samples

- 2.2.1 This method describes a technique for multi-element determination of trace elements in solution. A few microliters of the sample are first evaporated at a low temperature (sufficient heat to remove the solvent from the sample) and then ashed at a higher temperature on an electrically heated surface of carbon, tantalum, or other conducting material. The conductor can be formed as a hollow tube, a strip, a rod, a boat, or a trough. After ashing, the current is rapidly increased to several hundred amperes, which causes the temperature to rise to 2000-3000 °C; atomization of the sample occurs in a period of a few milliseconds to seconds. The absorption or fluorescence of the atomized particles can then be measured in the region above the heated conductor. At the wavelength at which absorbance (or fluorescence) occurs, the detector output rises to a maximum after a few seconds of ignition, followed by a rapid decay back to zero as the atomization products escape into the surroundings. The change is rapid enough to require a high speed recorder.
- 2.2.2 The matrix interference problem is one of the major causes of poor accuracy encountered with this method. It has been found empirically that some of the sample matrix effects and poor reproducibility associated with graphite furnace atomization can be alleviated by reducing the natural porosity of the graphite tube. A background correction technique is required to compensate for variable background contribution to the determination of trace elements.
- 2.2.3 Table 2 lists elements that may be analyzed by GFAA along with recommended wavelengths, estimated instrumental detection limits, and optimum concentration range. Table 3 lists recommended instrumental operating parameters.
- 2.2.4 For treatment of sludge samples, see Section 2.1.8.
- 2.3 Cold Vapor AA (CVAA) Techniques for Analysis of Mercury

- 2.3.1 Manual CVAA Technique for Analysis of Mercury in Water Samples
- 2.3.1.1 The flameless AA procedure is a method based on the absorption of radiation at 253.7 nm by mercury vapor. Mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.
- 2.3.1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heating step is required for methyl mercuric chloride when present in or spiked into a natural system. The heating step is not necessary for distilled water.
- 2.3.1.3 The working range of the method may be varied through instrument and/or recorder expansion. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved (see Section 7.2.3).
- 2.3.1.4 For treatment of sludge samples, see Section 2.1.8.
- 2.3.2 Automated CVAA Technique for Analysis of Mercury in Water Samples
- 2.3.2.1 See Section 2.3.1.1.
- 2.3.2.2 See Section 2.3.1.2.
- 2.3.2.3 The working range of the method is 0.2 to 20.0 ug Hg/L.
- 2.3.2.4 For treatment of sludge samples, see Section 2.1.8.
- 2.3.3 Manual CVAA Technique for Analysis of Mercury in Soil/Sediment Samples
- 2.3.3.1 A weighed portion of the sample is digested in acid for 2 minutes at 95 °C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique. An alternate digestion involving the use of an autoclave is described in Section 10.5.2.
- 2.3.3.2 The working 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/or recorder expansion.
- 2.3.3.3 For treatment of sludge samples, see Section 2.1.8.
- 3 INTERFERENCES
- 3.1 Interferences Observed with ICP-Atomic Emission Spectrometric Method
- 3.1.1 Three types of interference effects may contribute to inaccuracies in the determination of trace elements: spectral, physical, and chemical. These are summarized as follows.
- 3.1.1.1 Spectral interferences
- 3.1.1.1.1 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 for 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 for by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element 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.

3.1.1.1.2 Listed in Table 5 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 5 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 (USDOE, Iowa State University, Ames, Iowa 50011) is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element.

3.1.1.1.3 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 5, 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 5, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated, and the blank spaces in Table 5 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 6. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peak heights generated by the analyte concentrations also listed in Table 6.

3.1.1.1.4 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.

#### 3.1.1.2 Physical interferences

3.1.1.2.1 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Changes in properties such as 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 aerosol flow rate and causes instrumental drift. Internal standards may also be used to compensate for physical interferences.

3.1.1.2.2 Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution techniques 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. Nebulizers specifically designed for use with solutions containing high concentration of dissolved solids may be used.

3.1.1.3 Chemical interferences -- These 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.

3.1.2 The ICP Serial Dilution Analysis must be performed on 10% of the samples, or at least once for each set or Episode of samples. Samples identified as field blanks cannot be used for serial dilution analysis. If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five-fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all

affected analytes in the samples associated with that serial dilution must be flagged.

### 3.2 Interferences Observed with GFAA Spectroscopic Method

3.2.1 Interferences of three types are encountered in atomic absorption methods using electrothermal atomization: spectral, chemical, and physical. These interferences are summarized as follows.

#### 3.2.1.1 Spectral interferences

3.2.1.1.1 Spectral interferences arise when the absorption of an interfering species either overlaps or lies close to the analyte absorption. Then resolution by the monochromator becomes impossible. This effect can be compensated for by monitoring the presence of the interfering element.

3.2.1.1.2 Spectral interferences could also arise because of the presence of combustion products that exhibit broad band absorption or particulate products that scatter radiation. This problem can also originate in the sample matrix itself. If the source of interference is known, an excess of the interfering substance can be added to both the sample and standards. Provided that the excess is large with respect to the concentration from the sample matrix, the contribution from the sample matrix will become insignificant.

3.2.1.1.3 The matrix interference problem is greatly exacerbated with electrothermal atomization; this is one of the major causes for poor accuracy. Scattering by incompletely decomposed organic particles also occurs commonly. As a consequence, the need for background correction techniques is encountered with electrothermal atomization. The use of Zeeman or Smith-Hieftje background correction techniques is recommended.

3.2.1.2 Chemical interferences are more common than spectral ones. Their effects can be minimized by a suitable choice of operating conditions. These interferences can be categorized as: 1) formation of compounds of low volatility which reduces the rate at which the sample is atomized, 2) ionization of atoms and molecules, and 3) solute vaporization effects. These interferences can be minimized by varying

the temperature and addition of ionization suppressor or by standard addition technique. These interferences can be highly dependent on the matrix type and the specific analyte element.

3.2.1.3 Physical interferences are pronounced with samples containing high dissolved solids and/or acid concentration resulting in change in viscosity and surface tension. If these types of interferences are operative, they can be reduced by dilution of the sample.

3.2.2 Possible interferences observed during analysis of trace elements by GFAA spectroscopic methods and certain recommended instrumental parameters -- All furnace elements must be analyzed by method of standard addition (Section 8.15). The use of background correction is also required for all of these elements.

#### 3.2.2.1 Antimony

3.2.2.1.1 Nitrogen may also be used as the purge gas.

3.2.2.1.2 If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 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.

#### 3.2.2.2 Arsenic

3.2.2.2.1 The use of Zeeman or Smith-Hieftje background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (ie., Al, Fe). If conditions occur where significant interference is suspected, the laboratory must switch to an alternate wavelength or take other appropriate action to compensate for the interference effects.

3.2.2.2.2 The use of an electrodeless discharge lamp (EDL) for the light source is recommended.

#### 3.2.2.3 Beryllium

3.2.2.3.1 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

- 3.2.2.4 Cadmium concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.
- 3.2.2.4.1 Contamination from the work area is critical in cadmium analysis. Use pipette tips which are free of cadmium.
- 3.2.2.5 Chromium
- 3.2.2.5.1 Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to the solution at a level of at least 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.
- 3.2.2.5.2 Nitrogen should not be used as a purge gas because of possible CN band interference.
- 3.2.2.5.3 Pipette tips have been reported to be a possible source of contamination.
- 3.2.2.6 Lead
- 3.2.2.6.1 Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead Electrodeless Discharge Lamp at this lower wavelength has been found to be advantageous. Also, a lower atomization temperature (2400 °C) may be preferred.
- 3.2.2.6.2 To suppress sulfate interference (up to 1500 ppm) lanthanum nitrate is added to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976).
- 3.2.2.6.3 Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
- 3.2.2.7 Selenium
- 3.2.2.7.1 The use of Zeeman or Smith-Hieftje background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference is suspected, the laboratory must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
- 3.2.2.7.2 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with
- 3.2.2.7.3 The use of an electrodeless discharge lamp (EDL) for the light source is recommended.
- 3.2.2.8 Thallium
- 3.2.2.8.1 Nitrogen may also be used as the purge gas.
- 3.3 Interferences Observed with Cold Vapor AA (CVAA) Techniques for Analysis of Mercury
- 3.3.1 Manual CVAA technique for analysis of mercury in water
- 3.3.1.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.
- 3.3.1.2 Copper may interfere in the analysis of mercury; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 3.3.1.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the seawater using this technique.
- 3.3.1.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EPA laboratories have not encountered such samples to date. This is mentioned only to caution the analyst of the possibility.
- 3.3.2 Automated CVAA technique for analysis of mercury in water
- 3.3.2.1 Some seawaters and wastewaters high in chlorides have shown a positive interference, probably due to the formation of free chlorine. (See Section 3.3.1.3.)



- 3.3.2.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.
- 3.3.2.3 If total mercury values are to be reported, samples containing solids must be blended and then mixed while being sampled.
- 3.3.3 Manual CVAA technique for analysis of mercury in soil
  - 3.3.3.1 The same types of interferences that may occur in water samples are also possible with soils/sediments, i.e., sulfides, high copper, high chlorides, etc.
  - 3.3.3.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.
  - 3.3.3.3 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile material, purge the dead air space in the BOD bottle before the addition of stannous sulfate.
- 4 SAFETY
  - 4.1 The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. 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 data sheets should be made available to all personnel involved in the chemical analysis.
- 5 APPARATUS AND EQUIPMENT
  - 5.1 ICP-Atomic Emission Spectrometer
    - 5.1.1 Sequential ICP instruments (2 channel minimum) interfaced with a computerized data system capable of short sampling times and narrow survey windows necessary for the semiquantitative ICP screening procedure and facility for background correction.
    - 5.1.2 Radio frequency generator.
    - 5.1.3 Argon gas supply, welding grade or better.
  - 5.2 GFAA Spectrometer.
    - 5.2.1 Computer-controlled atomic absorption spectrometer with background correction.
    - 5.2.2 Argon gas supply, welding grade or better.
  - 5.3 For ICP-Atomic Emission and GFAA, the following is also required.
    - 5.3.1 250 mL beaker or other appropriate vessel.
    - 5.3.2 Watch glasses.
    - 5.3.3 Thermometer that covers range of 0 - 200 °C.
    - 5.3.4 Whatman No. 42 filter paper or equivalent.
  - 5.4 Apparatus for manual CVAA mercury analysis in water
    - 5.4.1 Atomic absorption spectrophotometer: 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: 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.
    - 5.4.2 Mercury hollow cathode lamp: Westinghouse WL-22847, argon-filled, or equivalent.
    - 5.4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.
    - 5.4.4 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. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" x 2" cards. One-inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

5.4.5 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.

5.4.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.4.7 Aeration tubing: A straight glass fit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.4.8 Drying tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate. The apparatus is assembled as shown in Figure 1. NOTE: 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.

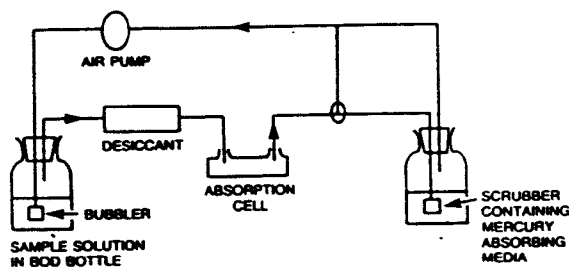


FIGURE 1 Apparatus for Flameless Mercury Determination

5.5 Apparatus for automated CVAA mercury analysis in water

5.5.1 Technicon auto analyzer or equivalent instrumentation consisting of:

5.5.1.1 Sampler II with provision for sample mixing.

5.5.1.2 Manifold.

5.5.1.3 Proportioning pump II or III.

5.5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.5.2 Vapor-liquid separator (Figure 2).

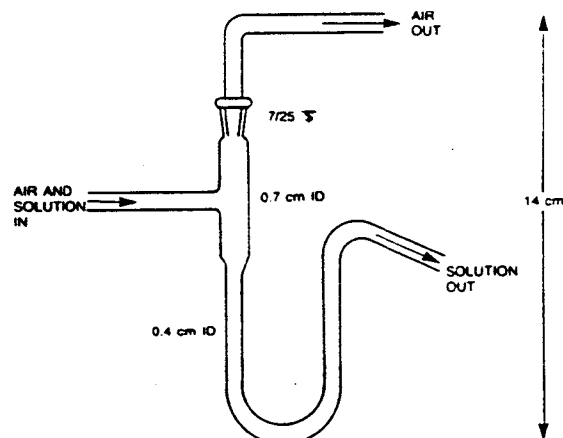


FIGURE 2 Vapor Liquid Separator

5.5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.5.4 Atomic absorption spectrophotometer (see Section 5.4.1).

5.5.5 Mercury hollow cathode lamp (see Section 5.4.2).

5.5.6 Recorder (see Section 5.4.3).

5.6 Apparatus for manual CVAA mercury analysis in soil/sediment

5.6.1 Atomic Absorption Spectrophotometer (see Section 5.4.1).

- 5.6.2 Mercury Hollow Cathode Lamp (see Section 5.4.2).
- 5.6.3 Recorder (see Section 5.4.3).
- 5.6.4 Absorption Cell (see Section 5.4.4).
- 5.6.5 Air Pump (see Section 5.4.5).
- 5.6.6 Flowmeter (See Section 5.4.6.).
- 5.6.7 Aeration tubing (see Section 5.4.7).
- 5.6.8 Drying tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see NOTE in Section 5.4.8).
- 6 REAGENTS AND STANDARDS
- 6.1 ICP-Atomic Absorption Spectrometry -- Quantitative screening of 21 elements
- 6.1.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.
- 6.1.1.1 Acetic acid, conc. (sp gr 1.06).
- 6.1.1.2 Hydrochloric acid, conc. (sp gr 1.19).
- 6.1.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized distilled water and dilute to 1 liter.
- 6.1.1.4 Nitric acid, conc. (sp gr 1.41).
- 6.1.1.5 Nitric acid, (1+1): Add 500 mL conc.  $\text{HNO}_3$  (sp gr 1.41) to 400 mL deionized distilled water and dilute to 1 liter.
- 6.1.2 Deionized 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.
- 6.1.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for one hour 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.
- 6.1.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 0.100 g aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc.  $\text{HNO}_3$  in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a one-liter flask, add an additional 10 mL (1+1) HCl, and dilute to 1000 mL with deionized distilled water.
- 6.1.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g  $\text{K(SbO)}_2\text{C}_4\text{H}_4\text{O}_6$  in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized distilled water.
- 6.1.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g  $\text{As}_2\text{O}_3$  in 100 mL deionized distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g  $\text{BaCl}_2$  (dried at 250 °C for 2 hours) in 10 mL deionized distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with deionized distilled water.
- 6.1.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  in deionized distilled water, add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.6 Boron solution, stock, 1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous  $\text{H}_3\text{BO}_3$  in deionized distilled water and dilute to 1000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.
- 6.1.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1)  $\text{HNO}_3$ . Heat to increase rate of dissolution. Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g  $\text{CaCO}_3$  (dried at 180 °C for one hour before weighing) in deionized distilled water, and dissolve cautiously with a minimum amount of (1+1)  $\text{HNO}_3$ . Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.

- 6.1.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g  $\text{CrO}_3$  in deionized distilled water. When solution is complete, acidify with 10 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.10 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1)  $\text{HNO}_3$ . Add 10.0 mL (1+1) HCl and dilute to 1000 mL with deionized distilled water.
- 6.1.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g  $\text{CuO}$  in a minimum amount of (1+1)  $\text{HNO}_3$ . Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g  $\text{Fe}_2\text{O}_3$  in a warm mixture of 20 mL (1+1) HCl and 2 mL conc.  $\text{HNO}_3$ . Cool, add an additional 5 mL conc.  $\text{HNO}_3$ , and dilute to 1000 mL with deionized distilled water.
- 6.1.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g  $\text{Pb}(\text{NO}_3)_2$  in a minimum amount of (1+1)  $\text{HNO}_3$ . Add 10.0 mL of conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g  $\text{MgO}$  in a minimum amount of (1+1)  $\text{HNO}_3$ . Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g manganese metal in 10 mL conc. HCl and 1 mL conc.  $\text{HNO}_3$ , and dilute to 1000 mL with deionized distilled water.
- 6.1.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g  $(\text{NH}_4)_2\text{MoO}_4$  in deionized distilled water and dilute to 1000 mL.
- 6.1.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc.  $\text{HNO}_3$ , cool and dilute to 1000 mL with deionized distilled water.
- 6.1.3.18 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g  $\text{H}_2\text{SeO}_3$  (actual assay 94.6%) in deionized distilled water and dilute to 1000 mL.
- 6.1.3.19 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g  $\text{AgNO}_3$  in 100 mL deionized distilled water and 10 mL conc.  $\text{HNO}_3$ . Dilute to 1000 mL with deionized distilled water.
- 6.1.3.20 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized distilled water. Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.21 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g  $\text{TlNO}_3$  in deionized distilled water. Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.22 Tin solution, stock, 1 mL = 100 ug Sn: Dissolve 0.1000 g of tin metal in 80 mL conc. HCl and dilute to 1000 mL with deionized distilled water. NOTE: It is preferable to maintain the tin standard in 8 - 20 percent HCl to overcome the problem of precipitation and colloidal formation.
- 6.1.3.23 Titanium, stock, 1 mL = 100 ug Ti: Dissolve 0.3220 g  $\text{TiCl}_3$  in 50 mL conc. HCl. Dilute to 1000 mL with deionized distilled water.
- 6.1.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297  $\text{NH}_4\text{VO}_3$  in a minimum amount of conc.  $\text{HNO}_3$ . Heat to increase rate of dissolution. Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.25 Yttrium solution, stock, 1 mL = 100 ug Y: Dissolve 0.43080 g  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in deionized distilled water. Add 50 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.3.26 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g  $\text{ZnO}$  in a minimum amount of dilute  $\text{HNO}_3$ . Add 10.0 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water.
- 6.1.4 Mixed calibration standard solutions
- 6.1.4.1 Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (Recommended solutions are given in Sections 6.1.4.4.1-6.1.4.4.5.). Add 2 mL (1+1)  $\text{HNO}_3$  and 10 mL (1+1) HCl, and dilute to 100 mL with deionized distilled water. (See NOTE in Section 6.1.4.4.5.)

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.

6.1.4.2 The calibration standards must contain the same acid concentration as the prepared sample. Fresh mixed standards should be prepared as needed, recognizing that concentration can change over time. 6.1.4.3 Calibration standards must be initially verified using an ICV standard and monitored weekly for stability (see Section 8.4.1.1).

6.1.4.4 Typical calibration standard combinations are given in Sections 6.1.4.4.1 through 6.1.4.4.5. Although not specifically required, these combinations are appropriate when using the specific wavelengths listed in Table 1.

6.1.4.4.1 Mixed standard solution I - Manganese, beryllium, cadmium, lead, and zinc.

6.1.4.4.2 Mixed standard solution II -- Barium, copper, iron, vanadium, yttrium, and cobalt.

6.1.4.4.3 Mixed standard solution III -- Molybdenum, arsenic, and selenium.

6.1.4.4.4 Mixed standard solution IV -- Calcium, sodium, aluminum, chromium and nickel.

6.1.4.4.5 Mixed standard solution V -- Antimony, boron, magnesium, silver, thallium, and titanium. NOTE: 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.

6.1.4.4.6 Standard solution VI -- Tin.

6.1.5 Initial calibration verification (ICV) standard solutions -- Prepared in the same

acid matrix as the calibration standards (see Section 6.1.4) and in accordance with the instructions provided by the supplier. Certified ICV standard solutions should be obtained from an outside source. If the certified solution of the ICV standard is not available from any source, analyses shall be conducted on an independent standard (defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration) at a concentration other than that used for instrument calibration but within the calibration range. NOTE: ICV standards for semiquantitative ICP screen elements are not available commercially at this time and should be prepared by the laboratory. The standards used must be traceable to EPA or NIST materials.

6.1.6 Continuing calibration verification (CCV) standard solutions -- Prepared by combining compatible elements at a concentration equivalent to the midpoints of their respective calibration curves. The aggregated CCV standard solutions must contain all analytes. The CCV standard may be an outside standard of NIST or EPA materials, NIST SRM 1643a, or laboratory-prepared standards traceable to EPA or NIST.

6.1.7 ICP interference check sample (ICS) -- The ICP ICS consists of two solutions: Solution A (interferents) and Solution AB (analytes mixed with the interferents). The materials used in the ICS must be traceable to NIST or EPA material.

6.1.7.1 If the ICP ICS is not available from any source, the laboratory must prepare independent ICP check samples with interferent and analyte concentrations at the levels specified in Table 11.

6.1.7.2 The mean value and standard deviation of independent ICP check samples must be established by initially analyzing the check samples at least five times repetitively for each parameter in Table 11. Results must fall within the control limit of  $\pm 20\%$  of the established mean value.

6.1.8 Blanks -- Two types of blanks are required. Initial and continuing calibration blanks are used in establishing the analytical curve; the preparation (reagent) blank is used to

correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.1.8.1 Initial and continuing calibration blanks -- Prepared by diluting 2 mL of (1+1)  $\text{HNO}_3$  and 10 mL of (1+1)  $\text{HCl}$  to 100 mL with deionized distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples. The calibration blank must contain the same acid concentration as the prepared sample solution.

6.1.8.2 Preparation (reagent) blank -- Must contain all the reagents and in the same volumes as used in the processing of the samples. The preparation 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.

6.1.9 Laboratory control sample -- Should be obtained from an outside source. If unavailable, the ICV standard solutions may be used. The laboratory control sample must contain all analytes of interest. Standards used must be traceable to NIST or EPA material.

6.2 ICP-Atomic Absorption Spectrometry -- Semiquantitative screening of 42 elements

6.2.1 Individual stock solution (1000 mg/L) for the elements listed in Table 4 may be prepared by the laboratory or purchased from a commercial source. These solutions are available from J.T. Baker Alfa Products and other suppliers.

6.2.1.1 Osmium stock solution: Osmium stock solution can be prepared from osmium chloride (available from Alfa Products or other suppliers). Dissolve 1.559 g  $\text{OsCl}_3$  in 6 mL conc.  $\text{HCl}$  + 2 mL conc.  $\text{HNO}_3$ , and dilute to 1 liter to yield 1000 mg/L stock solution.

6.2.1.2 Sulfur stock solution: Can be prepared from ammonium sulfate (available from J. T. Baker or other suppliers). Dissolve 4.122 g of anhydrous ammonium sulfate in deionized water and dilute to 1 liter to yield 1000 mg/L stock solution.

6.2.1.3 Uranium stock solution: Made from uranyl nitrate (available from Alfa Products or other suppliers). Dissolve 2.110 g uranyl nitrate hexahydrate in 6 mL conc.  $\text{HCl}$  + 2

mL conc.  $\text{HNO}_3$  and dilute to 1 liter to give 1000 mg/L.

6.2.2 Mixed calibration solution -- Prepare a mixed working (calibration) standard directly from the individual stock solutions to give final concentrations for each analyte as listed in Table 7. It is recommended that a micro-pipette with disposable plastic tips be used to transfer each stock solution to the volumetric flask. The stability of this solution is limited, but can be extended by storing it in a dark brown plastic bottle away from light. Care should be taken to include analyte contribution from other stock standards. For example: a number of the stock standards are prepared from potassium salts. If alternative solutions are not available, the final solution (Section 6.2.2) must be analyzed quantitatively by ICP to derive its true concentration. The resulting calibration standard must contain the same acid concentration as the prepared sample solution.

6.2.3 ICV standard solutions (see Section 6.1.5), CCV standard solutions (see Section 6.1.6), and interference check samples (see Section 6.1.7) are also required.

6.2.4 Two types of blanks are required -- Initial and continuing calibration blanks and the preparation blank (see Section 6.1.8).

6.3 GFAA Spectrophotometric Method

6.3.1 Antimony

6.3.1.1 Stock solution: Carefully weigh 2.669 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized water. 1 mL = 1 mg Sb (1000 mg/L).

6.3.1.2 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."

6.3.1.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

- 6.3.2 Arsenic
- 6.3.2.1 Stock solution: Dissolve 1.320 g arsenic trioxide,  $\text{As}_2\text{O}_3$  (analytical reagent grade) in 100 mL deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL conc.  $\text{HNO}_3$  and dilute to 1 liter. 1 mL = 1 mg As (1000 mg/L).
- 6.3.2.2 Nickel nitrate solution, 5%: Dissolve 24.770 g ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in deionized distilled water and make up to 100 mL.
- 6.3.2.3 Nickel nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
- 6.3.2.4 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 conc.  $\text{HNO}_3$ , 2 mL 30%  $\text{H}_2\text{O}_2$ , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.
- 6.3.3 Lead
- 6.3.3.1 Stock solution: Carefully weigh 1.599 g lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled  $\text{HNO}_3$  and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Pb (1000 mg/L).
- 6.3.3.2 Lanthanum nitrate solution: Dissolve 58.639 g of ACS reagent grade  $\text{La}_2\text{O}_3$  in 100 mL conc.  $\text{HNO}_3$  and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
- 6.3.3.3 Working lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard, add 10 mL of the lanthanum nitrate solution.
- 6.3.4 Selenium
- 6.3.4.1 Stock selenium solution: Dissolve 0.3453 g selenous acid (actual assay 94.6%  $\text{H}_2\text{SeO}_3$ ) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).
- 6.3.4.2 Nickel nitrate solution, 5%: Dissolve 24.770 g ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in deionized distilled water and make up to 100 mL.
- 6.3.4.3 Nickel nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
- 6.3.4.4 Working selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 mL conc.  $\text{HNO}_3$ , 2 mL 30%  $\text{H}_2\text{O}_2$ , and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.
- 6.3.5 Thallium
- 6.3.5.1 Stock solution: Dissolve 1.303 g thallium nitrate,  $\text{TlNO}_3$  (analytical reagent grade) in deionized distilled water. Add 10 mL conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).
- 6.3.5.2 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."
- 6.3.5.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.
- 6.4 Mercury Analysis in Water by Manual Cold Vapor Technique
- 6.4.1 Sulfuric acid, conc: Reagent grade.
- 6.4.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL conc. sulfuric acid to 1.0 liter.
- 6.4.2 Nitric acid, conc: Reagent grade of low mercury content. NOTE: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.
- 6.4.3 Stannous sulfate: Add 25 g stannous sulfate to 250 mL 0.5 N sulfuric acid. This mixture is a suspension and should be

stirred continuously during use. NOTE: Stannous chloride may be used in place of stannous sulfate.

- 6.4.4 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g sodium chloride and 12 g hydroxylamine sulfate in deionized distilled water, and dilute to 100 mL. NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)
- 6.4.5 Potassium permanganate: 5% solution, w/v. Dissolve 5 g potassium permanganate in 100 mL distilled water.
- 6.4.6 Potassium persulfate: 5% solution, w/v. Dissolve 5 g potassium persulfate in 100 mL distilled water.
- 6.4.7 Stock mercury solution: Dissolve 0.1354 g mercuric chloride in 75 mL deionized distilled water. Add 10 mL conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.
- 6.4.8 Working mercury solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution 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.
- 6.5 Mercury Analysis in Water by Automated Cold Vapor Technique
  - 6.5.1 Sulfuric acid, conc: Reagent grade.
    - 6.5.1.1 Sulfuric acid, 2 N: Dilute 56 mL conc. sulfuric acid to 1 liter with deionized distilled water.
    - 6.5.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with deionized distilled water.
  - 6.5.2 Nitric acid, conc: Reagent grade of low mercury content.
    - 6.5.2.1 Nitric acid, 0.5% wash solution: Dilute 5 mL conc. nitric acid to 1 liter with deionized distilled water.
  - 6.5.3 Stannous sulfate: Add 50 g stannous sulfate to 500 mL 2N sulfuric acid (Section 6.5.1.1). This mixture is a suspension and should be stirred

continuously during use. NOTE: Stannous chloride may be used in place of stannous sulfate.

- 6.5.4 Sodium chloride-hydroxylamine sulfate solution: Dissolve 30 g sodium chloride and 30 g hydroxylamine sulfate in deionized distilled water and dilute to 1 liter. NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.
- 6.5.5 Potassium permanganate: See Section 6.4.5.
- 6.5.6 Potassium permanganate, 0.1N: Dissolve 3.16 g potassium permanganate in deionized distilled water and dilute to 1 liter.
- 6.5.7 Potassium persulfate: See Section 6.4.6.
- 6.5.8 Stock mercury solution: See Section 6.4.7.
- 6.5.9 Working mercury solution: See Section 6.4.8. From this solution, prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 ug Hg/L.
- 6.5.10 Air scrubber solution: Mix equal volumes of 0.1 N potassium permanganate (Section 6.5.6) and 10% sulfuric acid (Section 6.5.1.2).
- 6.6 Mercury Analysis in Soil/Sediments by Manual Cold Vapor Technique
  - 6.6.1 Sulfuric acid, conc: Reagent grade of low mercury content.
  - 6.6.2 Nitric acid, conc: See Section 6.4.2.
  - 6.6.3 Stannous sulfate: See Section 6.4.3.
  - 6.6.4 Sodium chloride-hydroxylamine sulfate: See Section 6.4.4.
  - 6.6.5 Potassium permanganate: See Section 6.4.5.
  - 6.6.6 Potassium persulfate: See Section 6.4.6.
  - 6.6.7 Stock mercury solution: See Section 6.4.7.
  - 6.6.8 Working mercury solution: See Section 6.4.8.



## 7 CALIBRATION

### 7.1 ICP and GFAA Spectroscopic Methods

7.1.1 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. All measurements must be within the instrument linear range where correction factors are valid.

7.1.2 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.

### 7.2 Analysis of Mercury in Water by Cold Vapor Technique

7.2.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL conc. sulfuric acid (Section 6.4.1) and 2.5 mL conc. nitric acid (Section 6.4.2) to each bottle. Add 15 mL  $\text{KMnO}_4$  (Section 6.4.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL potassium persulfate (Section 6.4.6) to each bottle and heat for 2 hours in a water bath maintained at 95 °C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120 °C and 15 psi. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (Section 6.4.4) to reduce the excess permanganate. When the solution has been decolorized, wait 30 seconds, add 5 mL of the stannous sulfate solution (Section 6.4.3), and immediately attach the bottle to the aeration apparatus forming a closed system. At this point, the sample is allowed to stand quietly without manual agitation.

7.2.2 The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see NOTE 1). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see NOTE 2). Close the bypass valve, remove the stopper and frit 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 1: An open system (where the mercury vapor is passed through the absorption cell only once) may be used instead of the closed system.

NOTE 2: Because of the toxic nature of mercury vapor, precautions 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 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$ , or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will adsorb mercury vapor is available.

7.2.3 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise.

### 7.3 Analysis of Mercury in Soil/Sediments by Cold Vapor Technique

7.3.1 Transfer 0, 0.5, 1.0, 5.0, and 10 mL aliquots of the working mercury solutions (Section 6.6.8) containing 0-1.0 ug mercury to a series of 300 mL BOD bottles. Add enough deionized distilled water to each bottle to make a total volume of 100 mL. Add 5 mL conc.  $\text{H}_2\text{SO}_4$  (Section 6.6.1) and 2.5 mL conc.  $\text{HNO}_3$  (Section 6.6.2), and heat for 2 minutes in a water bath at 95 °C. Allow the sample to cool. Add 50 mL deionized distilled water, 15 mL  $\text{KMnO}_4$  solution (Section 6.6.5), and 8 mL potassium persulfate solution (Section 6.6.6) to each bottle and return bottles to the water bath for 30 minutes. Cool and add 6 mL sodium chloride-hydroxylamine sulfate solution (Section 6.6.4) to reduce the excess permanganate. Add 50 mL deionized distilled water. Treating each

bottle individually, add 5 mL stannous sulfate solution (Section 6.6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation.

- 7.3.2 The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see NOTE 1 in Section 7.2.2). 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 valve and continue the aeration until the absorbance returns to its minimum value (see NOTE 2 in Section 7.2.2). Close the bypass valve, 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.

## 8 QUALITY ASSURANCE/QUALITY CONTROL

- 8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of: 1) an initial demonstration of laboratory capability, 2) analysis of samples spiked with the analytes of interest to evaluate and document data quality, and 3) 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 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.

- 8.2 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 analysis of samples containing low solids (aqueous samples), prepare four 500 mL aliquots of reagent water spiked with the 27 elements listed in Tables 1-2 at concentrations at or near the MLs given in Table 9. Digest these samples according to the procedures in Section 10.1.1 and analyze the samples according to the ICP, GFAA and Hg procedures in Sections 10.1.3, 10.3, and 10.4, respectively.

- 8.2.2 For analysis of samples containing high solids, prepare four aliquots of reagent water containing the 27 elements at concentrations at or near the detection limits given in Tables 1-2. Digest these samples according to the procedures for water samples in Section 10.1.1, but analyze them as if they were soil samples according to Sections 10.1.3, 10.3, and 10.4, and calculate the concentrations of the analytes as if the original sample weight was 1 g of soil.

- 8.2.3 Using the results of the set of four analyses (from Section 8.2.1 or 8.2.2), compute the average percent recovery ( $\bar{x}$ ) and the coefficient of variation ( $s$ ) of the percent recovery(ies) for each element.

- 8.2.4 For each element, compare  $s$  and  $\bar{x}$  with the corresponding limits in Table 8. If  $s$  and  $\bar{x}$  for all elements 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  $\bar{x}$  falls outside the range for accuracy, system performance is unacceptable for the element. In this case, correct the problem and repeat the test.

## 8.3 Instrument Calibration

- 8.3.1 Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Section 7. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

- 8.3.2 For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis.

- 8.3.3 Calibration standards**
- 8.3.3.1** For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.
- 8.3.3.2 AA Systems**
- 8.3.3.2.1** Calibration standards for AA procedures must be prepared by dilution of the stock solutions (Section 6.3).
- 8.3.3.2.2** Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the minimum level (see Table 9), except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.
- 8.3.3.2.3** Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required four-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within  $\pm 5\%$  of the true value. Each standard concentration and the calculations to show that the  $\pm 5\%$  criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary. NOTE: The  $\pm 5\%$  criteria does not apply to the atomic absorption calibration standard at the minimum level.
- 8.3.3.2.4** Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by continuing calibration verification and continuing calibration blank analyses.
- 8.3.4** Mercury analysis techniques -- Follow the calibration procedures outlined in Section 7.
- 8.4 Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)**
- 8.4.1 Initial Calibration Verification (ICV)**
- 8.4.1.1** The accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of an ICV standard (Sections 6.1.5 and 6.2.3) at each wavelength used for analysis. If the results are not within  $\pm 10\%$  of the true value, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. NOTE: For semiquantitative ICP analysis, 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.
- 8.4.1.2** ICV standard solutions must be run immediately after each of the ICP and AA systems have been calibrated and each time the system is set up. The ICV standard solution(s) must be run for each analyte at each wavelength used for analysis.
- 8.4.2 Continuing Calibration Verification (CCV)**
- 8.4.2.1** To ensure calibration accuracy during each analysis run, a CCV standard (Sections 6.1.6 and 6.2.3) is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The CCV standard must also be analyzed and reported for every wavelength used for analysis of each analyte at the beginning of the run and after the last analytical sample.
- 8.4.2.2** The same continuing calibration standard must be used throughout the analysis run for each set or Episode of samples received.
- 8.4.2.3** Each CCV standard analysis must reflect the conditions of analysis of all associated analytical samples (all preceding analytical samples up to the previous CCV standard analysis). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV standard to a greater extent than the extent applied to the associated

analytical samples. For instance, the difference in time between a CCV standard analysis and the blank immediately following it, as well as the difference in time between the CCV standard analysis and the analytical sample immediately preceding it, may not exceed the lowest difference in time between analysis of any two consecutive analytical samples associated with the CCV.

- 8.4.2.4 If the deviation of the continuing calibration verification is greater than the control limits specified in Table 10, the analysis must be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and the preceding samples analyzed since the last good calibration verification reanalyzed for the analytes affected.
- 8.5 Minimum Level (ML) Standards for ICP (CRI) and AA (CRA)
  - 8.5.1 To verify linearity near the ML for ICP analysis, analyze an ICP standard (CRI) at 2x ML (Table 9) or 2x IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8-hour working shift, whichever is more frequent, but not before initial calibration verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.
  - 8.5.2 To verify linearity near the ML for AA analysis, analyze an AA standard (CRA) at the ML or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the initial calibration verification.
  - 8.5.3 If any GFAA element exceeds the ICP ML by 2x, it can be analyzed by ICP rather than GFAA.
  - 8.5.4 Report percent recoveries for the CRI and CRA standards. Specific acceptance criteria for these standards will be set by EPA in the future.
- 8.6 Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
  - 8.6.1 Initial and continuing calibration blank analyses -- A calibration blank (Section 6.1.8.1 and 6.2.4) must be analyzed at each wavelength used for analysis,

immediately after every initial and continuing calibration verification, at a frequency of 10% or each time the instrument is calibrated, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. NOTE: A CCB must be run after the last CCV that was run after the last analytical sample of the run.

- 8.6.1.1 For quantitative ICP analysis, if the absolute value blank result exceeds the ML (Table 9), terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last acceptable calibration blank analysis.
- 8.6.1.2 For semiquantitative ICP analysis, the absolute value of the blank result must be less than the lower threshold limit (Table 4). If the result is not within the LTL, terminate the analysis, correct the problem, and recalibrate the instrument.
- 8.6.2 Preparation blank analysis -- At least one preparation (reagent) blank (Sections 6.1.8.2 and 6.2.4) must be prepared and analyzed with each batch of samples (group of samples prepared at the same time) digested. This blank is to be reported for each batch of samples and used in all analyses to ascertain whether sample concentrations reflect contamination.
- 8.6.2.1 If the absolute value of the concentration of the blank is less than or equal to the ML (Table 9), no correction of sample results is performed.
- 8.6.2.2 If any analyte concentration in the blank is above the ML (Table 9), the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the ML, must be redigested and reanalyzed for that analyte. The sample concentration is not to be corrected for the blank value.
- 8.6.2.3 If the concentration of the blank is below the negative ML, then all samples reported below 10x ML associated with the blank must be redigested and reanalyzed.

## 8.7 ICP Interference Check Sample (ICS) Analysis

- 8.7.1 To verify inter-element and background correction factors, analyze and report the results for the ICP ICS (Sections 6.1.7 and 6.2.3) at the beginning and end of each analysis run or a minimum of twice per 8-hour working shift, whichever is more frequent, but not before initial calibration verification.
- 8.7.2 The ICP ICS consists of two solutions: Solution A (interferents) and Solution AB (analytes mixed with the interferents). An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.
- 8.7.3 Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of  $\pm 20\%$  of the true value for the analytes included in the ICS. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last acceptable ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analyte(s). This mean determination must be made during an analytical run where the results for the previously-analyzed ICS met all method specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

## 8.8 Spike Sample Analysis (Matrix Spike)

- 8.8.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps. Spike sample analyses shall be performed on 10% of the samples analyzed, or at least one spike sample analysis (matrix spike) shall be performed for each set or Episode of samples, whichever is more frequent.
- 8.8.2 If the spike analysis is performed on the same sample that is chosen for the

duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see Section 8.9). The average of the duplicate results cannot be used for the purpose of determining percent recovery. NOTE: Samples identified as field blanks cannot be used for the spike sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

- 8.8.3 Analyze an aliquot of the sample by the ICP parameters for all elements listed in Table 1 to determine the background concentration of each element.

- 8.8.4 Using these concentrations, prepare a QC spike standard containing the analytes. The standard shall produce a concentration in the sample of  $1x - 5x$  the background level determined above. For not-detected analytes, the spike shall be in the range of  $5x - 50x$  the detection limit.

- 8.8.5 Spike a second sample aliquot with the QC spike concentrate and analyze it to determine the concentration in the sample after spiking of each analyte.

- 8.8.6 Calculate the percent recovery of each analyte as follows:

$$P = \frac{A - B}{T} \times 100$$

Where,

A = Concentration of element in the sample after spiking.

B = Background concentration of each element in the sample. NOTE: When B is less than the instrument detection limit, use B=0 only for the purpose of calculation.

T = Known true value of the spike.

- 8.8.7 The acceptable range for recovery of the predigested spike is 75-125 percent for all analytes. EPA will develop recovery limits based on single or interlaboratory data when sufficient data have been accumulated. Report the result for each analyte that falls within the 75-125 percent recovery limits.

- 8.8.8 If the recovery limit is not met for any analyte, proceed as follows.

- 8.8.8.1 For ICP elements, repeat the test. If the recovery is still outside the range, the

instrument conditions should be verified by running the CCV. If the calibration criteria are not met, the instrument should be recalibrated and the spike recovery test repeated. If after recalibration, the spike recovery remains outside of 75 - 125% limits, the sample should be diluted by a factor of 10 and the test repeated. Report and qualify the results.

8.8.8.2 For AA elements, analyze the sample by the method of standard addition (MSA) (Section 8.15). If the correlation coefficient meets method requirements (Section 8.15.7), report and qualify the results. If these specifications are not met, dilute an aliquot of the original sample by a factor of 10 and repeat the analysis by MSA.

8.8.8.3 If correlation coefficient of the diluted analysis meets specifications, report and qualify the results. If these specifications are not met, recalibrate the instrument and repeat the analysis by MSA on the diluted sample. If the correlation coefficient specifications are not met, report and qualify the results.

#### 8.9 Duplicate Spike Sample Analysis (Matrix Spike Duplicate)

8.9.1 Duplicate spike analyses (matrix spike duplicate) shall be performed on 10% of the samples analyzed, or at least one duplicate analyses shall be performed for each set or Episode of samples, whichever is more frequent.

8.9.2 Repeat the spiking and analysis of a third aliquot of the same sample as used for determination of spike recovery (Section 8.8.5), using the same analysis scheme as used for analysis of the sample. For example, if an analyte determined by AA required dilute MSA analysis in order to meet the spike recovery limits, determine that metal in the duplicate spike analysis by dilute MSA analysis.

8.9.3 Samples identified as field blanks cannot be used for duplicate spike sample analysis. EPA may require that a specific sample be used for duplicate spike sample analysis.

8.9.4 The acceptable range for precision of the spike recovery is less than twenty percent relative percent difference (<20% RPD) for

all analytes. EPA will develop precision limits based on a single or inter-laboratory data when sufficient data have been accumulated. Report and qualify the result for each analyte that fails the RPD.

8.9.5 The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where,

RPD = Relative percent difference

S = First spike sample value (matrix spike)

D = Second spike sample value (matrix spike duplicate)

#### 8.10 Laboratory Control Sample (LCS) Analysis

8.10.1 Laboratory control samples (Section 6.1.9) must be analyzed for each analyte using the same sample preparation technique, analytical methods, and QA/QC procedures as employed in sample analysis. An LCS must be analyzed for each set or Episode of samples or for each standard stock batch.

8.10.2 If the percent recovery for the LCS falls outside the control limits of 80-120% (with the exception of Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed. For Ag and Sb, qualify the results.

#### 8.11 ICP Serial Dilution Analysis

8.11.1 For quantitative ICP analysis, prior to reporting concentration data for the analyte elements, analyze and report the results of the ICP serial dilution analysis. The ICP serial dilution analysis must be performed on 10% of the samples analyzed, or at least one serial dilution analysis shall be performed for each set or Episode of samples, whichever is more frequent. NOTE: Samples identified as field blanks cannot be used for serial dilution analysis.

8.11.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five-fold dilution) must then agree within 10% of the original

determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected and the data for all sample analyses associated with that serial dilution must be flagged.

- 8.11.3 The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where,

I = Initial Sample Result

S = Serial Dilution Result (Instrument Reading x 5)

- 8.11.4 In the instance where there is more than one serial dilution per sample set or Episode, if one serial dilution result is not within method specifications (see Section 8.11.2), flag all samples in the set or Episode that are associated with that serial dilution.

#### 8.12 Instrument Detection Limit (IDL) Determination

- 8.12.1 Before any field samples are analyzed under this method, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of analyses under this method and at least quarterly (every three calendar months), and must meet the MLs specified in Table 9.

- 8.12.2 The instrument detection limits (in ug/L) shall be determined by multiplying by three, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

- 8.12.3 The quarterly determined IDL for an instrument must always be used as the IDL

for that instrument during that quarter. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

- 8.12.4 IDLs must be reported for each instrument used. If multiple AA instruments are used for the analysis of an element within a sample set or Episode, the highest IDL for the AAs must be used for reporting concentration values for that sample set. The same reporting procedure must be used for multiple ICPs.

#### 8.13 Inter-element Corrections for ICP

- 8.13.1 Prior to the start of analysis under this method and at least annually thereafter, the ICP inter-element correction factors must be determined. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

- 8.13.2 If the instrument was adjusted in any way that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use.

- 8.14 Linear Range Analysis (LRA) -- For all quantitative ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every three calendar months) for each element for each wavelength used. The standard must be analyzed during a routine analytical run performed under this method. The analytically determined concentration of this standard must be within  $\pm 5\%$  of the true value. This concentration is the upper limit of the ICP linear range beyond which results should not be used without dilution of the analytical sample.

- 8.15 Method of standard addition (MSA) -- All GFAA elements must be analyzed by method of standard addition in all samples.

- 8.15.1 The standard addition technique 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 interferences which cause a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows.

- 8.15.1.1 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 non-analyte 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.

- 8.15.1.2 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, and 4) the signal must be corrected for any additive interference.
- 8.15.2 Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 8.15.3 The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the

MSA quantitation). Only single injections are required for MSA quantitation.

- 8.15.4 Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).
- 8.15.5 For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 8.15.6 Spikes must be prepared such that:
- 8.15.6.1 Spike 1 is approximately 50% of the sample absorbance.
- 8.15.6.2 Spike 2 is approximately 100% of the sample absorbance.
- 8.15.6.3 Spike 3 is approximately 150% of the sample absorbance.
- 8.15.7 The data for each MSA analysis should be clearly identified in the raw data using added concentration as the x-variable and absorbance as the y-variable, along with the slope, x-intercept, y-intercept, and correlation coefficient ( $r$ ) for the least squares fit of the data. If the correlation coefficient ( $r$ ) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, flag the result.

- 8.16 Quality control requirements for ICP semiquantitative screen of 42 elements -- Instrument calibration (Section 8.3) and performance of ICV (Section 8.4.1), CCV (Section 8.4.2), ICB and CCB (Section 8.6.1), PB (Section 8.6.2), and ICS (Section 8.7) analyses are required.

## 9 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

### 9.1 ICP and GFAA Spectroscopic Methods

#### 9.1.1 Water sample preservation

- 9.1.1.1 Samples should be stored in polyethylene or glass containers.
- 9.1.1.2 Samples are filtered immediately on site by the sampler before adding preservative for dissolved metals.



9.1.1.3	Sample preservation is performed by the sampler immediately following sample collection. The sample should be preserved with nitric acid to pH of less than 2.	10	PROCEDURES FOR SAMPLE PREPARATION AND ANALYSIS
9.1.1.4	Samples should be maintained at 4 °C (±2 °C) until analysis.	10.1	ICP and GFAA Spectroscopic Techniques
9.1.1.5	Sample analysis should be completed within six months of sample collection.	10.1.1	Water Sample Preparation
9.1.2	Soil/sediment sample preservation	10.1.1.1	Acid digestion procedure for GFAA -- Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL (1+1) HNO <sub>3</sub> and 2 mL 30% H <sub>2</sub> O <sub>2</sub> to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95 °C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering the sample, after dilution and mixing the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis. NOTE: If Sb is to be determined by furnace AA, use the digestate prepared for ICP analysis.
9.1.2.1	The preservation required for soil samples is maintenance at 4 °C (±2 °C) until analysis.	10.1.1.2	Acid digestion procedure for ICP analysis -- Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL (1+1) HNO <sub>3</sub> and 10 mL (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95 °C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering the sample, after dilution and mixing the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.
9.1.2.2	Sample analysis should be completed within six months of sample collection.	10.1.1.3	Sludge samples having less than 1% solids should be treated by the above method. Sludge samples having between 1 to 30% solids should be diluted to less than 1% solids and then treated by the above method.
9.2	Mercury Analysis by CVAA	10.1.2	Soil Sample Preparation -- This method is an acid digestion procedure used to prepare soils, sediments, and sludge samples containing more than 30% solids, for analysis by GFAA or by ICP. A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen
9.2.1	Analysis of Mercury in Water by Manual or Automated CVAA		
9.2.1.1	Until more conclusive data are obtained, samples are preserved at the time of collection by acidification with nitric acid to a pH of 2 or lower.		
9.2.1.2	Analysis for mercury should be completed within 28 days after collection of the sample.		
9.2.2	Analysis of Mercury in Soil/Sediment by Manual CVAA		
9.2.2.1	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.		
9.2.2.2	Refrigerate soil samples at 4 °C (±2 °C) upon collection until analysis.		
9.2.2.3	The sample should be analyzed without drying. A separate percent solids determination is required (Section 11.1.1).		
9.2.2.4	Analysis should be completed within 28 days after sample collection.		

peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a percent solids determination (Section 11.1.1).

10.1.2.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 - 1.5 g portion of sample and transfer it to a beaker.

10.1.2.2 Add 10 mL of 1:1 nitric acid ( $\text{HNO}_3$ ), mix the slurry, and cover with a watch glass. Heat the sample to 95 °C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of conc.  $\text{HNO}_3$ , replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL, while maintaining a covering of solution over the bottom of the beaker.

10.1.2.3 After the second reflux step has been completed and the sample has cooled, add 2 mL of deionized distilled water and 3 mL of 30%  $\text{H}_2\text{O}_2$ . Return the beaker to the hot plate for warming 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, then cool the beaker.

10.1.2.4 Continue to add 30%  $\text{H}_2\text{O}_2$  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%  $\text{H}_2\text{O}_2$ .

10.1.2.5 If the sample is being prepared for the furnace AA analysis of Sb, or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of deionized distilled water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with deionized distilled water. (NOTE: In place of filtering the sample,

after dilution and mixing the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v)  $\text{HNO}_3$ . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.

10.1.2.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of deionized distilled water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with deionized distilled water. (NOTE: In place of filtering the sample, after dilution and mixing the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) The diluted digestate solution contains approximately 2% (v/v)  $\text{HNO}_3$ . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

#### 10.1.3 Sample Analysis

10.1.3.1 Initiate the appropriate operating configuration of the computer.

10.1.3.2 Profile and calibrate the instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 6.1.4. Flush the system with the calibration blank (Section 6.1.8.1) between each standard. NOTE: For boron concentrations greater than 500 ug/L, extended flush times of 1 - 2 minutes may be required.

10.1.3.3 Begin the sample run, flushing the system with the calibration blank solution (Section 6.1.8.1) between each sample. (See NOTE in Section 10.1.3.2.) Analyze the CCV standard (Section 6.1.6) and the calibration blank (Section 6.1.8.1) following each 10 analytical samples.

- 10.1.3.4 A minimum of two replicate exposures are required for standardization and for all QC and sample analyses, except during MSA. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.
- 10.2 Semiquantitative Screen of 42 Elements by ICP
- 10.2.1 All element files should be set up with the narrowest possible survey and peak windows. Wherever possible, automatic or manual background correction for each element should be employed to compensate for interferences.
- 10.2.2 Wavelength calibration standards should be run as many times as needed to bring all analytes within the specified survey window. This may require as many as five replicate readings on the wavelength standard. The lower threshold limit (LTL) for each element is established by analyzing each analyte at a level of twice the expected LTL in seven replicates. The LTL is the value obtained by multiplying three times the standard deviation of the replicate readings.
- 10.2.3 Following wavelength calibration, instrument calibration standards and blanks are run. The system should be flushed with the calibration blank solution between readings.
- 10.2.4 Analysis of solutions following calibration can be performed using single readings. Wavelength profiles should be stored on a magnetic device for future reference.
- 10.3 Analysis of Mercury in Water by Manual Cold Vapor Technique
- 10.3.1 Transfer 100 mL of sample, or a sample aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid (Section 6.4.1) and 2.5 mL of conc. nitric acid (Section 6.4.2), mixing after each addition. Add 15 mL of potassium permanganate solution (Section 6.4.5) to each sample bottle. The same amount of  $\text{KMnO}_4$  added to the samples should be present in standards and blanks. (NOTE: For sewage samples additional permanganate may be required.) Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (Section 6.4.6) to each bottle and heat for 2 hours in a water bath at 95 °C
- 10.3.2 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (Section 6.4.4) to reduce the excess permanganate (NOTE: Add reductant in 6 mL increments until  $\text{KMnO}_4$  is completely reduced.) Purge the head space in the BOD bottle for at least 1 minute, add 5 mL of stannous sulfate (Section 6.4.3), and immediately attach the bottle to the aeration apparatus. Continue as described under Section 7.2.1.
- 10.3.3 Sludge samples having less than 1% solids should be treated by the above method. Whereas, sludge samples having between 1 to 30% solids should be diluted to less than 1% solids and then treated by the above method.
- 10.4 Analysis of Mercury in Water by Automated Cold Vapor Technique
- 10.4.1 Set up manifold as shown in Figure 3.
- 10.4.2 Feeding all the reagents through the system, with acid wash solution (Section 6.5.2.1) through the sample line, adjust heating bath to 105 °C.
- 10.4.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance, and place heat lamp (if used) directly over absorption cell.
- 10.4.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.
- 10.4.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.
- 10.4.6 After the analysis is complete put all lines except the  $\text{H}_2\text{SO}_4$  line in distilled water to wash out system. After flushing the system, wash out the  $\text{H}_2\text{SO}_4$  line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (Section 6.5.3) through the sample lines, followed by deionized distilled water. This will prevent build-up of oxides of

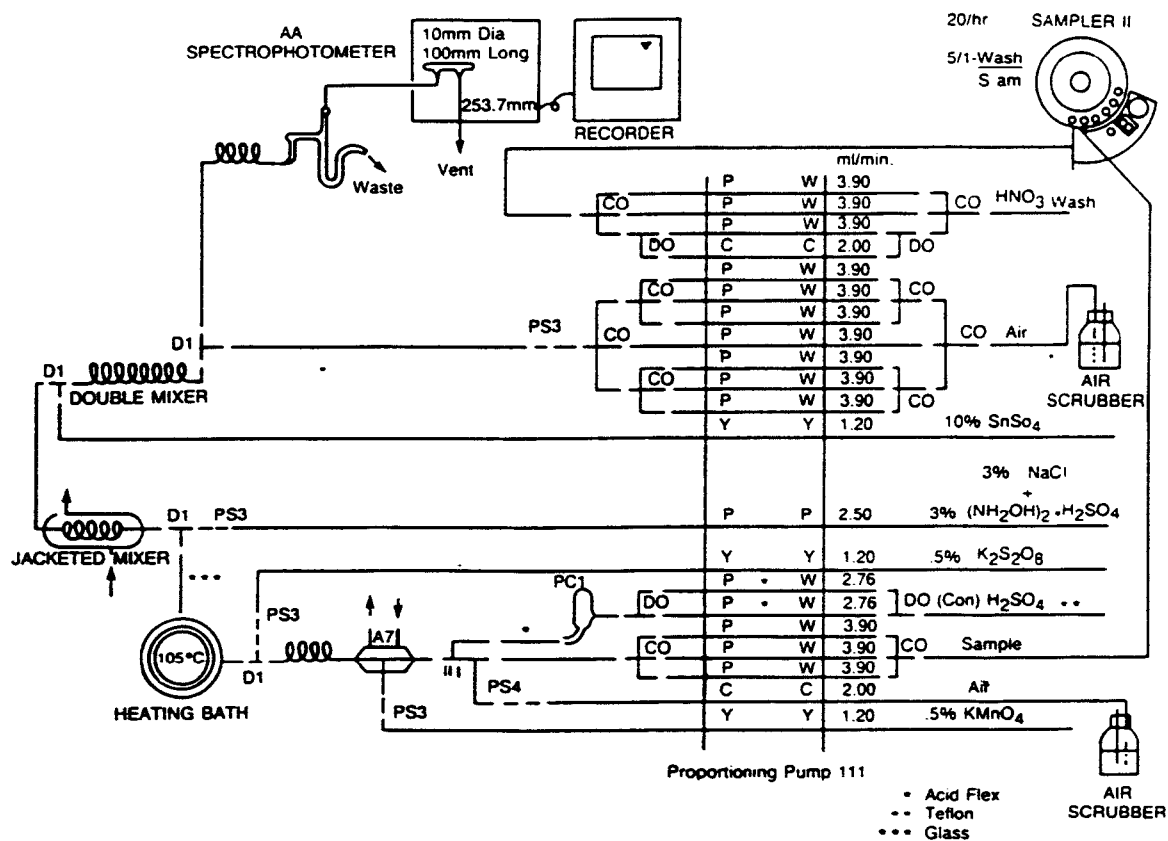


FIGURE 3 Mercury Manifold Setup

- manganese. Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as, equal volumes of 0.1 N  $\text{KMnO}_4$  (Section 6.5.6) and 10%  $\text{H}_2\text{SO}_4$  (Section 6.5.1.2), or 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.
- 10.4.7 For treatment of sludge samples, see Section 10.3.3.
- 10.5 Analysis of Mercury in Soil/Sediment by Manual Cold Vapor Technique
- 10.5.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a 800 bottle. Add 5 mL of sulfuric acid (Section 6.6.1) and 2.5 mL of conc. nitric acid (6.6.2), mixing after each addition. Heat two minutes in a water bath at 95 °C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (Section 6.6.5), and 8 mL of potassium persulfate solution (Section 6.6.6) 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 (Section 6.6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, purge the head space of the sample bottle for at least one minute, add 5 mL of stannous sulfate (Section 6.6.3), and immediately attach the bottle to the aeration apparatus. Continue as described under Section 7.3.1.
- 10.5.2 An alternate digestion procedure employing an autoclave may also be used. In this method, add 5 mL conc.  $\text{H}_2\text{SO}_4$  and 2 mL conc.  $\text{HNO}_3$  to the 0.2 g of sample. Then add 5 mL saturated  $\text{KMnO}_4$  solution and 8 mL potassium persulfate solution and cover the bottle with a piece of aluminum foil. Autoclave the sample at 121 °C and 15 psi 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 (Section 6.6.4) to reduce the excess permanganate. Purge the headspace of the sample bottle for at least 1 minute and continue as described under Section 7.3.1.
- 10.5.3 Sludge samples having more than 30% solids should be treated by this method.
- 11 QUANTITATION DETERMINATION
- 11.1 ICP and GFAA Spectroscopic Techniques
- 11.1.1 Analytical results for water samples are expressed in ug/L; for soil samples, analytical results are expressed as mg/kg on a dry weight basis. Therefore, a determination of percent solids is required for soils, sediments, and sludge samples containing greater than 30% solids, as follows.
- 11.1.1.1 Immediately following the weighing of the sample to be processed for analysis (see Section 10), add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.
- 11.1.1.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105 °C. NOTE: Sample handling and drying should be conducted in a well-ventilated area.
- 11.1.1.3 Dry the sample overnight (12-24 hours), but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained. Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.
- NOTE: Drying time is defined as the elapsed time in the oven. Therefore, time in and out of the oven should be recorded to document the 12-hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of one-hour drying time in each cycle. Constant weight is defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.
- 11.1.1.4 Calculate percent solids by the formula below. This value will be used for calculating analyte concentration on a dry weight basis.
- $$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$
- 11.1.2 The concentrations determined in the digest are to be reported on the basis of

the dry weight of the sample for soil/sediment samples and sludge samples containing greater than 30% solids.

$$\text{Concentration (dry wt) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Concentration (mg/L)

V = Final volume in liters after sample preparation

W = Weight in kg of wet sample

S = % Solids/100

- 11.1.2.1 For aqueous samples and sludge samples containing less than 30% solids, the concentration of the elements in the digest can determined as follows:

$$\text{Concentration (ug/L)} = \frac{C \times V_F}{V_I}$$

Where,

C = Concentration (ug/L)

V<sub>F</sub> = Final volume in liters after sample preparation

V<sub>I</sub> = Volume in liters of the sample digested.

- 11.1.3 Preparation (reagent) blanks should be treated as specified in Section 10.

- 11.1.4 If dilutions were performed, the appropriate factor must be applied to sample values.

- 11.1.5 Report results for semiquantitative ICP screen of 42 elements in ug/L or mg/kg, depending on the matrix. Samples are semiquantified by comparing each analyte result to the established LTL for that analyte. All "peak offsets" or similar designations reported by ICP should be searched through stored spectrum files or the data confirmed through sample spikes before reporting.

- 11.2 Analysis of Mercury in Water by Manual and Automated Cold Vapor Technique

- 11.2.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

- 11.2.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/L} = \frac{\text{ug Hg in aliquot}}{\text{volume of aliquot in mL}} \times 1000$$

- 11.2.3 Report mercury concentrations as follows: below 0.20 ug/L, to 0.20 U; between 0.20 and 10.0 ug/L, to two significant figures; equal to or above 10.0 ug/L, to three significant figures.

- 11.3 Analysis of Mercury in Soil/Sediments by Manual Cold Vapor Technique

- 11.3.1 Measure the height of the unknown peak from the chart and read the mercury value from the standard curve.

- 11.3.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in the aliquot}}{\text{wt of the aliquot in gms}}$$

(based upon dry weight of the sample)

- 11.3.3 Report mercury concentrations for soil/sediment samples converted to units of mg/kg. The sample result or the detection limit for each sample must be corrected for sample weight and percent solids before reporting.

## 12 ANALYSIS OF COMPLEX SAMPLES

- 12.1 Some samples may contain high levels (>1500 mg/L) of the compounds of interest, interfering compounds, and/or polymeric materials. These may lead to inaccuracies in the determination of trace elements.

- 12.2. Physical, chemical, and/or spectral interference effects may arise. These interferences can be overcome by dilution of the sample, matrix matching, varying the temperature or by employing the Method of Standard Addition. These effects are described in Section 3.

- 12.3 The acceptable range for recovery of the predigested spike is 75-125 percent for all analytes. If any analyte falls outside the QC limits, proceed as described in Section 8.8.

## 13 METHOD PERFORMANCE

- 13.1 In an EPA round robin study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrations. Table 12 lists the true values, the mean reported values, and the mean percent relative standard deviations from this study.

- 13.2 The precision data obtainable for the electrothermal atomization AA method is given in Table 13.
- 13.3 The precision data for CVAA technique for analysis of mercury is given in Table 14.
- 14 GLOSSARY OF TERMS
- 14.1 Calibration blank -- A volume of deionized distilled water acidified with  $\text{HNO}_3$  and  $\text{HCl}$  used in establishing the analytical curve.
- 14.2 Calibration standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).
- 14.3 Continuing calibration verification (CCV) standard solutions -- A multi-element standard of known concentrations prepared by the laboratory to monitor and verify instrument performance on a daily basis.
- 14.4 Dissolved elements -- Those elements which will pass through a 0.45  $\mu\text{m}$  membrane filter.
- 14.5 Initial calibration verification (ICV) standard solutions -- A solution obtained from an outside source having known concentration values, used to verify the calibration standards.
- 14.6 Instrumental detection limits (IDL) -- Determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3-5x IDL on three nonconsecutive days, with seven consecutive measurements per day.
- 14.7 Interference check sample (ICS) -- A solution containing both interfering and analyte elements of known concentration, used to verify background and inter-element correction factors.
- 14.8 Laboratory control sample -- A control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analysis methods employed for the analytical samples.
- 14.9 Linear range -- The concentration range over which the analytical curve remains linear.
- 14.10 Lower threshold limit (LTL) -- Based on signal-to-noise ration of 2:1 for each element, expressed as mg/L. Levels lower than LTL are considered "not detected." The LTL for each element is highly dependent on sample matrix.
- 14.1 Method of Standard Addition (MSA) -- The standard addition technique involves the use of the unknown and the unknown-plus-a-known amount of standard by adding known amounts of standard to one or more aliquots of the processed sample solution. The MSA procedure is described in Section 8.15.
- 14.12 Minimum level (ML) -- The minimum level is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The laboratory is required to achieve the ML listed for each element in Table 11.
- 14.13 Preparation (reagent) blank -- A volume of deionized distilled water containing the same acid matrix as the calibration standards, that is carried through the entire analytical scheme.
- 14.14 Sensitivity -- The slope of the analytical curve, i.e., functional relationship between emission intensity or absorption and concentration.
- 14.15 Serial dilution analysis -- A five-fold dilution analysis used to establish a chemical or physical interference effect.
- 14.16 Soil samples -- Soils, sediments, and sludge samples containing more than 30% solids.
- 14.17 Suspended elements -- Those elements which are retained by a 0.45  $\mu\text{m}$  membrane filter.
- 14.18 Total elements -- The concentration determined on an unfiltered sample following vigorous digestion.
- 14.19 Water samples -- Aqueous samples and sludge samples containing 30% or less solids which are diluted and treated as water samples.

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Table 1  
RECOMMENDED WAVELENGTHS AND ESTIMATED  
INSTRUMENTAL DETECTION LIMITS FOR ELEMENTS  
ANALYZED BY ICP

Element	Wavelength (1) nm	Estimated Detection Limit (2) ug/L
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
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
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Tin	189.989 (3)	30
Titanium	334.941	3
Vanadium	292.402	8
Yttrium	371.030	2.5
Zinc	213.856	2

- (1) These wavelengths 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 Section 3.1.1). The use of alternate wavelengths should be reported (in nm) with the sample data.
- (2) Estimated detection limits 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) Nitrogen purge used at this wavelength.

Table 2  
RECOMMENDED WAVELENGTHS, ESTIMATED INSTRUMENTAL  
DETECTION LIMITS, AND OPTIMUM CONCENTRATION RANGE FOR  
ELEMENTS ANALYZED BY AA SPECTROSCOPY (1)

Element	Wavelength (nm)	Estimated Detection Limit (2) (ug/L)	Optimum Concentration Range (2) (ug/L)
<u>GFAA</u>			
Antimony	217.6	3	20-300
Arsenic	193.7	1	5-100
Lead	283.3(3)	1	5-100
Selenium	196.0	2	5-100
Thallium	276.8	1	5-100
<u>CVAA</u>			
Mercury	253.7	0.2	0.2-20

- (1) Values are taken from Methods 204.2 (Sb), 206.2 (As), 210.2 (Se), 213.2 (Cd), 218.2 (Cr), 239.2 (Pb), 270.2 (Se), 272.2 (Ag), 279.2 (Tl), "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Metals-4.
- (2) Concentration values and instrument conditions given are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas, and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than these recommended settings.
- (3) The line at 217.0 nm is more intense, and is recommended for instruments with background correction.

Table 3  
RECOMMENDED INSTRUMENTAL PARAMETERS FOR ANALYSIS OF TRACE ELEMENTS BY GFAA SPECTROSCOPY (1)

Element	Drying		Ashing		Atomizing		Purge Gas Atmosphere
	Time (sec)	Temperature (°C)	Time (sec)	Temperature (°C)	Time (sec)	Temperature (°C)	
Antimony	30	125	30	800	10	2700	Argon (2)
Arsenic	30	125	30	1100	10	2700	Argon
Lead	30	125	30	500	10	2700	Argon
Selenium	30	125	30	1200	10	2700	Argon
Thallium	30	125	30	400	10	2400	Argon (2)

(1) Other operating parameters should be set as specified by the particular instrument manufacturer.

(2) Nitrogen may be substituted as the purge gas (see Section 3.2.2).

Table 4  
ICP SCREEN ELEMENTS, WAVELENGTHS, AND LOWER THRESHOLD  
LIMITS

Element	Symbol	Wavelength (1)	LTL (2) (mg/L)
Bismuth	Bi	396.152	0.1
Cerium	Ce	413.765	1
Dysprosium	Dy	353.170	0.1
Erbium	Er	349.910	0.1
Europium	Eu	381.967	0.1
Gadolinium	Gd	342.247	0.5
Gallium	Ga	294.364	0.5
Germanium	Ge	265.118	0.5
Gold	Au	242.765	1
Hafnium	Hf	277.336	1
Holmium	Ho	345.600	0.5
Indium	In	230.606	1
Iodine	I	183.038	1
Iridium	Ir	224.268	1
Lanthanum	La	379.478	0.1
Lithium	Li	670.781	0.1
Lutetium	Lu	261.542	0.1
Neodymium	Nd	309.418	0.5
Niobium	Nb	401.225	1
Osmium	Os	228.226	0.1
Palladium	Pd	340.458	0.5
Phosphorus	P	213.618	1
Platinum	Pt	214.423	1
Potassium	K	766.490	1
Praseodymium	Pr	390.844	1
Rhenium	Re	221.426	1
Rhodium	Rh	233.477	1
Ruthenium	Ru	240.272	1
Samarium	Sm	359.260	0.5
Scandium	Sc	361.384	0.1
Silicon	Si	251.611	0.1
Strontium	Sr	407.771	0.1
Sulfur	S	180.731	1
Tantalum	Ta	226.230	0.5
Tellurium	Te	214.281	1
Terbium	Tb	350.917	0.5
Thorium	Th	283.730	1
Thulium	Tm	313.126	0.5
Tungsten	W	207.911	1
Uranium	U	385.958	1
Ytterbium	Yb	328.937	0.1
Zirconium	Zr	343.823	0.1

(1) Wavelength: Most sensitive line for analysis. Line choice is dependent on sample matrix. Use of secondary lines is necessary for some elements for spectral interference confirmation.

(2) 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.

Table 5  
EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Element	Wavelength (nm)	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 6**  
**ANALYTE AND INTERFERENT ELEMENTAL CONCENTRATIONS USED**  
**FOR INTERFERENCE MEASUREMENTS IN TABLE 5**

Analytes	mg/L	Interferents	mg/L
Aluminum	10	Aluminum	1000
Antimony	10	Calcium	1000
Arsenic	10	Chromium	200
Barium	1	Copper	200
Beryllium	1	Iron	1000
Boron	10	Magnesium	1000
Cadmium	10	Manganese	200
Calcium	1	Nickel	200
Chromium	1	Titanium	200
Cobalt	1	Vanadium	200
Copper	1		
Iron	1		
Lead	10		
Magnesium	1		
Manganese	1		
Molybdenum	10		
Nickel	10		
Selenium	10		
Silicon	1		
Sodium	10		
Thallium	10		
Vanadium	1		
Zinc	10		

**Table 7**  
**WORKING STANDARD CONCENTRATIONS**

Element	Symbol	Working Standard (1) (mg/L)
Bismuth	Bi	1.0
Cerium	Ce	1.0
Dysprosium	Dy	1.0
Erbium	Er	1.0
Europium	Eu	1.0
Gadolinium	Gd	1.0
Gallium	Ga	1.0
Germanium	Ge	10.0
Gold	Au	10.0
Hafnium	Hf	10.0
Holmium	Ho	10.0
Indium	In	10.0
Iodine	I	10.0
Iridium	Ir	10.0
Lanthanum	La	1.0
Lithium	Li	1.0
Lutetium	Lu	1.0
Neodymium	Nd	1.0
Niobium	Nb	10.0
Osmium	Os	10.0
Palladium	Pd	1.0
Phosphorus	P	10.0
Platinum	Pt	10.0
Potassium	K	150.0
Praseodymium	Pr	10.0
Rhenium	Re	10.0
Rhodium	Rh	10.0
Ruthenium	Ru	10.0
Samarium	Sm	1.0
Scandium	Sc	1.0
Silicon	Si	1.0
Strontium	Sr	1.0
Sulfur	S	10.0
Tantalum	Ta	1.0
Tellurium	Te	10.0
Terbium	Tb	1.0
Thorium	Th	10.0
Thulium	Tm	1.0
Tungsten	W	1.0
Uranium	U	10.0
Ytterbium	Yb	1.0
Zirconium	Zr	1.0

(1) Working Standard: For each 1 mg/L of final concentration needed, pipette 1 mL of stock solution and dilute to 1 L final volume. For example, for a 10 mg/L final concentration, pipette 10.0 mL of stock solution.

**Table 8**  
**QC SPECIFICATIONS FOR ANALYSIS OF PRECISION AND**  
**ACCURACY STANDARDS (1)**

ICP Spectroscopy		GFAA Spectroscopy	
Element (2)	Mean % RSD (3)	Element (2)	Mean % RSD (4)
Aluminum	17.2	Arsenic (5)	12.83
Arsenic	15.83	Lead	2.73
Beryllium	70.07	Selenium (5)	9.7
Cadmium	14.67		
Chromium	8.37		
Cobalt	11.7		
Copper	17.67		
Iron	8		
Lead	20.67		
Manganese	4.23		
Nickel	10.27		
Selenium	24.07		
Vanadium	1.93		
Zinc	20		

- (1) Acceptable range of percent recovery for all elements is 75-125%. As more data becomes available, these limits will be re-evaluated.
- (2) Other elements will be added as data becomes available to EPA.
- (3) Values derived from 21 determinations.
- (4) Values derived from 30 determinations, except for Pb. A total of 36 determinations were made for Pb.
- (5) Automated sample injection.

**Table 9**  
**MINIMUM LEVELS (ML) OF DETECTION**

ICP Analytes	ML (ug/L)	AA Analytes	ML (ug/L)
Aluminum	200	Antimony	20
Barium	200	Arsenic	10
Beryllium	5	Lead	5
Boron	10	Selenium	5
Cadmium	5	Thallium	10
Calcium	5000	Mercury	0.2
Chromium	10		
Cobalt	50		
Copper	25		
Iron	100		
Magnesium	5000		
Manganese	15		
Molybdenum	10		
Nickel	40		
Silver	10		
Sodium	5000		
Tin	30		
Titanium	5		
Vanadium	50		
Yttrium	5		
Zinc	20		

**Table 10**  
**INITIAL AND CONTINUING CALIBRATION VERIFICATION**  
**CONTROL LIMITS**

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP (1)/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120

- (1) Limits apply to quantitative ICP and semiquantitative ICP screen of 42 elements.

**Table 11**  
**ANALYTE AND INTERFERENT ELEMENTAL CONCENTRATIONS USED**  
**FOR ICP INTERFERENCE CHECK SAMPLE**

Analytes	mg/L	Interferents	mg/L
Barium	0.5	Aluminum	500
Beryllium	0.5	Calcium	500
Cadmium	1.0	Iron	200
Chromium	0.5	Magnesium	500
Cobalt	0.5		
Copper	0.5		
Lead	1.0		
Manganese	0.5		
Nickel	1.0		
Silver	1.0		
Vanadium	0.5		
Zinc	1.0		

Table 12  
ICP PRECISION AND ACCURACY DATA (1)

Element	Sample #1			Sample #2			Sample #3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean Percent RSD	True Value (ug/L)	Mean Reported Value (ug/L)	Mean Percent RSD	True Value (ug/L)	Mean Reported Value (ug/L)	Mean Percent RSD
Aluminum	700	696	5.6	60	62	33	160	161	13
Arsenic	200	208	7.5	22	19	23	60	63	17
Beryllium	750	733	6.2	20	20	9.8	180	176	5.2
Cadmium	50	48	12	2.5	2.9	16	14	13	16
Chromium	150	149	3.8	10	10	18	50	50	3.3
Cobalt	500	512	10	20	20	4.1	120	108	21
Copper	250	235	5.1	11	11	40	70	67	7.9
Iron	600	594	3.0	20	19	15	180	178	6.0
Lead	250	236	16	24	30	32	80	80	14
Manganese	350	345	2.7	15	15	6.7	100	99	3.3
Nickel	250	245	5.8	30	28	11	60	55	14
Selenium	40	32	21.9	6	8.5	42	10	8.5	8.3
Vanadium	750	749	1.8	70	69	2.9	170	169	1.1
Zinc	200	201	5.6	16	19	45	80	82	9.4

(1) Not all elements were analyzed by all laboratories.

Table 13  
PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS (1)

Element (2)	Wavelength (nm)	Sample Size (uL)	No. of Replicate Determinations	Mean Concentration (ug/L)	Relative Standard Deviation
Arsenic (3)	193.7	50	10	12.5	17.6
		50	10	28.4	13.7
		50	10	58.4	7.2
Lead	217.0	25	12	36.6	3.8
		25	12	103	2.9
		25	12	161	1.5
Selenium (3)	196.0	50	10	12.5	17.6
		50	10	29.6	5.6
		50	10	55.8	5.9

(1) Values taken from "Standard Methods for the Examination of Water and Wastewater," 16th edition, p 179 (1985).

(2) Other elements will be added as data becomes available to EPA.

(3) Automated sample injection.

Table 14  
PRECISION DATA FOR CVAA TECHNIQUE FOR ANALYSIS OF MERCURY (1)

Metal (Dissolved)	Metal Concentration (ug/L)	Relative Standard Deviation (%)	Relative Error (%)	Number of Participants
Inorganic	0.34	0.077	21	23
	4.2	0.56	14.4	21
Organic	4.2	0.36	8.4	21

(1) Data from Kopp, J.F., M.C. Longbottom, and L. B. Lobring, 1972, "Cold Vapour Method for Determining Mercury," J. Amer. Water Works Ass. 64:20, for distilled water samples.



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**EPA METHOD 160.3**  
**RESIDUE, TOTAL**  
**GRAVIMETRIC, DRIED AT 103-105 °C**

**Modification to Method 160.3 for analysis of solids:**

Accurately weigh approximately 50 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Proceed with drying the sample at 103-105 °C per Section 7.3.

## 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/l to 20,000 mg/l.
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**

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 91, Method 208A, (1975).

**EPA METHOD 335.2**  
**CYANIDE, TOTAL**  
**TITRIMETRIC, SPECTROPHOTOMETRIC**

**Modification to Method 335.2 for analysis of solids:**

Accurately weigh approximately 5 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Transfer the sample quantitatively into the CN distillation flask. Add deionized distilled water to bring the sample to the required 500 mL volume. Proceed with analysis starting with Section 8.2.1.



## 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/l (0.25 mg/250 ml of absorbing liquid).
  - 1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l.
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 ( $\text{pH} \geq 12$ ) 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 Bubber #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 11-164-50).
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  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$  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  $\text{H}_2\text{SO}_4$  to 500 ml of distilled water.
- 7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  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  $\text{AgNO}_3$ . 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  $\mu\text{g}$ ).
- 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  $\mu\text{g}$  CN.
- 7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g  $\text{AgNO}_3$  crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried  $\text{AgNO}_3$ , dissolve in distilled water, and dilute to 1000 ml (1 ml = 1 mg 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: Weigh 510 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  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  $\text{NO}_3$  and or  $\text{NO}_2$  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  $\text{H}_2\text{SO}_4$ .
- 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-pyrazolone 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 $\mu$ g CN)	Conc. $\mu$ g 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  $\pm 10\%$  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  $\mu$ g/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  $\mu\text{g/l}$ , in the original sample as follows:

$$\text{CN, } \mu\text{g/l} = \frac{A \times 1,000 \times 50}{B \times C}$$

where:

A =  $\mu\text{g}$  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<sub>3</sub> for titration of sample.

B = volume of AgNO<sub>3</sub> for titration of blank.

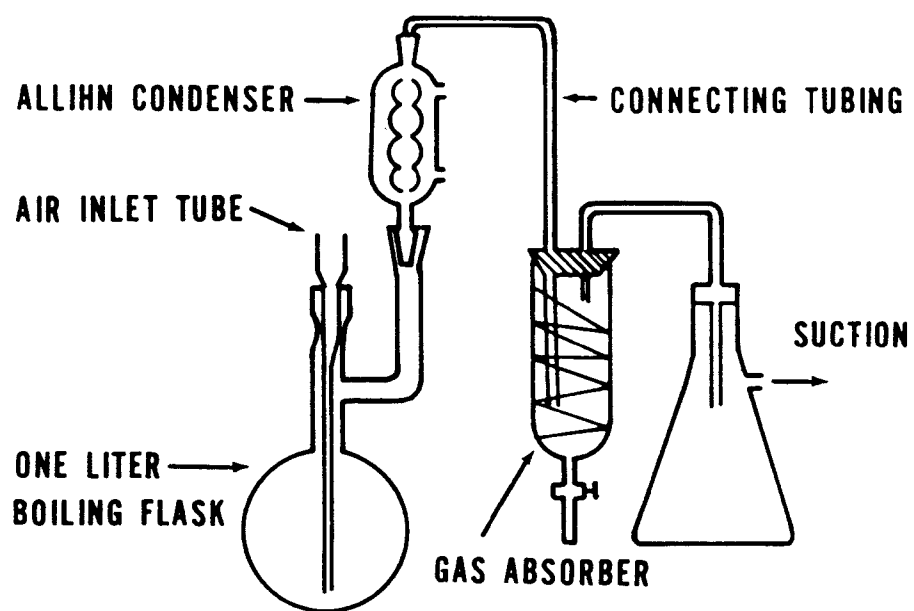
10. Precision and Accuracy

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  $\pm 0.005$ ,  $\pm 0.007$ ,  $\pm 0.031$  and  $\pm 0.094$ , 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.

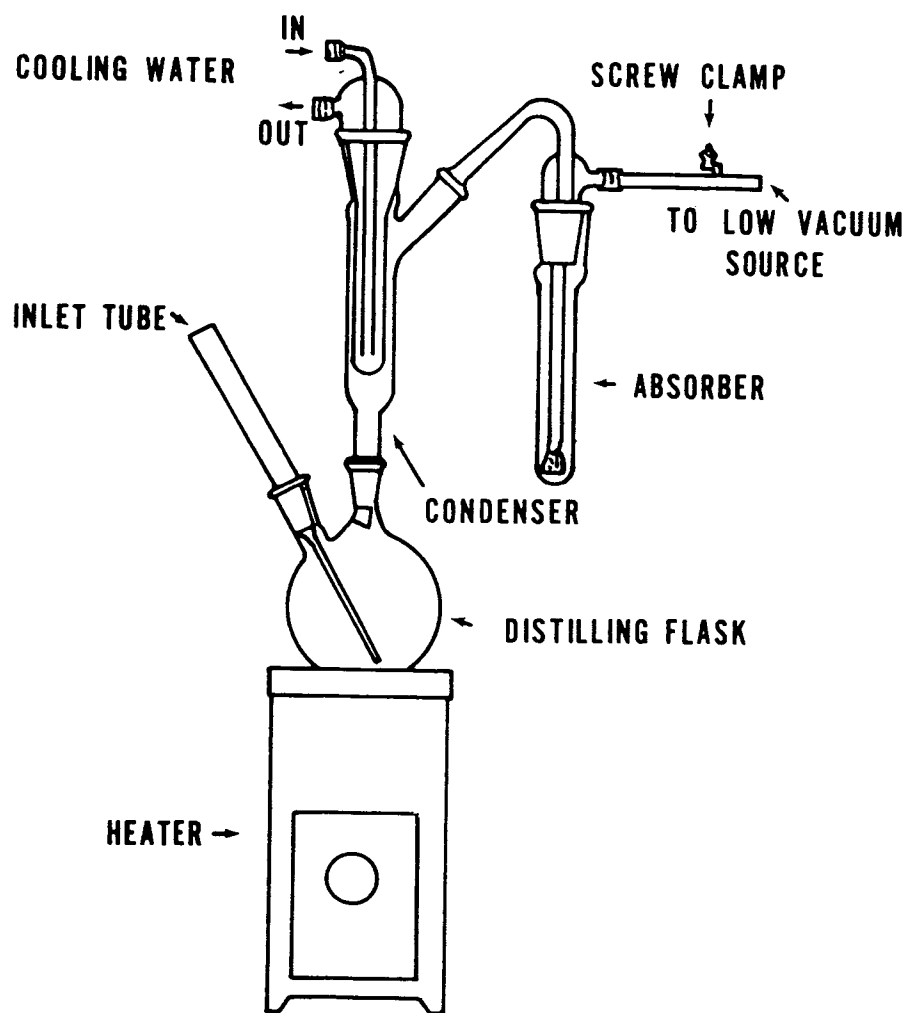
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**FIGURE 1**  
**CYANIDE DISTILLATION APPARATUS**





**FIGURE 2**  
**CYANIDE DISTILLATION APPARATUS**



**EPA METHOD 340.2**  
**FLUORIDE**  
**POTENTIOMETRIC, ION SELECTIVE ELECTRODE**

**Modification to Method 340.2 for analysis of solids:**

For determination of total fluoride in solids, Bellack distillation (Section 1.4) is necessary. Accurately weigh 5 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Quantitatively transfer the sample into the distillation flask. Add deionized distilled water to bring sample to 50 mL volume. Perform Bellack distillation per EPA Method 340.1, Section 6.1, using a stirring heating mantle as the heat source. To prevent bumping, place a stirring bar into the flask and stir the contents during the heating process. After distillation is complete, proceed with analysis by Method 340.2.

NOTE: Method 340.1 is included as part of this modification.

## FLUORIDE, TOTAL

### Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)

STORET NO. Total 00951

Dissolved 00950

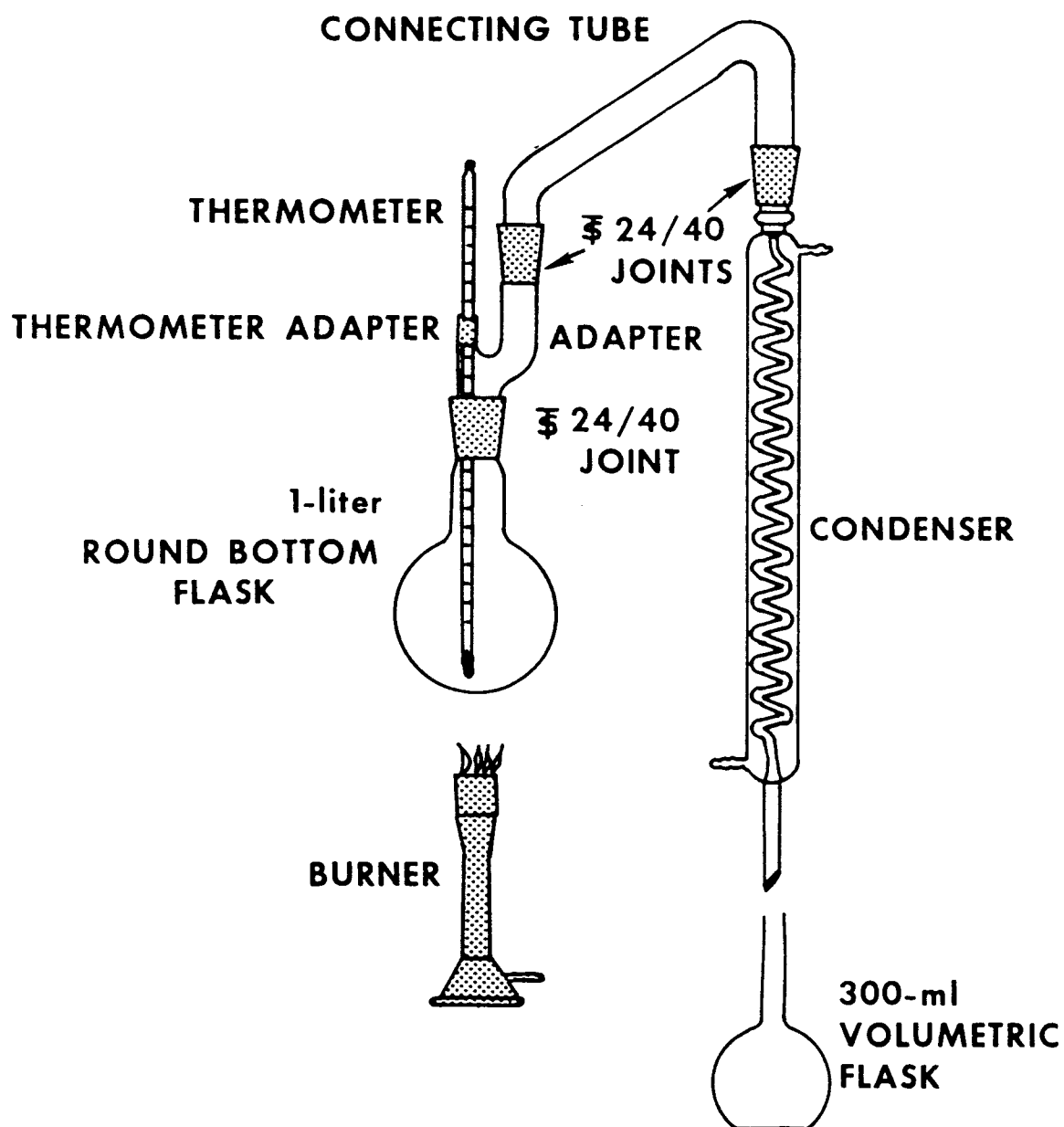
1. Scope and Application
  - 1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
  - 1.2 The method covers the range from 0.1 to about 1.4 mg/l F. This range may be extended to 1000 mg/l using the Fluoride Ion Selective Electrode Method (340.2) after distillation.
2. Summary of Method
  - 2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
  - 3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.
  - 3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Apparatus
  - 4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.
  - 4.2 Colorimeter: One of the following
    - 4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.
    - 4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.
5. Reagents
  - 5.1 Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, conc.

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Editorial revision 1974 and 1978

- 5.2 Silver sulfate,  $\text{Ag}_2\text{SO}_4$  crystals.
- 5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride,  $\text{NaF}$ , in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F.
- 5.4 Standard fluoride solution: Place 100 ml stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F.
- 5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 ml volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.
- 5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in approximately 25 ml distilled water in a 500 ml volumetric flask. Add 350 ml conc  $\text{HCl}$  and dilute to the mark with distilled water.
- 5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.
- 5.8 Reference solution: Add 10 ml SPADNS solution (5.5) to 100 ml distilled water. Dilute 7 ml conc  $\text{HCl}$  to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.
- 5.9 Sodium arsenite solution: Dissolve 5.0 g  $\text{NaAsO}_2$  in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).
6. Procedure
  - 6.1 Preliminary distillation
    - 6.1.1 Place 400 ml distilled water in the distilling flask.
    - 6.1.2 Carefully add 200 ml conc.  $\text{H}_2\text{SO}_4$  and swirl until contents are homogeneous.
    - 6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1) making sure all joints are tight.
    - 6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly  $180^\circ\text{C}$ . Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.
    - 6.1.5 Cool to  $120^\circ\text{C}$  or below.
    - 6.1.6 Add 300 ml sample, mix thoroughly, distill as in 6.1.4 until temperature reaches  $180^\circ\text{C}$ . Do not heat above  $180^\circ\text{C}$  to prevent sulfate carryover.
    - 6.1.7 Add  $\text{Ag}_2\text{SO}_4$  (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.
    - 6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.
    - 6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.
  - 6.2 Colorimetric Determination:
    - 6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/l by diluting appropriate quantities of standard fluoride solution (5.4) to 50 ml with distilled water.



**FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.**

- 6.2.2 Pipet 5.00 ml each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.
- 6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.
- 6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.
- 6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) NaAsO<sub>2</sub> solution (5.9) per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/l produce an error of 0.1 mg/l at 1.0 mg/l F.
- 6.2.6 Use a 50 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve.
- 6.2.7 Perform step 6.2.2 and 6.2.3.

## 7. Calculations

- 7.1 Read the concentration in the 50 ml sample using the standard curve (6.2.4)
- 7.2 Calculate as follows:

$$\text{mg/l F} = \frac{\text{mgF} \times 1,000}{\text{ml sample}}$$

- 7.3 When a sample (ml sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg/l F} = \frac{\text{mgF} \times 1,000}{\text{ml sample}} \times \frac{B}{C}$$

## 8. Precision and Accuracy

- 8.1 On a sample containing 0.83 mg/l F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/l F with a standard deviation of  $\pm 0.089$  mg/l.
- 8.2 On a sample containing 0.57 mg/l F (with 200 mg/l SO<sub>4</sub> and 10 mg/l Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/l F with a standard deviation of  $\pm 0.103$  mg/l.
- 8.3 On a sample containing 0.68 mg/l F (with 200 mg/l SO<sub>4</sub>, 2 mg/l Al and 2.5 mg/l [Na(PO<sub>3</sub>)<sub>6</sub>] as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/l F with a standard deviation of  $\pm 0.092$  mg/l. (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

## Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389–390 (Method No. 414A, Preliminary Distillation Step) and p. 393–394 (Method 414C SPADNS) 14th Edition, (1975).
2. Annual Book of ASTM Standards, Part 31, “Water”, Standard D 1179–72, Method A, p. 310 (1976).



# 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  $\text{Ag/Ag Cl, Cl}^-(0.3), \text{F}^-(0.001) \text{LaF/test solution/SCE/}$ .
3. Interferences
  - 3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of  $\text{Si}^{+4}$ ,  $\text{Fe}^{+3}$  and  $\text{Al}^{+3}$  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<sup>(1)</sup>
  - 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<sup>(2)</sup>. 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/l 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  $\pm 0.03$  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  $\pm 0.036$  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 351.3**  
**NITROGEN, KJELDAHL, TOTAL**  
**COLORIMETRIC; TITRIMETRIC; POTENTIOMETRIC**

**Modification to Method 351.3 for analysis of solids:**

Accurately weigh approximately 10 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Quantitatively transfer the sample to an 800 mL flask. Add deionized distilled water to bring the sample to 500 mL volume. Proceed with analysis.

# NITROGEN, KJELDAHL, TOTAL

## Method 351.3 (Colorimetric; Titrimetric; Potentiometric)

STORET NO. 00625

1. Scope and Application
  - 1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline 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 nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.
  - 1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/l.
  - 1.3 This method is described for macro and micro glassware systems.
2. Definitions
  - 2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ , under the conditions of digestion described below.
  - 2.2 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. This may be determined directly by removal of ammonia before digestion.
3. Summary of Method
  - 3.1 The sample is heated in the presence of conc. sulfuric acid,  $\text{K}_2\text{SO}_4$  and  $\text{HgSO}_4$  and evaporated until  $\text{SO}_3$  fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.
4. Sample Handling and Preservation
  - 4.1 Samples may be preserved by addition of 2 ml of conc.  $\text{H}_2\text{SO}_4$  per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.
5. Interference
  - 5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

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## 6. Apparatus

- 6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove  $\text{SO}_3$  fumes and water.
- 6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.
- 6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

## 7. Reagents

- 7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

**NOTE 1:** All solutions must be made with ammonia-free water.

- 7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide ( $\text{HgO}$ ) in 50 ml of 1:4 sulfuric acid (10.0 ml conc.  $\text{H}_2\text{SO}_4$  : 40 ml distilled water) and dilute to 100 ml with distilled water.
- 7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g  $\text{K}_2\text{SO}_4$  in 1300 ml distilled water and 400 ml conc.  $\text{H}_2\text{SO}_4$ . Add 50 ml mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.
- 7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g  $\text{NaOH}$  and 25 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in distilled water and dilute to 1 liter.
- 7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.
- 7.6 Boric acid solution: Dissolve 20 g boric acid,  $\text{H}_3\text{BO}_3$ , in water and dilute to 1 liter with distilled water.
- 7.7 Sulfuric acid, standard solution: (0.02 N) 1 ml = 0.28 mg  $\text{NH}_3\text{-N}$ . Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc.  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 1 liter with  $\text{CO}_2$ -free distilled water. Dilute 200 ml of this solution to 1 liter with  $\text{CO}_2$ -free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N  $\text{Na}_2\text{CO}_3$  solution. This last solution is prepared by dissolving 1.060 g anhydrous  $\text{Na}_2\text{CO}_3$ , oven-dried at  $140^\circ\text{C}$ , and diluting to 1 liter with  $\text{CO}_2$ -free distilled water.  
**NOTE 2:** An alternate and perhaps preferable method is to standardize the approximately 0.1 N  $\text{H}_2\text{SO}_4$  solution against a 0.100 N  $\text{Na}_2\text{CO}_3$  solution. By proper dilution the 0.02 N acid can be prepared.
- 7.8 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg  $\text{NH}_3\text{-N}$ . Dissolve 3.819 g  $\text{NH}_4\text{Cl}$  in water and make up to 1 liter in a volumetric flask with distilled water.
- 7.9 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg  $\text{NH}_3\text{-N}$ . Dilute 10.0 ml of the stock solution (7.8) with distilled water to 1 liter in a volumetric flask.
- 7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of  $\text{NaOH}$  in 500 ml of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.



**NOTE 3:** Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8. Procedure

8.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0-5	500
5-10	250
10-20	100
20-50	50.0
50-500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until  $\text{SO}_3$  fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide – thiosulfate solution (7.4) without mixing.

**NOTE 5:** Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 ml at the rate of 6–10 ml/min., into 50 ml of 2% boric acid (7.6) contained in a 500 ml Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/l, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

### 8.3 Micro Kjeldahl system

8.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until  $\text{SO}_3$  fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxide-thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 ml short-form Nessler tube.

8.3.4 Steam distill 30 ml at the rate of 6–10 ml/min., into 5 ml of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 ml. For concentrations above 1 mg/l the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N  $\text{H}_2\text{SO}_4$  (7.7), matching the endpoint against a blank containing the same volume of distilled water and  $\text{H}_3\text{BO}_3$  (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg $\text{NH}_3\text{-N}$	mg $\text{NH}_3\text{-N}/50.0$ ml
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg  $\text{NH}_3\text{-N}$  for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg  $\text{NH}_3\text{-N}$  from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method, (Method 350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled,

and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9. Calculation

- 9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{(A - B)N \times F \times 1,000}{S}$$

where:

A = milliliters of standard 0.020 N H<sub>2</sub>SO<sub>4</sub> solution used in titrating sample.

B = milliliters of standard 0.020 N H<sub>2</sub>SO<sub>4</sub> solution used in titrating blank.

N = normality of sulfuric acid solution.

F = milliequivalent weight of nitrogen (14 mg).

S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A - B) \times 280}{S}$$

- 9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1,000}{D} \times \frac{B}{C}$$

where:

A = mg NH<sub>3</sub>-N read from curve.

B = ml total distillate collected including the H<sub>3</sub>BO<sub>3</sub>.

C = ml distillate taken for Nesslerization.

D = ml of original sample taken.

- 9.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:

Organic Kjeldahl Nitrogen = TKN - (NH<sub>3</sub>-N.)

- 9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{B}{D} \times A$$

where:

A = mg NH<sub>3</sub>-N/l from electrode method standard curve.

B = volume of diluted distillate in ml.

D = ml of original sample taken.

#### 10. Precision

- 10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.20	0.197	+ 15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	- 1.67	-0.08

(FWPCA Method Study 2, Nutrient Analyses)

#### Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7-77-017.

**EPA METHOD 353.2**  
**NITROGEN, NITRATE-NITRITE**  
**COLORIMETRIC, AUTOMATED, CADMIUM REDUCTION**

**Modification to Method 353.2 for analysis of solids:**

Accurately weigh 5 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Add deionized distilled water to bring the sample to 100 mL volume. Place the mixture on a shaker for 4 hours, then filter through Whatman #40 (or equivalent). Proceed with analysis starting with Section 7.1.

## 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<sub>2</sub>SO<sub>4</sub> 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 AAI) consisting of the following components:
    - 5.1.1 Sampler.
    - 5.1.2 Manifold (AAI) or analytical cartridge (AAI).
    - 5.1.3 Proportioning Pump
    - 5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
    - 5.1.5 Recorder.

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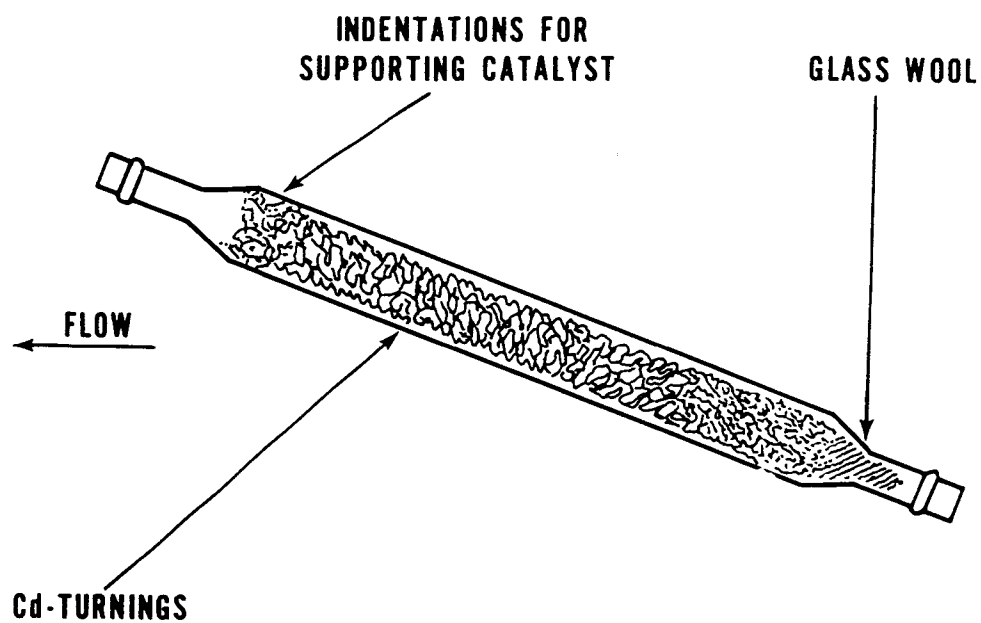
5.1.6 Digital printer for AAI (Optional).

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 AAI: 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  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  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  $\text{H}_2\text{SO}_4$ , use 2 ml  $\text{H}_2\text{SO}_4$  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  $\text{KNO}_3$  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  $\text{NO}_3\text{-N}$ .
- 6.12 Stock nitrite solution: Dissolve 6.072 g  $\text{KNO}_2$  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  $\text{NO}_2\text{-N}$ .
- 6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg  $\text{NO}_3\text{-N}$ . 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  $\text{NO}_2\text{-N}$ . 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., mg $\text{NO}_2\text{-N}$ or $\text{NO}_3\text{-N/l}$	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:

$\text{NaCl}$ - 24.53 g/l	$\text{MgCl}_2$ - 5.20 g/l	$\text{Na}_2\text{SO}_4$ - 4.09 g/l
$\text{CaCl}_2$ - 1.16 g/l	$\text{KCl}$ - 0.70 g/l	$\text{NaHCO}_3$ - 0.20 g/l
$\text{KBr}$ - 0.10 g/l	$\text{H}_3\text{BO}_3$ - 0.03 g/l	$\text{SrCl}_2$ - 0.03 g/l
$\text{NaF}$ - 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.  $\text{HCl}$  or conc.  $\text{NH}_4\text{OH}$ .
- 7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in  $20^\circ$  incline position (AAI). Care should be taken not to introduce air into reduction column on the AAI.
- 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 AAI, 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  $\text{NO}_2$  and/or  $\text{NO}_3$  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, %	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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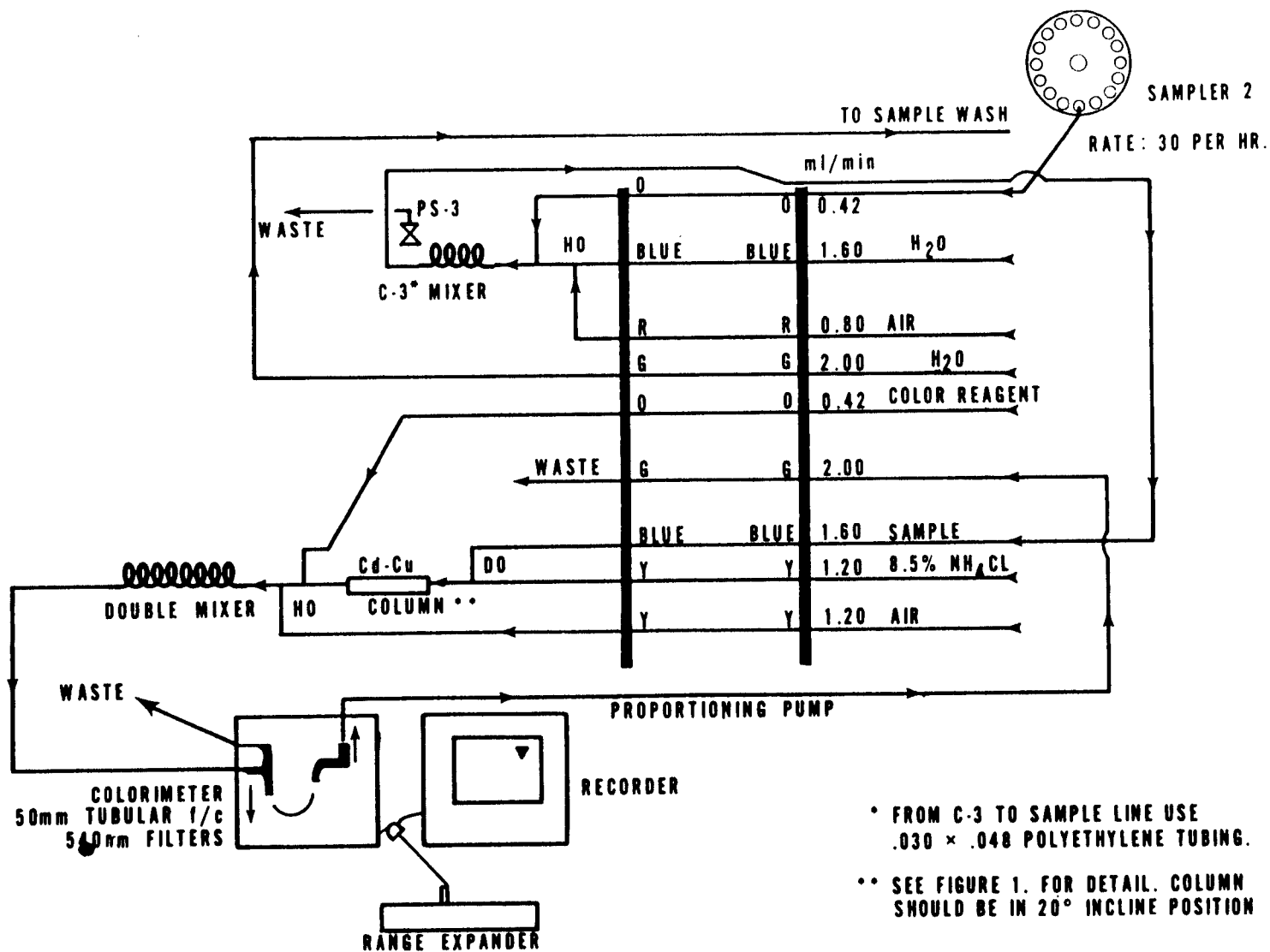


FIGURE 2. NITRATE - NITRITE MANIFOLD AA-1

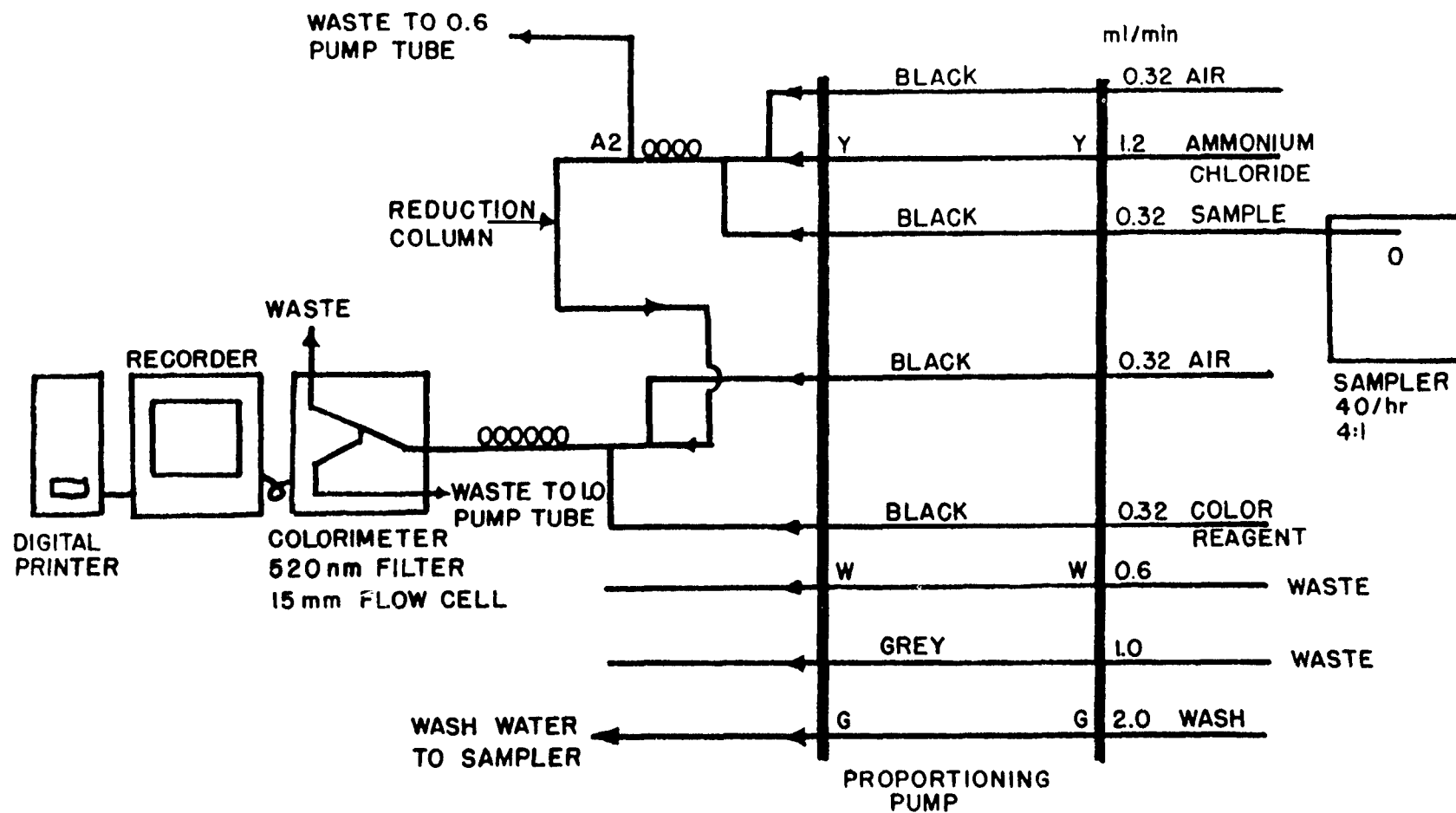


FIGURE 3 NITRATE-NITRITE MANIFOLD AA II



**EPA METHOD 365.2**  
**PHOSPHORUS, ALL FORMS**  
**COLORIMETRIC, ASCORBIC ACID, SINGLE REAGENT**

**Modification to Method 365.2 for analysis of solids:**

Accurately weigh approximately 0.5 grams of soil, sediment, or sludge sample to the nearest 0.1 mg. Transfer the sample quantitatively to a 125 mL Erlenmeyer flask. Add deionized distilled water to bring the sample to the required 50 mL volume. Proceed with analysis starting with Section 8.1.



## PHOSPHORUS, ALL FORMS

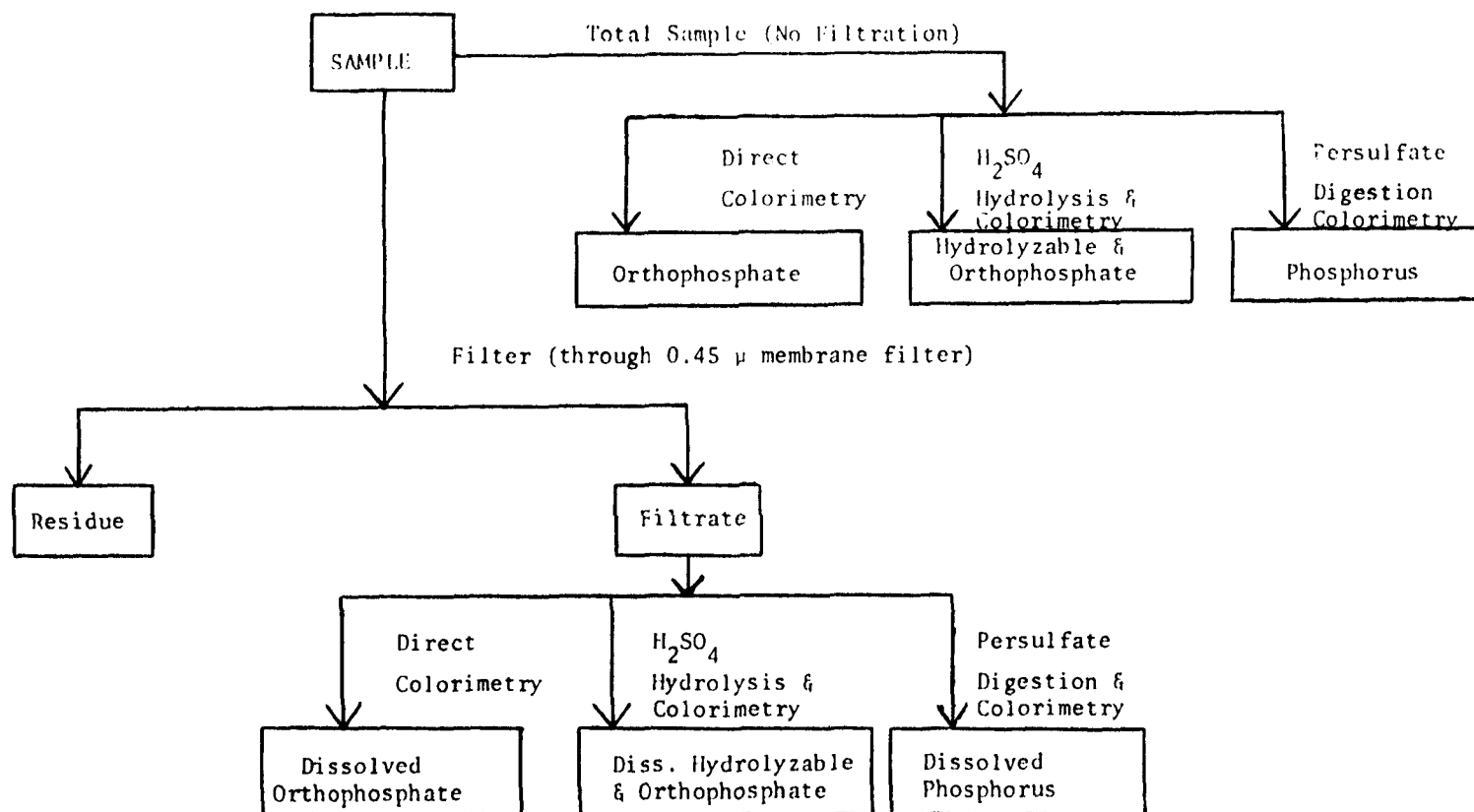
### Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent)

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<sup>(2)</sup>.
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.  $\text{H}_2\text{SO}_4$  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  $[(\text{PO}_4)^{-3}]$  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 polyphosphorus.  $[(\text{P}_2\text{O}_7)^{-4}, (\text{P}_3\text{O}_{10})^{-5}, \text{etc.}]$  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.  $\text{H}_2\text{SO}_4$  with distilled water to 500 ml.
- 7.2 Antimony potassium tartrate solution: Weigh 1.3715 g  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$ , dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at  $4^\circ\text{C}$  in a dark, glass-stoppered bottle.
- 7.3 Ammonium molybdate solution: Dissolve 20 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 500 ml of distilled water. Store in a plastic bottle at  $4^\circ\text{C}$ .
- 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  $4^\circ\text{C}$ .
- 7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N  $\text{H}_2\text{SO}_4$ , (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.  $\text{H}_2\text{SO}_4$  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,  $\text{KH}_2\text{PO}_4$ , which has been dried in an oven at  $105^\circ\text{C}$ . 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  $\mu\text{g}$  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  $\text{H}_2\text{SO}_4$  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  $121^\circ\text{C}$  (15–20 psi).

8.1.4 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to  $7.0 \pm 0.2$  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  $\text{H}_2\text{SO}_4$  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  $121^\circ\text{C}$  (15–20 psi).

8.2.3 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to  $7.0 \pm 0.2$  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  $7 \pm 0.2$  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  $\pm 2\%$  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/l. 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, %	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, %	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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