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

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Method 1624: Volatile Organic Compounds by Isotope Dilution GCMS

Method 1625: 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 semivolatile, 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.

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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_6	666-52-4	616 V
acrolein	34210	107-02-8	002 V	001 V	d_4	33984-05-3	202 V
acrylonitrile	34215	107-13-1	003 V	002 V	d_3	53807-26-4	203 V
benzene	34030	71-43-2	004 V	003 V	d_6	1076-43-3	204 V
bromodichloromethane	32101	75-27-4	048 V	012 V	^{13}C	93952-10-4	248 V
bromoform	32104	75-25-2	047 V	005 V	^{13}C	72802-81-4	247 V
bromomethane	34413	74-83-9	046 V	020 V	d_3	1111-88-2	246 V
carbon tetrachloride	32102	56-23-5	006 V	006 V	^{13}C	32488-50-9	206 V
chlorobenzene	34301	108-90-7	007 V	007 V	d_5	3114-55-4	207 V
chloroethane	34311	75-00-3	016 V	009 V	d_5	19199-91-8	216 V
2-chloroethylvinyl ether	34576	110-75-8	019 V	010 V			
chloroform	32106	67-66-3	023 V	011 V	^{13}C	31717-44-9	223 V
chloromethane	34418	74-87-3	045 V	021 V	d_3	1111-89-3	245 V
dibromochloromethane	32105	124-48-1	051 V	008 V	^{13}C	93951-99-6	251 V
1,1-dichloroethane	34496	75-34-3	013 V	014 V	d_3	56912-77-7	213 V
1,2-dichloroethane	32103	107-06-2	010 V	015 V	d_4	17070-07-0	210 V
1,1-dichloroethene	34501	75-35-4	029 V	016 V	d_2	22280-73-5	229 V
trans-1,2-dichlorethene	34546	156-60-5	030 V	026 V	d_3	42366-47-2	230 V
1,2-dichloropropane	34541	78-87-5	032 V	017 V	d_6	93952-08-0	232 V
trans-1,3-dichloropropene	34699	10061-02-6	033 V		d_4	93951-86-1	233 V
diethyl ether	81576	60-29-7	515 V		d_{10}	2679-89-2	615 V
p-dioxane	81582	123-91-1	527 V		d_8	17647-74-4	627 V
ethylbenzene	34371	100-41-4	038 V	019 V	d_{10}	25837-05-2	238 V
methylene chloride	34423	75-09-2	044 V	022 V	d_2	1665-00-5	244 V
methyl ethyl ketone	81595	78-93-3	514 V		d_3	53389-26-7	614 V
1,1,2,2-tetrachloroethane	34516	79-34-5	015 V	023 V	d_2	33685-54-0	215 V
tetrachloroethene	34475	127-18-4	085 V	024 V	$^{13}C_2$	32488-49-6	285 V
toluene	34010	108-88-3	086 V	025 V	d_8	2037-26-5	286 V
1,1,1-trichloroethane	34506	71-55-6	011 V	027 V	d_3	2747-58-2	211 V
1,1,2-trichloroethane	34511	79-00-5	014 V	028 V	$^{13}C_2$	93952-09-1	214 V
trichloroethene	39180	79-01-6	087 V	029 V	$^{13}C_2$	93952-00-2	287 V
vinyl chloride	39175	75-01-4	088 V	031 V	d_3	6745-35-3	288 V

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
532	allyl alcohol*	107-18-6
533	carbon disulfide	75-15-0
534	2-chloro-1,3-butadiene (chloroprene)	126-99-8
535	chloroacetonitrile*	107-14-2
536	3-chloropropene	107-05-1
537	crotonaldehyde*	123-73-9
538	1,2-dibromoethane (EDB)	106-93-4
539	dibromomethane	74-95-3
540	trans-1,4-dichloro-2-butene	110-57-6
541	1,3-dichloropropane	142-28-9
542	cis-1,3-dichloropropene	10061-01-5
543	ethyl cyanide*	107-12-0
544	ethyl methacrylate	97-63-2
545	2-hexanone	591-78-6
546	iodomethane	74-88-4
547	isobutyl alcohol*	78-83-1
548	methacrylonitrile	126-98-7
549	methyl methacrylate	78-83-1
550	4-methyl-2-pentanone	108-10-1
551	1,1,1,2-tetrachloroethane	630-20-6
552	trichlorofluoromethane	75-69-4
553	1,2,3-trichloropropane	96-18-4
554	vinyl acetate	108-05-4
951	m-xylene	108-38-3
952	o- + p-xylene	

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

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: Mean (sec)	Retention time: EGD Ref	Retention time: Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4): low solids (ug/kg)	Method Detection Limit (4): high solids (ug/kg)
245	chloromethane-d_3	147	181	0.141 - 0.270	50		
345	chloromethane	148	245	0.922 - 1.210	50	207*	13
246	bromomethane-d_3	243	181	0.233 - 0.423	50		
346	bromomethane	246	246	0.898 - 1.195	50	148*	11
288	vinyl chloride-d_3	301	181	0.286 - 0.501	50		
388	vinyl chloride	304	288	0.946 - 1.023	10	190*	11
216	chloroethane-d_5	378	181	0.373 - 0.620	50		
316	chloroethane	386	216	0.999 - 1.060	50	789*	24
244	methylene chloride-d_2	512	181	0.582 - 0.813	10		
344	methylene chloride	517	244	0.999 - 1.017	10	566*	280*
546	iodomethane	498	181	0.68			
616	acetone-d_6	554	181	0.628 - 0.889	50		
716	acetone	565	616	0.984 - 1.019	50	3561*	322*
202	acrolein-d_4	564	181	0.641 - 0.903	(5)	50	

Table 3 (continued)

GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Retention time Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	Method Detection Limit (4) high solids (ug/kg)
302	acrolein	566	202	0.984 - 1.018 (5)	50	377*	18
203	acrylonitrile-d_3	606	181	0.735 - 0.926	50		
303	acrylonitrile	612	203	0.985 - 1.030	50	360*	9
533	carbon disulfide	631	181	0.86			
552	trichlorofluoromethane	663	181	0.91			
543	ethyl cyanide	672	181	0.92			
229	1,1-dichloroethene-d_2	696	181	0.903 - 0.976	10		
329	1,1-dichloroethene	696	229	0.999 - 1.011	10	31	5
536	3-chloropropene	696	181	0.95			
532	allyl alcohol	703	181	0.96			
181	bromochloromethane (I.S.)	730	181	1.000 - 1.000	10		
213	1,1-dichloroethane-d_3	778	181	1.031 - 1.119	10		
313	1,1-dichloroethane	786	213	0.999 - 1.014	10	16	1
615	diethyl ether-d_{10}	804	181	1.067 - 1.254	50		
715	diethyl ether	820	615	1.010 - 1.048	50	63	12
230	trans-1,2-dichloroethene-d_2	821	181	1.056 - 1.228	10		
330	trans-1,2-dichloroethene	821	230	0.996 - 1.011	10	41	3
614	methyl ethyl ketone-d_3	840	181	0.646 - 1.202	50		
714	methyl ethyl ketone	848	614	0.992 - 1.055	50	241*	80*
223	chloroform-$^{13}C_1$	861	181	1.092 - 1.322	10		
323	chloroform	861	223	0.961 - 1.009	10	21	2
535	chloroacetonitrile	884	181	1.21			
210	1,2-dichloroethane-d_4	901	181	1.187 - 1.416	10		
310	1,2-dichloroethane	910	210	0.973 - 1.032	10	23	3
539	dibromomethane	910	181	1.25			
548	methacrylonitrile	921	181	1.26			
547	isobutyl alcohol	962	181	1.32			
211	1,1,1-trichloroethane-$^{13}C_2$	989	181	1.293 - 1.598	10		
311	1,1,1-trichloroethane	999	211	0.989 - 1.044	10	16	4
627	p-dioxane-d_8	982	181	1.262 - 1.448 (5)	50		
727	p-dioxane	1001	627	1.008 - 1.040 (5)	50	--	140*
206	carbon tetrachloride-$^{13}C_1$	1018	182	0.754 - 0.805	10		
306	carbon tetrachloride	1018	206	0.938 - 1.005	10	87	9
554	vinyl acetate	1031	182	0.79			
248	bromodichloromethane-$^{13}C_1$	1045	182	0.766 - 0.825	10		
348	bromodichloromethane	1045	248	0.978 - 1.013	10	28	3
534	2-chloro-1,3-butadiene	1084	182	0.83			
537	crotonaldehyde	1098	182	0.84			
232	1,2-dichloropropane-d_6	1123	182	0.830 - 0.880	10		
332	1,2-dichloropropane	1134	232	0.984 - 1.018	10	29	5
542	cis-1,3-dichloropropene	1138	182	0.87			
287	trichloroethene-$^{13}C_2$	1172	182	0.897 - 0.917	10		
387	trichloroethene	1187	287	0.991 - 1.037	10	41	2
541	1,3-dichloropropane	1196	182	0.92			
204	benzene-d_6	1200	182	0.888 - 0.952	10		
304	benzene	1212	204	1.002 - 1.026	10	23	8
251	chlorodibromomethane-$^{13}C_1$	1222	182	0.915 - 0.949	10		
351	chlorodibromomethane	1222	251	0.989 - 1.030	10	15	2
214	1,1,2-trichloroethane-$^{13}C_2$	1224	182	0.922 - 0.953	10		
314	1,1,2-trichloroethane	1224	214	0.975 - 1.027	10	26	1

Table 3 (continued)

GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS

EGD No. (1)	Compound	Retention time			Minimum 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_4	1226	182	0.922 - 0.959	10		
333	trans-1,3-dichloropropene	1226	233	0.993 - 1.016	10	(6)*	(6)*
019	2-chloroethylvinyl ether	1278	182	0.983 - 1.026	10	122	21
538	1,2-dibromoethane	1279	182	0.98			
182	2-bromo-1-chloropropane (I.S.	1306	182	1.000 - 1.000	10		
549	methyl methacrylate	1379	182	1.06			
247	bromoform-$^{13}C_1$	1386	182	1.048 - 1.087	10		
347	bromoform	1386	247	0.992 - 1.003	10	91	7
551	1,1,1,2-tetrachloroethane	1408	182	1.08			
550	4-methyl-2-pentanone	1435	183	0.92			
553	1,2,3-trichloropropane	1520	183	0.98			
215	1,1,2,2-tetrachloroethane-d_2	1525	183	0.969 - 0.996	10		
315	1,1,2,2-tetrachloroethane	1525	215	0.890 - 1.016	10	20	6
545	2-hexanone	1525	183	0.98			
285	tetrachloroethene-$^{13}C_2$	1528	183	0.966 - 0.996	10		
385	tetrachloroethene	1528	285	0.997 - 1.003	10	106	10
540	trans-1,4-dichloro-2-butene	1551	183	1.00			
183	1,4-dichlorobutane (int std)	1555	183	1.000 - 1.000	10		
544	ethyl methacrylate	1594	183	1.03			
286	toluene-d_8	1603	183	1.016 - 1.054	10		
386	toluene	1619	286	1.001 - 1.019	10	27	4
207	chlorobenzene-d_5	1679	183	1.066 - 1.135	10		
307	chlorobenzene	1679	207	0.914 - 1.019	10	21	58*
238	ethylbenzene-d_{10}	1802	183	1.144 - 1.293	10		
338	ethylbenzene	1820	238	0.981 - 1.018	10	28	4
185	bromofluorobenzene	1985	183	1.255 - 1.290	10		
951	m-xylene	2348	183	1.51	10		
952	o- + p-xylene	2446	183	1.57	10		

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

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

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

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

(5) Specification derived from related compound.

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

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

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

Carrier gas: helium at 40 mL/min.

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

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

4 SAFETY

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

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

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

5 APPARATUS AND MATERIALS

5.1 Sample bottles for discrete sampling

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

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

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

5.2.1 Purging devices for water and soil samples

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

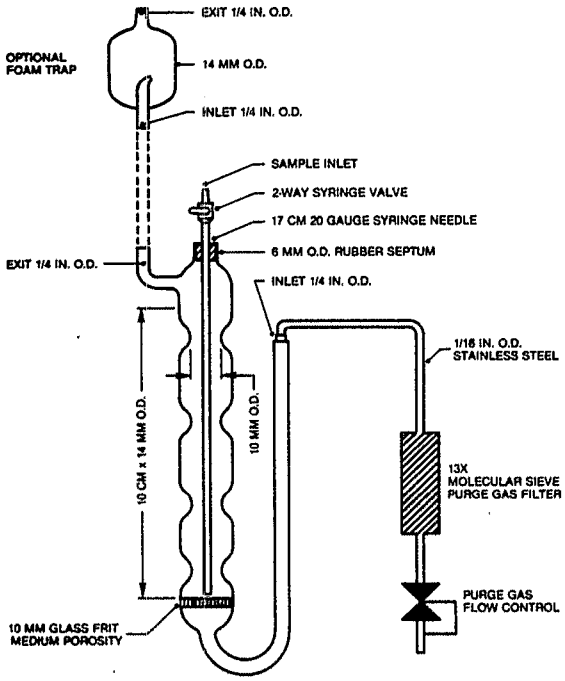

FIGURE 1 Purging Device for Waters

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

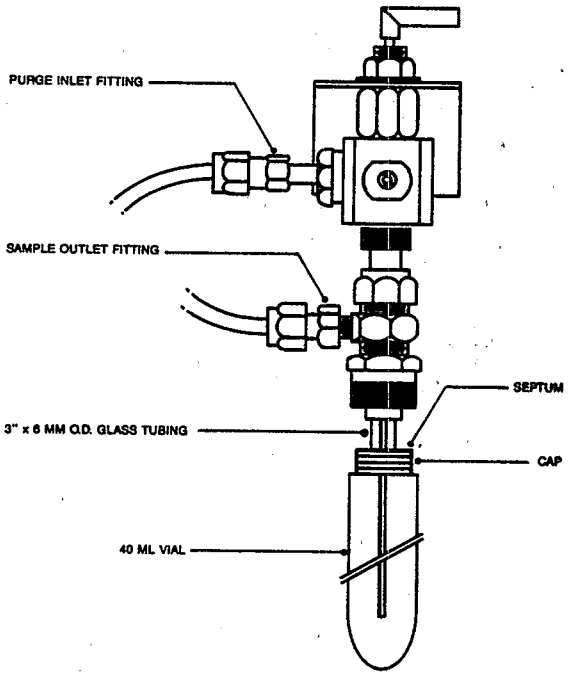

FIGURE 2 Purging Device for Soils or Waters

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

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

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

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

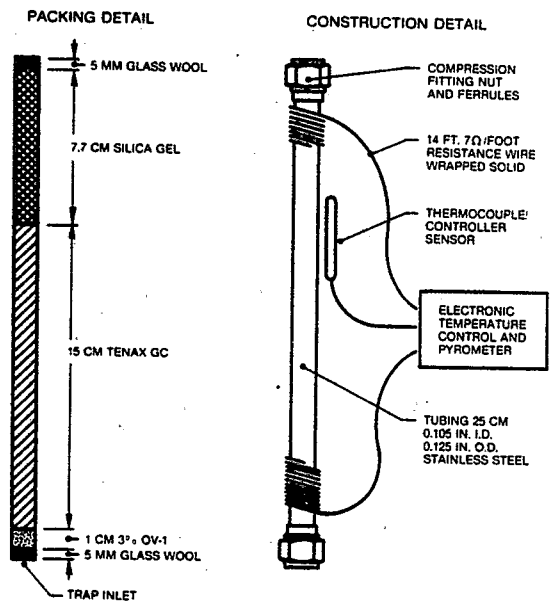

FIGURE 3 Trap Construction and Packings

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.

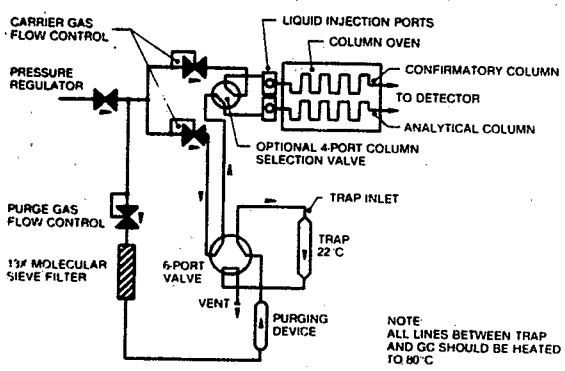

FIGURE 4 Schematic of Purge and Trap Device--Purge Mode

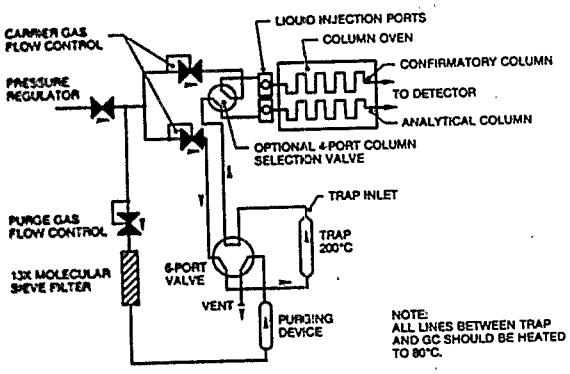

FIGURE 5 Schematic of Purge and Trap Device--Desorb Mode

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

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

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

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

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

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

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

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

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

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

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

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

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

5.11 Balances

5.11.1 Analytical, capable of weighing 0.1 mg.

5.11.2 Top loading, capable of weighing 10 mg.

5.12 Equipment for determining percent moisture

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

5.12.2 Dessicator.

5.12.3 Beakers--50 - 100 mL.

6 REAGENTS AND STANDARDS

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

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

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

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

6.2 Sodium thiosulfate--ACS granular.

6.3 Methanol--pesticide quality or equivalent.

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

6.5 Preparation of stock solutions--prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in Section 4.

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

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

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

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

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

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

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

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

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

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards

that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

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

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

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

6.7.2 Aqueous performance standard--an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (Section 11). This standard shall contain either 20 or 100 ug/L of the labeled and pollutant gases and water soluble compounds, 10 ug/L BFB, and 20 ug/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 ug/L aqueous calibration standard (Section 6.7.1).

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

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

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

7 CALIBRATION

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

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

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

7.2.1 For the compounds in Table 1 and other compounds for which the GCMS is to be calibrated, obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. 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_6	58/64			
acrolein	d_4	56/60			
acrylonitrile	d_3	53/56			
allyl alcohol		57	181	(3)	0.20
benzene	d_6	78/84			
2-bromo-1-chloropropane (4)		77			
bromochloromethane (4)		128			
bromodichloromethane	^{13}C	83/86			
bromoform	^{13}C	173/176			
bromomethane	d_3	96/99			
carbon disulfide		76	181	1.93	2.02
carbon tetrachloride	^{13}C	47/48			
2-chloro-1,3-butadiene		53	182	0.29	0.50
chloroacetonitrile		75	181	(3)	1.12
chlorobenzene	d_5	112/117			
chloroethane	d_5	64/71			
2-chloroethylvinyl ether	d_7	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}C	85/86			
chloromethane	d_3	50/53			
3-chloropropene		76	181	0.43	0.63
crotonaldehyde		70	182	(3)	0.090
dibromochloromethane	^{13}C	129/130			
1,2-dibromoethane		107	182	0.86	0.68
dibromomethane		93	181	1.35	1.91
1,4-dichlorobutane (4)		55			
trans-1,4-dichloro-2-butene		75	183	0.093	0.14
1,1-dichloroethane	d_3	63/66			
1,2-dichloroethane	d_4	62/67			
1,1-dichloroethene	d_2	61/65			
trans-1,2-dichlorethene	d_2	61/65			
1,2-dichloropropane	d_6	63/67			
1,3-dichloropropane		76	182	0.89	0.88
cis-1,3-dichloropropene		75	182	0.29	0.41
trans-1,3-dichloropropene	d_4	75/79			
diethyl ether	d_{10}	74/84			
p-dioxane	d_8	88/96			
ethyl cyanide		54	181	(3)	1.26
ethyl methacrylate		69	183	0.69	0.52
ethylbenzene	d_{10}	106/116			
2-hexanone		58	183	0.076	0.33
iodomethane		142	181	4.55	2.55
isobutyl alcohol		74	181	(3)	0.22
methylene chloride	d_2	84/88			
methyl ethyl ketone	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	d_2	83/84			
tetrachloroethene	$^{13}C_2$	164/172			
toluene	d_8	92/100			
1,1,1-trichloroethane	d_3	97/102			
1,1,2-trichloroethane	$^{13}C_2$	83/84			
trichloroethene	$^{13}C_2$	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	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 (ug/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d_8 is given in Figure 6.

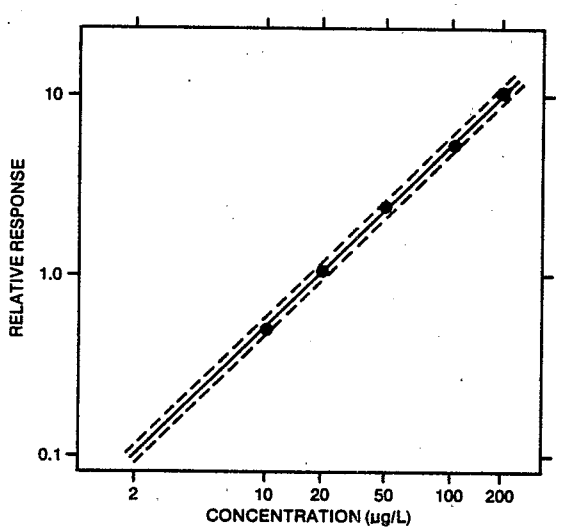

FIGURE 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window

Also shown are the ± 10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration (Section 7.4.4).

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).

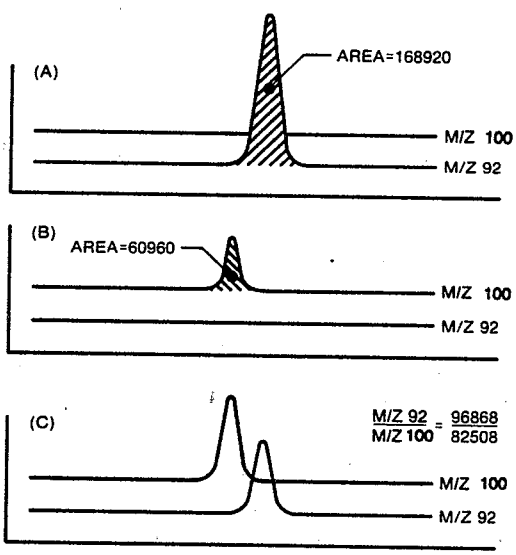

FIGURE 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-d8, and (C) a Mixture of Toluene and Toluene-d8

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:

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

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

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

The RR for the above data is then calculated using the equation given in Section 7.4.1. For the example, 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 ± 2 °C (Section 10). For these samples, the analytical system may be calibrated using a purge temperature of 40 ± 2 °C in order to more closely approximate the behavior of the compounds of interest in high solids samples.

8 QUALITY ASSURANCE/QUALITY CONTROL

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

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

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

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

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (Section 14.2).

8.1.5 The laboratory shall, on an 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 (X) in ug/L and the standard deviation of the recovery (s) in ug/L for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

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

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

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

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

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

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

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

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

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

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

8.5.1 The level at which the purge and trap system will carry greater than 5 ug/L of a pollutant of interest (Tables 1 and 2) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds.

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) s (ug/L)	X (ug/L)	Labeled compound recovery (Sect. 8.3 and 14.2) P (%)	Labeled and native compound on-going accuracy (Sect. 11.5) 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 ± 5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

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

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

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

10.4 Samples containing less than one percent solids

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

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

10.4.3 Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber. Purge the sample per Section 10.7.

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

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

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

10.5.5 Add an appropriate amount of the labeled compound spiking solution (Section 6.6) to the sample in the purge vessel. Place a cap on the purging vessel and and shake vigorously to further disperse the sample. Attach the purge vessel to the purging device, 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 ± 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 ± 0.1 minutes at 20 - 25 °C for samples containing less than one percent solids. Purge samples containing one percent solids or greater at 40 ± 2 °C. If the compounds in Table 2 that do not purge at 20 - 40 °C are to be determined, a purge temperature of 80 ± 5 °C is used.

10.8 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 °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 °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 °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 on-going accuracy in Table 6.

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

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

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

11.5.1.2 Compute the concentration for only those compounds which failed the first test (Section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds, and analyses of blanks and samples may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the system (Section 7), and repeat the entire test (Section 11.1) for all compounds.

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

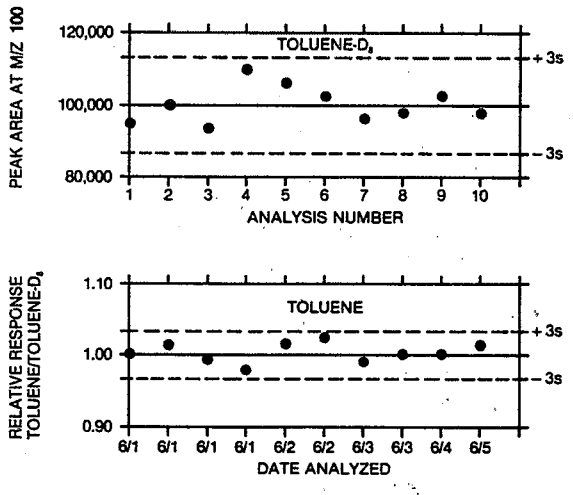

FIGURE 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d_8 (lower graph) Plotted as Function of Time or Analysis Number

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 ± 60 seconds or ± 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:

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.

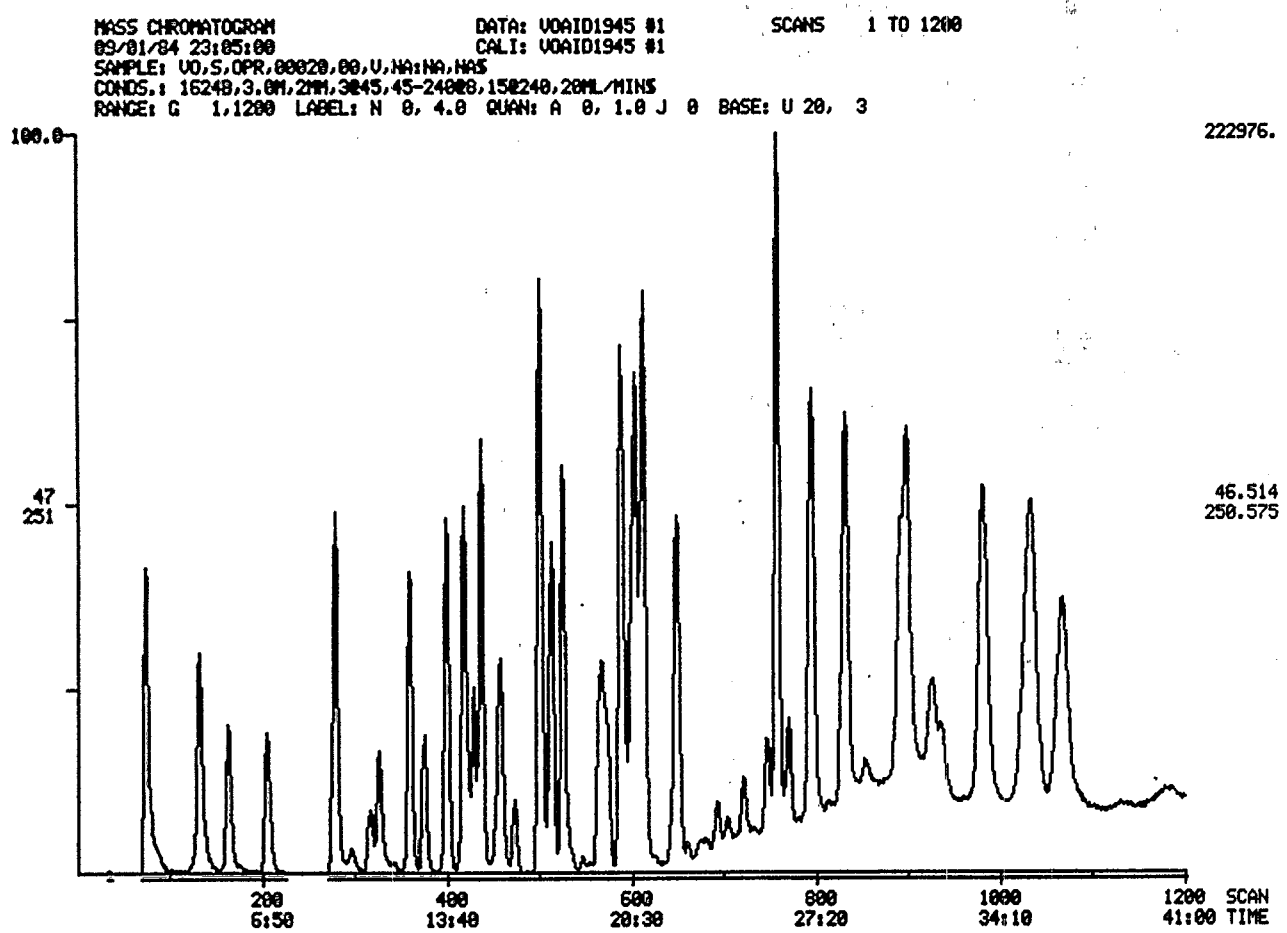

FIGURE 9 Chromatogram of Aqueous Performance Standard

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

532 allyl alcohol

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

533 carbon disulfide

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

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

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

535 chloroacetonitrile

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

536 3-chloropropene

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

537 crotonaldehyde

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

538 1,2-dibromoethane (EDB)

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

539 dibromomethane

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

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

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

541 1,3-dichloropropane

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

542 cis-1,3-dichloropropene

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

543 ethyl cyanide

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

544 ethyl methacrylate

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

545 2-hexanone (methyl butyl ketone)

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

546 iodomethane

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

547 isobutyl alcohol

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

548 methacrylonitrile

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

549 methyl methacrylate

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

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

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

551 1,1,1,2-tetrachloroethane

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

552 trichlorofluoromethane

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

553 1,2,3-trichloropropane

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

554 vinyl acetate

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

951 m-xylene

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

951 o- + p-xylene

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

Method 1625 Revision C June 1989

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

	Pollutant				Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
acenaphthene	34205	83-32-9	001 B	001 B	d_{10}	15067-20-2	201 B
acenaphthylene	34200	208-96-8	077 B	002 B	d_8	93951-97-4	277 B
anthracene	34220	120-12-7	078 B	003 B	d_{10}	1719-06-8	278 B
benzidine	39120	92-87-5	005 B	004 B	d_8	92890-63-6	205 B
benzo(a)anthracene	34526	56-55-3	072 B	005 B	d_{12}	1718-53-2	272 B
benzo(b)fluoranthene	34230	205-99-2	074 B	007 B	d_{12}	93951-98-5	274 B
benzo(k)fluoranthene	34242	207-08-9	075 B	009 B	d_{12}	93952-01-3	275 B
benzo(a)pyrene	34247	50-32-8	073 B	006 B	d_{12}	63466-71-7	273 B
benzo(ghi)perylene	34521	191-24-2	079 B	008 B	d_{12}	93951-66-7	279 B
biphenyl (Appendix C)	81513	92-52-4	512 B		d_{10}	1486-01-7	612 B
bis(2-chloroethyl) ether	34273	111-44-4	018 B	011 B	d_8	93952-02-4	218 B
bis(2-chloroethoxy)methane	34278	111-91-1	043 B	010 B	d_8	93966-78-0	243 B
bis(2-chloroisopropyl) ether	34283	108-60-1	042 B	012 B	d_{12}	93951-67-8	242 B
bis(2-ethylhexyl) phthalate	39100	117-81-7	066 B	013 B	d_4	93951-87-2	266 B
4-bromophenyl phenyl ether	34636	101-55-3	041 B	014 B	d_5	93951-83-8	241 B
butyl benzyl phthalate	34292	85-68-7	067 B	015 B	d_4	93951-88-3	267 B
n-C10 (Appendix C)	77427	124-18-5	517 B		d_{22}	16416-29-8	617 B
n-C12 (Appendix C)	77588	112-40-3	506 B		d_{26}	16416-30-1	606 B
n-C14 (Appendix C)	77691	629-59-4	518 B	618 B			
n-C16 (Appendix C)	77757	544-76-3	519 B		d_{34}	15716-08-2	619 B
n-C18 (Appendix C)	77804	593-45-3	520 B	620 B			
n-C20 (Appendix C)	77830	112-95-8	521 B		d_{42}	62369-67-9	621 B
n-C22 (Appendix C)	77859	629-97-0	522 B	622 B			
n-C24 (Appendix C)	77886	646-31-1	523 B		d_{50}	16416-32-3	623 B
n-C26 (Appendix C)	77901	630-01-3	524 B	624 B			
n-C28 (Appendix C)	78116	630-02-4	525 B	625 B			
n-C30 (Appendix C)	78117	638-68-6	526 B		d_{62}	93952-07-9	626 B

Table 1 (continued)

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

	Pollutant				Labeled Compound		
Compound	Storet	CAS Registry	EPA-EGD	NPDES	Analog	CAS Registry	EPA-EGD
carbazole (4c)	77571	86-74-8	528 B		d_8	38537-24-5	628 B
2-chloronaphthalene	34581	91-58-7	020 B	016 B	d_7	93951-84-9	220 B
4-chlorophenyl phenyl ether	34641	7005-72-3	040 B	017 B	d_5	93951-85-0	240 B
chrysene	34320	218-01-9	076 B	018 B	d_{12}	1719-03-5	276 B
p-cymene (Appendix C)	77356	99-87-6	513 B		d_{14}	93952-03-5	613 B
dibenzo(a,h)anthracene	34556	53-70-3	082 B	019 B	d_{14}	13250-98-1	282 B
dibenzofuran (Appendix C & 4c)	81302	132-64-9	505 B		d_8	93952-04-6	605 B
dibenzothiophene (Synfuel)	77639	132-65-0	504 B		d_8	33262-29-2	604 B
di-n-butyl phthalate	39110	84-74-2	068 B	026 B	d_4	93952-11-5	268 B
1,2-dichlorobenzene	34536	95-50-1	025 B	020 B	d_4	2199-69-1	225 B
1,3-dichlorobenzene	34566	541-73-1	026 B	021 B	d_4	2199-70-4	226 B
1,4-dichlorobenzene	34571	106-46-7	027 B	022 B	d_4	3855-82-1	227 B
3,3'-dichlorobenzidine	34631	91-94-1	028 B	023 B	d_6	93951-91-8	228 B
diethyl phthalate	34336	84-66-2	070 B	024 B	d_4	93952-12-6	270 B
2,4-dimethylphenol	34606	105-67-9	034 A	003 A	d_3	93951-75-8	234 A
dimethyl phthalate	34341	131-11-3	071 B	025 B	d_4	93951-89-4	271 B
2,4-dinitrotoluene	34611	121-14-2	035 B	027 B	d_3	93951-68-9	235 B
2,6-dinitrotoluene	34626	606-20-2	036 B	028 B	d_3	93951-90-7	236 B
di-n-octyl phthalate	34596	117-84-0	069 B	029 B	d_4	93952-13-7	269 B
diphenylamine (Appendix C)	77579	122-39-4	507 B		d_{10}	37055-51-9	607 B
diphenyl ether (Appendix C)	77587	101-84-8	508 B		d_{10}	93952-05-7	608 B
1,2-diphenylhydrazine	34346	122-66-7	037 B	030 B	d_{10}	93951-92-9	237 B
fluoranthene	34376	206-44-0	039 B	031 B	d_{10}	93951-69-0	231 B
fluorene	34381	86-73-7	080 B	032 B	d_{10}	81103-79-9	280 B
hexachlorobenzene	39700	118-74-1	009 B	033 B	$^{13}C_6$	93952-14-8	209 B
hexachlorobutadiene	34391	87-68-3	052 B	034 B	$^{13}C_4$	93951-70-3	252 B
hexachloroethane	34396	67-72-1	012 B	036 B	^{13}C	93952-15-9	212 B
hexachlorocyclopentadiene	34386	77-47-4	053 B	035 B	$^{13}C_4$	93951-71-4	253 B
indeno(1,2,3-cd)pyrene	34403	193-39-5	083 B	057 B			
isophorone	34408	78-59-1	054 B	038 B	d_8	93952-16-0	254 B
naphthalene	34696	91-20-3	055 B	039 B	d_8	1146-65-2	255 B
beta-naphthylamine (Appendix C)	82553	91-59-8	502 B		d_7	93951-94-1	602 B
nitrobenzene	34447	98-95-3	056 B	040 B	d_5	4165-60-0	256 B
N-nitrosodimethylamine	34438	62-75-9	061 B	041 B	d_6	17829-05-9	261 B
N-nitrosodi-n-proplyamine	34428	621-64-7	063 B	042 B	d_{14}	93951-96-3	263 B
N-nitrosodiphenylamine	34433	86-30-6	062 B	043 B	d_6	93951-95-2	262 B
phenanthrene	34461	85-01-8	081 B	044 B	d_{10}	1517-22-2	281 B
phenol	34694	108-95-2	065 A	010 A	d_5	4165-62-2	265 A
alpha-picoline (Synfuel)	77088	109-06-8	503 B		d_7	93951-93-0	603 B
pyrene	34469	129-00-0	084 B	045 B	d_{10}	1718-52-1	284 B
styrene (Appendix C)	77128	100-42-5	510 B		d_5	5161-29-5	610 B
alpha-terpineol (Appendix C)	77493	98-55-5	509 B		d_3	93952-06-8	609 B
1,2,3-trichlorobenzene (4c)	77613	87-61-6	529 B		d_3	3907-98-0	629 B
1,2,4-trichlorobenzene	34551	120-82-1	008 B	046 B	d_3	2199-72-6	208 B

Table 2

ACID EXTRACTABLE COMPOUNDS DETERMINED BY 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_2	93951-72-5	222 A
2-chlorophenol	34586	95-57-8	024 A	001 A	d_4	93951-73-6	224 A
2,4-dichlorophenol	34601	120-83-2	031 A	002 A	d_3	93951-74-7	231 A
2,4-dinitrophenol	34616	51-28-5	059 A	005 A	d_3	93951-77-0	259 A
2-methyl-4,6-dinitrophenol	34657	534-52-1	060 A	004 A	d_2	93951-76-9	260 A
2-nitrophenol	34591	88-75-5	057 A	006 A	d_4	93951-75-1	257 A
4-nitrophenol	34646	100-02-7	058 A	007 A	d_4	93951-79-2	258 A
pentachlorophenol	39032	87-86-5	064 A	009 A	$^{13}C_6$	85380-74-1	264 A
2,3,6-trichlorophenol (4c)	77688	933-75-5	530 A		d_2	93951-81-6	630 A
2,4,5-trichlorophenol (4c)		95-95-4	531 A		d_2	93951-82-7	631 A
2,4,6-trichlorophenol	34621	88-06-2	021 A	011 A	d_2	93951-80-5	221 A

Table 3

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

EGD No.	Compound	CAS Registry	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-isopropylnaphthalene	2027-17-0
562	benzenethiol	108-98-5	594	isosafrole	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-methylbenzothioazole	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

Table 4
ACID EXTRACTABLE COMPOUNDS TO BE DETERMINED BY REVERSE SEARCH AND QUANTITATION USING KNOWN RETENTION TIMES, RESPONSE FACTORS, REFERENCE COMPOUND, AND MASS SPECTRA

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

2 SUMMARY OF METHOD

2.1 The percent solids content of a sample is determined. Stable isotopically labeled analogs of the compounds of interest are added to the sample. If the solids content is less than one percent, a one liter sample is extracted at pH 12 - 13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is 30 percent percent or less, the sample is diluted to one percent solids with reagent water, homogenized ultrasonically, and extracted at pH 12-13, then at pH <2 with methylene chloride using continuous extraction techniques. If the solids content is greater than 30 percent, the sample is extracted using ultrasonic techniques. Each extract is dried over sodium sulfate, concentrated to a volume of five mL, cleaned up using gel permeation chromatography (GPC), if necessary, and concentrated. 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			Minimum 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_6 (5)	378	164	0.286 - 0.364	50		
361	N-nitrosodimethylamine (5)	385	261	1.006 - 1.028	50	16	27
585	N,N-dimethylformamide	407	164	0.350			
580	1,2:3,4-diepoxybutane	409	164	0.352			
603	alpha picoline-d_7	417	164	0.326 - 0.393	50		
703	alpha picoline	426	603	1.006 - 1.028	50	25	87
917	N-nitrosomethylethylamine	451	164	0.338			
598	methyl methanesulfonate	511	164	0.439			
610	styrene-d_5	546	164	0.450 - 0.488	10		
710	styrene	549	610	1.002 - 1.009	10	149*	17
916	N-nitrosodiethylamine	570	164	0.490			
577	1,3-dichloro-2-propanol	589	164	0.506			
589	ethyl methanesulfonate	637	164	0.548			
582	dimethyl sulfone	649	164	0.558			
562	benzenethiol	667	164	0.574			
922	pentachloroethane	680	164	0.585			
557	aniline	694	164	0.597			
613	p-cymene-d_{14}	742	164	0.624 - 0.652	10		
713	p-cymene	755	613	1.008 - 1.023	10	426*	912*
265	phenol-d_5	696	164	0.584 - 0.613	10		
365	phenol	700	265	0.995 - 1.010	10	2501*	757*
218	bis(2-chloroethyl) ether-d_8	696	164	0.584 - 0.607	10		
318	bis(2-chloroethyl) ether	704	218	1.007 - 1.016	10	32	22
617	n-C10-d_{22}	698	164	0.585 - 0.615	10		
717	n-C10	720	617	1.022 - 1.038	10	299*	1188*
226	1,3-dichlorobenzene-d_4	722	164	0.605 - 0.636	10		
326	1,3-dichlorobenzene	724	226	0.998 - 1.008	10	46	26
227	1,4-dichlorobenzene-d_4	737	164	0.601 - 0.666	10		
327	1,4-dichlorobenzene	740	227	0.997 - 1.009	10	35	20
225	1,2-dichlorobenzene-d_4	758	164	0.632 - 0.667	10		
325	1,2-dichlorobenzene	760	225	0.995 - 1.008	10	63	16
935	thioacetamide	768	164	0.660			
564	benzyl alcohol	785	164	0.675			
242	bis(2-chloroisopropyl) ether-d_{12}	788	164	0.664 - 0.691	10		
342	bis(2-chloroisopropyl) ether	799	242	1.010 - 1.016	10	24	39
571	o-cresol	814	164	0.700			
263	N-nitrosodi-n-propylamine-d_{14} (5)	817	164	0.689 - 0.716	20		
363	N-nitrosodi-n-propylamine (5)	830	263	1.008 - 1.023	20	46	47
555	acetophenone	818	164	0.703			
212	hexachloroethane-^{13}C	819	164	0.690 - 0.717	10		
312	hexachloroethane	823	212	0.999 - 1.001	10	58	55
937	o-toluidine	830	164	0.714			
919	N-nitrosomorpholine	834	164	0.717			

Table 5 (continued)

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

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Retention time Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	Method Detection Limit (4) high solids (ug/kg)
575	1,2-dibromo-3-chloropropane	839	164	0.721			
256	nitrobenzene-d_5	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_8	881	164	0.747 - 0.767	10		
354	isophorone	889	254	0.999 - 1.017	10	8	5
942	1,3,5-trithiane	889	164	0.764			
920	N-nitrosopiperidine	895	164	0.770			
234	2,4-dimethylphenol-d_3	921	164	0.781 - 0.803	10		
334	2,4-dimethylphenol	924	234	0.999 - 1.003	10	26	13
243	bis(2-chloroethoxy) methane-d_6 (5)	933	164	0.792 - 0.807	10		
343	bis(2-chloroethoxy) methane (5)	939	243	1.000 - 1.013	10	26	23
208	1,2,4-trichlorobenzene-d_3	955	164	0.813 - 0.830	10		
308	1,2,4-trichlorobenzene	958	208	1.000 - 1.005	10	49	24
558	o-anisidine	962	164	0.827			
255	naphthalene-d_8	963	164	0.819 - 0.836	10		
355	naphthalene	967	255	1.001 - 1.006	10	62	42
934	thianapthene	971	164	0.835			
609	alpha-terpineol-d_3	973	164	0.829 - 0.844	10		
709	alpha-terpineol	975	609	0.998 - 1.008	10	nd	nd
606	n-C12-d_{26}	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_3 (5)	1000	164	0.852 - 0.868	10		
729	1,2,3-trichlorobenzene (5)	1003	629	1.000 - 1.005	10	260*	164*
252	hexachlorobutadiene-$^{13}C_4$	1005	164	0.856 - 0.871	10		
352	hexachlorobutadiene	1006	252	0.999 - 1.002	10	46	22
918	N-nitrosomethylphenylamine	1006	164	0.865			
592	hexachloropropene	1013	164	0.871			
569	4-chloroaniline	1016	164	0.874			
570	3-chloronitrobenzene	1018	164	0.875			
915	N-nitrosodi-n-butylamine	1063	164	0.914			
923	pentamethylbenzene	1083	164	0.931			
561	1,3-benzenediol	1088	164	0.936			
931	safrole	1090	164	0.937			
939	2,4,5-trimethylaniline	1091	164	0.938			
904	2-methylnaphthalene	1098	164	0.944			
599	2-methylbenzothiazole	1099	164	0.945			
568	5-chloro-o-toluidine	1101	164	0.947			
938	1,2,3-trimethoxybenzene	1128	164	0.970			
933	1,2,4,5-tetrachlorobenzene	1141	164	0.981			
253	hexachlorocyclopentadiene-$^{13}C_4$	1147	164	0.976 - 0.986	10		
353	hexachlorocyclopentadiene	1142	253	0.999 - 1.001	10	nd	nd
594	isosafrole (cis or trans)	1147	164	0.986			
594	isosafrole (cis or trans)	1190	164	1.023			
578	2,3-dichloroaniline	1160	164	0.997			
574	2,4-diaminotoluene	1187	164	1.021			
220	2-chloronaphthalene-d_7	1185	164	1.014 - 1.024	10		
320	2-chloronaphthalene	1200	220	0.997 - 1.007	10	80	59

Table 5 (continued)

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

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Retention time Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	Method Detection Limit (4) high solids (ug/kg)
518	n-C14	1203	164	1.034	10	256	3533
612	biphenyl-d_{10}	1195	164	1.016 - 1.027	10		
712	biphenyl	1205	612	1.001 - 1.006	10	67	55
608	diphenyl ether-d_{10}	1211	164	1.036 - 1.047	10		
708	diphenyl ether	1216	608	0.997 - 1.009	10	44	12
579	2,3-dichloronitrobenzene	1214	164	1.044			
911	2-nitroaniline	1218	164	1.047			
908	1,4-naphthoquinone	1224	164	1.052			
595	longifolene	1225	164	1.053			
277	acenaphthylene-d_8	1265	164	1.080 - 1.095	10		
377	acenaphthylene	1247	277	1.000 - 1.004	10	57	18
593	2-isopropylnaphthalene	1254	164	1.078			
587	1,4-dinitrobenzene	1255	164	1.079			
576	2,6-dichloro-4-nitroaniline	1259	164	1.083			
271	dimethyl phthalate-d_4	1269	164	1.083 - 1.102	10		
371	dimethyl phthalate	1273	271	0.998 - 1.005	10	62	21
573	2,6-di-t-butyl-p-benzoquinone	1273	164	1.095			
236	2,6-dinitrotoluene-d_3	1283	164	1.090 - 1.112	10		
336	2,6-dinitrotoluene	1300	236	1.001 - 1.005	10	55	47
912	3-nitroaniline	1297	164	1.115			
201	acenaphthene-d_{10}	1298	164	1.107 - 1.125	10		
301	acenaphthene	1304	201	0.999 - 1.009	10	64	55
605	dibenzofuran-d_8	1331	164	1.134 - 1.155	10		
705	dibenzofuran	1335	605	0.998 - 1.007	10	77	210*
921	pentachlorobenzene	1340	164	1.152			
909	alpha-naphthylamine	1358	164	1.168			
235	2,4-dinitrotoluene-d_3	1359	164	1.152 - 1.181	10		
335	2,4-dinitrotoluene	1364	235	1.000 - 1.002	10	65	209*
602	beta-naphthylamine-d_7	1368	164	1.163 - 1.189	50		
702	beta-naphthylamine	1371	602	0.996 - 1.007	50	49	37
590	ethylenethiourea	1381	164	1.187			
280	fluorene-d_{10}	1395	164	1.185 - 1.214	10		
380	fluorene	1401	281	0.999 - 1.008	10	69	61
240	4-chlorophenyl phenyl ether-d_5	1406	164	1.194 - 1.223	10		
340	4-chlorophenyl phenyl ether	1409	240	0.990 - 1.015	10	73	59
270	diethyl phthalate-d_4	1409	164	1.197 - 1.229	10		
370	diethyl phthalate	1414	270	0.996 - 1.006	10	52	16
906	2-(methylthio)benzothiazole	1415	164	1.217			
567	4-chloro-2-nitroaniline	1421	164	1.222			
910	5-nitro-o-toluidine	1422	164	1.223			
913	4-nitroaniline	1430	164	1.230			
619	n-C16-d_{34}	1447	164	1.010 - 1.478	10		
719	n-C16	1469	619	1.013 - 1.020	10	116*	644*
237	1,2-diphenylhydrazine-d_8	1433	164	1.216 - 1.248	20		
337	1,2-diphenylhydrazine (6)	1439	237	0.999 - 1.009	20	48	27
607	diphenylamine-d_{10}	1437	164	1.213 - 1.249	20		
707	diphenylamine	1439	607	1.000 - 1.007	20	58	54
262	N-nitrosodiphenylamine-d_6	1447	164	1.225 - 1.252	20		
362	N-nitrosodiphenylamine (7)	1464	262	1.000 - 1.002	20	55	36
241	4-bromophenyl phenyl ether-d_5 (5)	1495	164	1.271 - 1.307	10		
341	4-bromophenyl phenyl ether (5)	1498	241	0.990 - 1.015	10	55	17

Table 5 (continued)

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

EGD No. (1)	Compound	Retention time Mean (sec)	Retention time EGD Ref	Retention time Relative (2)	Minimum Level (3) (ug/mL)	Method Detection Limit (4) low solids (ug/kg)	Method Detection Limit (4) high solids (ug/kg)
925	phenacetin	1512	164	1.300			
903	1-methylfluorene	1514	164	1.302			
209	hexachlorobenzene-$^{13}C_6$	1521	164	1.288 - 1.327	10		
309	hexachlorobenzene	1522	209	0.999 - 1.001	10	51	48
556	4-aminobiphenyl	1551	164	1.334			
929	pronamide	1578	164	1.357			
281	phenanthrene-d_{10}	1578	164	1.334 - 1.380	10		
520	n-C18	1580	164	1.359	10	134*	844*
381	phenanthrene	1583	281	1.000 - 1.005	10	42	22
278	anthracene-d_{10}	1588	164	1.342 - 1.388	10		
378	anthracene	1592	278	0.998 - 1.006	10	52	21
604	dibenzothiophene-d_8	1559	164	1.314 - 1.361	10		
704	dibenzothiophene	1564	604	1.000 - 1.006	10	72	71
588	diphenyldisulfide	1623	164	1.396			
914	4-nitrobiphenyl	1639	164	1.409			
927	1-phenylnaphthalene	1643	164	1.413			
628	carbazole-d_8 (5)	1645	164	1.388 - 1.439	20		
728	carbazole (5)	1650	628	1.000 - 1.006	20	47	24
621	n-C20-d_{42}	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_4	1719	164	1.446 - 1.510	10		
368	di-n-butyl phthalate	1723	268	1.000 - 1.003	10	64	80
928	2-phenylnaphthalene	1733	164	1.490			
586	3,6-dimethylphenanthrene	1763	164	1.516			
597	methapyrilene	1781	164	1.531			
926	phenothiazine	1796	164	1.544			
239	fluoranthene-d_{10}	1813	164	1.522 - 1.596	10		
339	fluoranthene	1817	239	1.000 - 1.004	10	54	22
572	crotoxyphos	1822	164	1.567			
936	thioxanthone	1836	164	1.579			
284	pyrene-d_{10}	1844	164	1.523 - 1.644	10		
384	pyrene	1852	284	1.001 - 1.003	10	40	48
205	benzidine-d_8	1854	164	1.549 - 1.632	50		
305	benzidine	1853	205	1.000 - 1.002	50	nd	nd
522	n-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_{50}	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_4 (5)	2058	164	1.715 - 1.824	10		
367	butylbenzyl phthalate (5)	2060	267	1.000 - 1.002	10	60	65
276	chrysene-d_{12}	2081	164	1.743 - 1.837	10		
376	chrysene	2083	276	1.000 - 1.004	10	51	48
901	4,4'methylenebis(2-chloroaniline)	2083	164	1.791			
272	benzo(a)anthracene-d_{12}	2082	164	1.735 - 1.846	10		

Table 5 (continued)

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

EGD No. (1)	Compound	Retention time			Minimum 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_6	2088	164	1.744 - 1.848	50		
328	3,3'-dichlorobenzidine	2086	228	1.000 - 1.001	50	62	111
940	triphenylene	2088	164	1.795			
560	benzanthrone	2106	164	1.811			
266	bis(2-ethylhexyl) phthalate-d_4	2123	164	1.771 - 1.880	10		
366	bis(2-ethylhexyl) phthalate	2124	266	1.000 - 1.002	10	553*	1310*
524	n-C26	2147	164	1.846	10	609*	886*
591	ethynylestradiol 3-methyl ether	2209	164	1.899			
269	di-n-octyl phthalate-d_4	2239	164	1.867 - 1.982	10		
369	di-n-octyl phthalate	2240	269	1.000 - 1.002	10	72	62
525	n-C28	2272	164	1.954	10	492*	1810*
584	7,12-dimethylbenz(a)anthracene	2284	164	1.964			
274	benzo(b)fluoranthene-d_{12}	2281	164	1.902 - 2.025	10		
374	benzo(b)fluoranthene	2293	274	1.000 - 1.005	10	54	30
275	benzo(k)fluoranthene-d_{12}	2287	164	1.906 - 2.033	10		
375	benzo(k)fluoranthene	2293	275	1.000 - 1.005	10	95	20
924	perylene	2349	164	2.020			
273	benzo(a)pyrene-d_{12}	2351	164	1.954 - 2.088	10		
373	benzo(a)pyrene	2350	273	1.000 - 1.004	10	52	15
626	n-C30-d_{62}	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_{14} (5)	2649	164	2.107 - 2.445	20		
382	dibenzo(a,h)anthracene (5)	2660	282	1.000 - 1.007	20	49	125
279	benzo(ghi)perylene-d_{12}	2741	164	2.187 - 2.524	20		
379	benzo(ghi)perylene	2750	279	1.001 - 1.006	20	44	nd

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

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

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

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

(5) Specification derived from related compound.

(6) Detected as azobenzene

(7) Detected as diphenylamine

nd = not detected when spiked into the sludge tested

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

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

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

Gas velocity: 30 +/- 5 cm/sec at 30°C

Table 6

GAS CHROMATOGRAPHIC RETENTION TIMES AND DETECTION LIMITS FOR ACID EXTRACTABLE COMPOUNDS

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

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

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

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

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

(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 ± 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 (± 2 °C), installed in a fume hood.

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

5.9 Balances

5.9.1 Analytical--capable of weighing 0.1 mg.

5.9.2 Top loading--capable of weighing 10 mg.

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

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

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

5.10.2.1 Schmadzu, 5 mm path length

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

5.10.2.3 Pharmacia UV-1, 3 mm flow cell

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

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

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

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

Table 7
DFTPP MASS-INTENSITY SPECIFICATIONS*

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

*Reference 6

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

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

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

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

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

6 REAGENTS AND STANDARDS

6.1 Reagents for adjusting sample pH

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

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

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

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

6.4 GPC calibration solution -- containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl)

phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur.

6.5 Reference matrices

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

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

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

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

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

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

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

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

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

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

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

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

6.13 Calibration solutions--combine 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 ± 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 DFTPP tuning conditions (Section 7.1 and Table 7) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. The spectrum may be further edited to remove common 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)
acenaphthene	d_{10}	154/164	
acenaphthylene	d_8	152/160	
acetophenone		105	0.79
4-aminobiphenyl		169	0.81
aniline		93	1.04
o-anisidine		108	0.43
anthracene	d_{10}	178/188	
aramite		185	0.19
benzanthrone		230	0.15
1,3-benzenediol		110	0.78
benzenethiol		110	0.18
benzidine	d_8	184/192	
benzo(a)anthracene	d_{12}	228/240	
benzo(b)fluoranthene	d_{12}	252/264	
benzo(k)fluoranthene	d_{12}	252/264	
benzo(a)pyrene	d_{12}	252/264	
benzo(ghi)perylene	d_{12}	276/288	
2,3-benzofluorene		216	0.35
benzoic acid		105	0.16
benzyl alcohol		79	0.47
biphenyl	d_{10}	154/164	
bis(2-chloroethyl) ether	d_8	93/101	
bis(2-chloroethoxy)methane	d_6	93/99	
bis(2-chloroisopropyl) ether	d_{12}	121/131	
bis(2-ethylhexyl) phthalate	d_4	149/153	
2-bromochlorobenzene		111	0.33
3-bromochlorobenzene		192	0.40
4-bromophenyl phenyl ether	d_5	248/253	
butyl benzyl phthalate	d_4	149/153	
n-C10	d_{22}	57/82	
n-C12	d_{26}	57/66	
n-C14		57	
n-C16	d_{34}	57/66	
n-C18		57	
n-C20	d_{42}	57/66	
n-C22		57	
n-C24	d_{50}	57/66	
n-C26		57	
n-C28		57	
n-C30	d_{62}	57/66	
carbazole	d_8	167/175	
4-chloro-2-nitroaniline		172	0.20
5-chloro-o-toluidine		106	0.50
4-chloroaniline		127	0.73
2-chloronaphthalene	d_7	162/169	
3-chloronitrobenzene		157	0.18
4-chlorophenyl phenyl ether	d_5	204/209	
3-chloropropionitrile		54	0.42
chrysene	d_{12}	228/240	
o-cresol		108	0.59
crotoxyphos		127	0.017
p-cymene	d_{14}	119/130	
2,6-di-tert-butyl-p-benzoquinone		220	0.078
di-n-butyl phthalate	d_4	149/153	
2,4-diaminotoluene		122	0.059
dibenzo(a,h)anthracene	d_{14}	278/292	
dibenzofuran	d_8	168/176	
dibenzothiophene	d_8	184/192	
1,2-dibromo-3-chloropropane		157	0.22
2,6-dichloro-4-nitroaniline		124	0.019
1,3-dichloro-2-propanol		79	0.68
2,3-dichloroaniline		161	0.47
1,2-dichlorobenzene	d_4	146/152	
1,3-dichlorobenzene	d_4	146/152	
1,4-dichlorobenzene	d_4	146/152	
3,3'-dichlorobenzidine	d_6	252/258	
2,2'-difluorobiphenyl (int std)		190	
2,3-dichloronitrobenzene		191	0.11
1,2:3,4-diepoxybutane		55	0.27
diethyl phthalate	d_4	149/153	
3,3'-dimethoxybenzidine		244	0.19
dimethyl phthalate	d_4	163/167	
dimethyl sulfone		79	0.40
p-dimethylaminoazobenzene		120	0.23
7,12-dimethylbenz(a) anthracene		256	0.58
N,N-dimethylformamide		73	0.51
3,6-dimethylphenanthrene		206	0.72
2,4-dimethylphenol	d_3	122/125	
1,4-dinitrobenzene		168	0.24
2,4-dinitrotoluene	d_3	165/168	
2,6-dinitrotoluene	d_3	165/167	
di-n-octyl phthalate	d_4	149/153	
diphenylamine	d_{10}	169/179	
diphenyl ether	d_{10}	170/180	
diphenyldisulfide		218	0.25
1,2-diphenylhydrazine (3)	d_{10}	77/82	
ethyl methanesulfonate		109	0.28
ethylenethiourea		102	0.22

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

Compound	Labeled Analog	Primary m/z (1)	Response Factor (2)
ethynylestradiol 3-methyl ether		227	0.28
fluoranthene	d_{10}	202/212	
fluorene	d_{10}	166/176	
hexachlorobenzene	$^{13}C_6$	284/292	
hexachlorobutadiene	$^{13}C_4$	225/231	
hexachloroethane	$^{13}C_2$	201/204	
hexachlorocyclopentadiene	$^{13}C_4$	237/241	
hexachloropropene		213	0.23
indeno(1,2,3-cd)pyrene		276	
isophorone	d_8	82/88	
2-isopropylnaphthalene		170	0.32
isosafrole		162	0.33
longifolene		161	0.14
malachite green		330	
methapyrilene		97	0.43
methyl methanesulfonate		80	0.20
2-methylbenzothiazole		149	0.59
3-methylcholanthrene		268	0.59
4,4'-methylenebis (2-chloroaniline)		231	0.21
4,5-methylenephenanthrene		190	0.44
1-methylfluorene		180	0.37
2-methylnaphthalene		142	0.99
1-methylphenanthrene		192	0.65
2-(methylthio)benzothiazole		181	0.42
naphthalene	d_8	128/136	
1,5-naphthalenediamine		158	0.085
1,4-naphthoquinone		158	0.021
alpha-naphthylamine		143	0.89
beta-naphthylamine	d_7	143/150	
5-nitro-o-toluidine		152	0.31
2-nitroaniline		138	0.39
3-nitroaniline		138	0.27
4-nitroaniline		138	0.11
nitrobenzene	d_5	123/128	
4-nitrobiphenyl		199	0.35
N-nitrosodi-n-butylamine		84	0.47
N-nitrosodi-n-propylamine	d_{14}	70/78	
N-nitrosodiethylamine		102	0.45
N-nitrosodimethylamine	d_6	74/80	
N-nitrosodiphenylamine (4)	d_6	169/175	
N-nitrosomethylethylamine	88	0.33	
N-nitrosomethylphenylamine	106	0.024	
N-nitrosomorpholine	56	0.49	
N-nitrosopiperidine		114	0.41
pentachlorobenzene		248	0.25
pentachloroethane		117	0.20
pentamethylbenzene		148	0.42
perylene		252	0.30
phenacetin		108	0.38
phenanthrene	d_{10}	178/188	
phenol	d_5	94/71	
phenothiazine		199	0.15
1-phenylnaphthalene		204	0.48
2-phenylnaphthalene		204	0.73
alpha-picoline	d_7	93/100	
pronamide		173	0.31
pyrene	d_{10}	202/212	
pyridine		79	0.68
safrole		162	0.45
squalene		69	0.042
styrene	d_5	104/109	
alpha-terpineol	d_3	59/62	
1,2,4,5-tetrachlorobenzene		216	0.43
thianaphthene		134	1.52
thioacetamide		75	0.28
thioxanthone		212	0.23
o-toluidine		106	1.04
1,2,3-trichlorobenzene	d_3	180/183	
1,2,4-trichlorobenzene	d_3	180/183	
1,2,3-trimethoxybenzene		168	0.48
2,4,5-trimethylaniline		120	0.28
triphenylene		228	1.32
tripropylene glycol methyl ether		59	0.092
1,3,5-trithiane		138	0.15

(1) native/labeled
(2) referenced to 2,2'-difluorobiphenyl
(3) detected as azobenzene
(4) detected as diphenylamine

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.

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_2	107/109	
2-chlorophenol	d_4	128/132	
p-cresol		108	0.61
3,5-dibromo-4-hydroxybenzonitrile		277	0.12
2,4-dichlorophenol	d_3	162/167	
2,6-dichlorophenol		162	0.42
2,4-dinitrophenol	d_3	184/187	
hexanoic acid		60	0.62
2-methyl-4,6-dinitrophenol	d_2	198/200	
2-nitrophenol	d_4	65/109	
4-nitrophenol	d_4	65/109	
pentachlorophenol	$^{13}C_6$	266/272	
2,3,4,6-tetrachlorophenol		232	0.17
2,3,6-trichlorophenol	d_2	196/200	
2,4,5-trichlorophenol	d_2	196/200	
2,4,6-trichlorophenol	d_2	196/200	

(1) 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

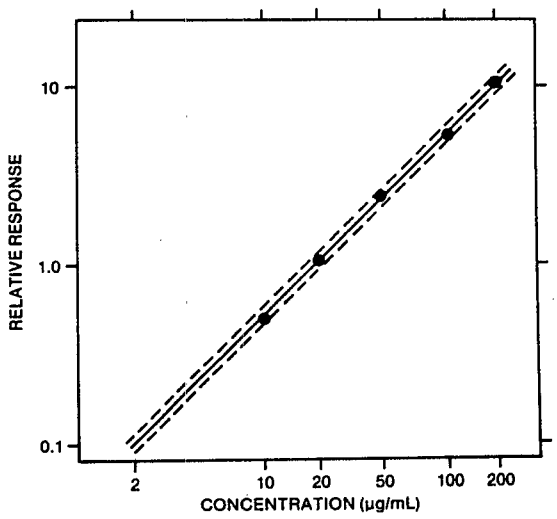

FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a ± 10 Percent Error Window.

a calibration curve for phenol using phenol-d_5 as the isotopic diluent. Also shown are the ± 10 percent error limits (dotted lines). Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

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

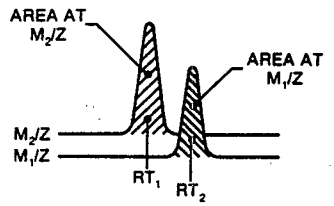

FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled (m_2/z) and Unlabeled (m_1/z) Pairs.

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

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

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

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,

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

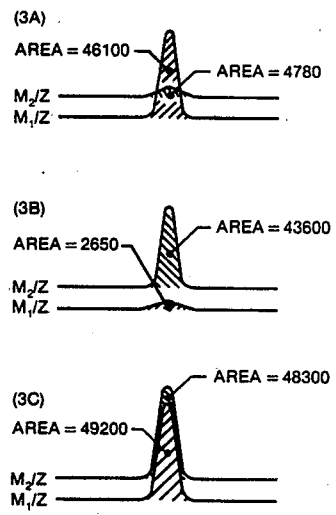

FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

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

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

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 uL aliquot of each of the calibration standards (Section 6.13) using the procedure in Section 11. Compute the RR at each concentration.

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

calibration curve for that compound shall be used over the 5 point calibration range.

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

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

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

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. (1)	Compound	Labeled and native compound initial precision and accuracy (Sec 8.2.3) (ug/L) s	X	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)
301	acenaphthene	21	79 - 134		80 - 125	72 - 144
201	acenaphthene-d_{10}	38	38 - 147	20 - 270	71 - 141	30 - 180
377	acenaphthylene	38	69 - 186		60 - 166	61 - 207
277	acenaphthylene-d_8	31	39 - 146	23 - 239	66 - 152	33 - 168
378	anthracene	41	58 - 174		60 - 168	50 - 199
278	anthracene-d_{10}	49	31 - 194	14 - 419	58 - 171	23 - 242
305	benzidine	119	16 - 518		34 - 296	11 - 672
205	benzidine-d_8	269	ns(2) ns	ns - ns	ns - ns	ns - ns
372	benzo(a)anthracene	20	65 - 168		70 - 142	62 - 176
272	benzo(a)anthracene-d_{12}	41	25 - 298	12 - 605	28 - 357	22 - 329
374	benzo(b)fluoranthene	183	32 - 545		61 - 164	20 - ns
274	benzo(b)fluoranthene-d_{12}	168	11 - 577	ns - ns	14 - ns	ns - ns
375	benzo(k)fluoranthene	26	59 - 143		13 - ns	53 - 155
275	benzo(k)fluoranthene-d_{12}	114	15 - 514	ns - ns	13 - ns	ns - 685
373	benzo(a)pyrene	26	62 - 195		78 - 129	59 - 206
273	benzo(a)pyrene-d_{12}	24	35 - 181	21 - 290	12 - ns	32 - 194
379	benzo(ghi)perylene	21	72 - 160		69 - 145	58 - 168
279	benzo(ghi)perylene-d_{12}	45	29 - 268	14 - 529	13 - ns	25 - 303
712	biphenyl (Appendix C)	41	75 - 148		58 - 171	62 - 176
612	biphenyl-d_{10}	43	28 - 165	ns - ns	52 - 192	17 - 267
318	bis(2-chloroethyl) ether	34	55 - 196		61 - 164	50 - 213
218	bis(2-chloroethyl) ether-d_8	33	29 - 196	15 - 372	52 - 194	25 - 222
343	bis(2-chloroethoxy)methane	27	43 - 153		44 - 228	39 - 166
243	bis(2-chloroethoxy)methane (3)	33	29 - 196	15 - 372	52 - 194	25 - 222
342	bis(2-chloroisopropyl) ether	17	81 - 138		67 - 148	77 - 145
242	bis(2-chloroisopropyl)ether-d_{12}	27	35 - 149	20 - 260	44 - 229	30 - 169
366	bis(2-ethylhexyl) phthalate	31	69 - 220		76 - 131	64 - 232
266	bis(2-ethylhexyl) phthalate-d_4	29	32 - 205	18 - 364	43 - 232	28 - 224
341	4-bromophenyl phenyl ether	44	44 - 140		52 - 193	35 - 172
241	4-bromophenylphenyl ether-d_5(3)	52	40 - 161	19 - 325	57 - 175	29 - 212
367	butyl benzyl phthalate	31	19 - 233		22 - 450	35 - 170
267	butyl benzyl phthalate-d_4 (3)	29	32 - 205	18 - 364	43 - 232	28 - 224
717	n-C10 (Appendix C)	51	24 - 195		42 - 235	19 - 237
617	n-C10-d_{22}	70	ns - 298	ns - ns	44 - 227	ns - 504
706	n-C12 (Appendix C)	74	35 - 369		60 - 166	29 - 424
606	n-C12-d_{26}	53	ns - 331	ns - ns	41 - 242	ns - 408
518	n-C14 (Appendix C) (3)	109	ns - ns		37 - 268	ns - ns
719	n-C16 (Appendix C)	33	80 - 162		72 - 138	71 - 181
619	n-C16-d_{34}	46	37 - 162	18 - 308	54 - 186	28 - 202
520	n-C18 (Appendix C) (3)	39	42 - 131		40 - 249	35 - 167
721	n-C20 (Appendix C)	59	53 - 263		54 - 184	46 - 301
621	n-C20-d_{42}	34	34 - 172	19 - 306	62 - 162	29 - 198
522	n-C22 (Appendix C) (3)	31	45 - 152		40 - 249	39 - 195
723	n-C24 (Appendix C)	11	80 - 139		65 - 154	78 - 142
623	n-C24-d_{50}	28	27 - 211	15 - 376	50 - 199	25 - 229
524	n-C26 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212

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) s	X	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)
525	n-C28 (Appendix C) (3)	35	35 - 193		26 - 392	31 - 212
726	n-C30 (Appendix C)	32	61 - 200		66 - 152	56 - 215
626	n-C30-d_{62}	41	27 - 242	13 - 479	24 - 423	23 - 274
728	carbazole (4c)	38	36 - 165		44 - 227	31 - 188
628	carbazole-d_8 (3)	31	48 - 130	29 - 215	69 - 145	40 - 156
320	2-chloronaphthalene	100	46 - 357		58 - 171	35 - 442
220	2-chloronaphthalene-d_7	41	30 - 168	15 - 324	72 - 139	24 - 204
322	4-chloro-3-methylphenol	37	76 - 131		85 - 115	62 - 159
222	4-chloro-3-methylphenol-d_2	111	30 - 174	ns - 613	68 - 147	14 - 314
324	2-chlorophenol	13	79 - 135		78 - 129	76 - 138
224	2-chlorophenol-d_4	24	36 - 162	23 - 255	55 - 180	33 - 176
340	4-chlorophenyl phenyl ether	42	75 - 166		71 - 142	63 - 194
240	4-chlorophenyl phenyl ether-d_5	52	40 - 161	19 - 325	57 - 175	29 - 212
376	chrysene	51	59 - 186		70 - 142	48 - 221
276	chrysene-d_{12}	69	33 - 219	13 - 512	24 - 411	23 - 290
713	p-cymene (Appendix C)	18	76 - 140		79 - 127	72 - 147
613	p-cymene-d_{14}	67	ns - 359	ns - ns	66 - 152	ns - 468
382	dibenzo(a,h)anthracene	55	23 - 299		13 - 761	19 - 340
282	dibenzo(a,h)anthracene-d_{14} (3)	45	29 - 268	14 - 529	13 - ns	25 - 303
705	dibenzofuran (Appendix C)	20	85 - 136		73 - 136	79 - 146
605	dibenzofuran-d_8	31	47 - 136	28 - 220	66 - 150	39 - 160
704	dibenzothiophene (Synfuel)	31	79 - 150		72 - 140	70 - 168
604	dibenzothiophene-d_8	31	48 - 130	29 - 215	69 - 145	40 - 156
368	di-n-butyl phthalate	15	76 - 165		71 - 142	74 - 169
268	di-n-butyl phthalate-d_4	23	23 - 195	13 - 346	52 - 192	22 - 209
325	1,2-dichlorobenzene	17	73 - 146		74 - 135	70 - 152
225	1,2-dichlorobenzene-d_4	35	14 - 212	ns - 494	61 - 164	11 - 247
326	1,3-dichlorobenzene	43	63 - 201		65 - 154	55 - 225
226	1,3-dichlorobenzene-d_4	48	13 - 203	ns - 550	52 - 192	ns - 260
327	1,4-dichlorobenzene	42	61 - 194		62 - 161	53 - 219
227	1,4-dichlorobenzene-d_4	48	15 - 193	ns - 474	65 - 153	11 - 245
328	3,3'-dichlorobenzidine	26	68 - 174		77 - 130	64 - 185
228	3,3'-dichlorobenzidine-d_6	80	ns - 562	ns - ns	18 - 558	ns - ns
331	2,4-dichlorophenol	12	85 - 131		67 - 149	83 - 135
231	2,4-dichlorophenol-d_3	28	38 - 164	24 - 260	64 - 157	34 - 182
370	diethyl phthalate	44	75 - 196		74 - 135	65 - 222
270	diethyl phthalate-d_4	78	ns - 260	ns - ns	47 - 211	ns - ns
334	2,4-dimethylphenol	13	62 - 153		67 - 150	60 - 156
234	2,4-dimethylphenol-d_3	22	15 - 228	ns - 449	58 - 172	14 - 242
371	dimethyl phthalate	36	74 - 188		73 - 137	67 - 207
271	dimethyl phthalate-d_4	108	ns - 640	ns - ns	50 - 201	ns - ns
359	2,4-dinitrophenol	18	72 - 134		75 - 133	68 - 141
259	2,4-dinitrophenol-d_3	66	22 - 308	ns - ns	39 - 256	17 - 378
335	2,4-dinitrotoluene	18	75 - 158		79 - 127	72 - 164
235	2,4-dinitrotoluene-d_3	37	22 - 245	10 - 514	53 - 187	19 - 275
336	2,6-dinitrotoluene	30	80 - 141		55 - 183	70 - 159
236	2,6-dinitrotoluene-d_3	59	44 - 184	17 - 442	36 - 278	31 - 250

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) s	X	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)
369	di-n-octyl phthalate	16	77 - 161		71 - 140	74 - 166
269	di-n-octyl phthalate-d_4	46	12 - 383	ns - ns	21 - 467	10 - 433
707	diphenylamine (Appendix C)	45	58 - 205		57 - 176	51 - 231
607	diphenylamine-d_{10}	42	27 - 206	11 - 488	59 - 169	21 - 249
708	diphenyl ether (Appendix C)	19	82 - 136		83 - 120	77 - 144
608	diphenyl ether-d_{10}	37	36 - 155	19 - 281	77 - 129	29 - 186
337	1,2-diphenylhydrazine	73	49 - 308		75 - 134	40 - 360
237	1,2-diphenylhydrazine-d_{10}	35	31 - 173	17 - 316	58 - 174	26 - 200
339	fluoranthene	33	71 - 177		67 - 149	64 - 194
239	fluoranthene-d_{10}	35	36 - 161	20 - 278	47 - 215	30 - 187
380	fluorene	29	81 - 132		74 - 135	70 - 151
280	fluorene-d_{10}	43	51 - 131	27 - 238	61 - 164	38 - 172
309	hexachlorobenzene	16	90 - 124		78 - 128	85 - 132
209	hexachlorobenzene-$^{13}C_6$	81	36 - 228	13 - 595	38 - 265	23 - 321
352	hexachlorobutadiene	56	51 - 251		74 - 135	43 - 287
252	hexachlorobutadiene-$^{13}C_4$	63	ns - 316	ns - ns	68 - 148	ns - 413
312	hexachloroethane	227	21 - ns		71 - 141	13 - ns
212	hexachloroethane-^{13}C	77	ns - 400	ns - ns	47 - 212	ns - 563
353	hexachlorocyclopentadiene	15	69 - 144		77 - 129	67 - 148
253	hexachlorocyclopentadiene-$^{13}C_4$	60	ns - ns	ns - ns	47 - 211	ns - ns
083	ideno(1,2,3-cd)pyrene (3)	55	23 - 299		13 - 761	19 - 340
354	isophorone	25	76 - 156		70 - 142	70 - 168
254	isophorone-d_8	23	49 - 133	33 - 193	52 - 194	44 - 147
360	2-methyl-4,6-dinitrophenol	19	77 - 133		69 - 145	72 - 142
260	2-methyl-4,6-dinitrophenol-d_2	64	36 - 247	16 - 527	56 - 177	28 - 307
355	naphthalene	20	80 - 139		73 - 137	75 - 149
255	naphthalene-d_8	39	28 - 157	14 - 305	71 - 141	22 - 192
702	beta-naphthylamine (Appendix C)	49	10 - ns		39 - 256	ns - ns
602	beta-naphthylamine-d_7	33	ns - ns	ns - ns	44 - 230	ns - ns
356	nitrobenzene	25	69 - 161		85 - 115	65 - 169
256	nitrobenzene-d_5	28	18 - 265	ns - ns	46 - 219	15 - 314
357	2-nitrophenol	15	78 - 140		77 - 129	75 - 145
257	2-nitrophenol-d_4	23	41 - 145	27 - 217	61 - 163	37 - 158
358	4-nitrophenol	42	62 - 146		55 - 183	51 - 175
258	4-nitrophenol-d_4	188	14 - 398	ns - ns	35 - 287	ns - ns
361	N-nitrosodimethylamine	49	10 - ns		39 - 256	ns - ns
261	N-nitrosodimethylamine-d_6 (3)	33	ns - ns	ns - ns	44 - 230	ns - ns
363	N-nitrosodi-n-propylamine	45	65 - 142		68 - 148	53 - 173
263	N-nitrosodi-n-propylamine (3)	37	54 - 126	26 - 256	59 - 170	40 - 166
362	N-nitrosodiphenylamine	45	65 - 142		68 - 148	53 - 173
262	N-nitrosodiphenylamine-d_6	37	54 - 126	26 - 256	59 - 170	40 - 166
364	pentachlorophenol	21	76 - 140		77 - 130	71 - 150
264	pentachlorophenol-$^{13}C_6$	49	37 - 212	18 - 412	42 - 237	29 - 254
381	phenanthrene	13	93 - 119		75 - 133	87 - 126
281	phenanthrene-d_{10}	40	45 - 130	24 - 241	67 - 149	34 - 168
365	phenol	36	77 - 127		65 - 155	62 - 154
265	phenol-d_5	161	21 - 210	ns - ns	48 - 208	ns - ns

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) s	X	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)
703	alpha-picoline (Synfuel)	38	59 - 149		60 - 165	50 - 174
603	alpha-picoline-d_7	138	11 - 380	ns - ns	31 - 324	ns - 608
384	pyrene	19	76 - 152		76 - 132	72 - 159
284	pyrene-d_{10}	29	32 - 176	18 - 303	48 - 210	28 - 196
710	styrene (Appendix C)	42	53 - 221		65 - 153	48 - 244
610	styrene-d_5	49	ns - 281	ns - ns	44 - 228	ns - 348
709	alpha-terpineol (Appendix C)	44	42 - 234		54 - 186	38 - 258
609	alpha-terpineol-d_3	48	22 - 292	ns - 672	20 - 502	18 - 339
729	1,2,3-trichlorobenzene (4c)	69	15 - 229		60 - 167	11 - 297
629	1,2,3-trichlorobenzene-d_3 (3)	57	15 - 212	ns - 592	61 - 163	10 - 282
308	1,2,4-trichlorobenzene	19	82 - 136		78 - 128	77 - 144
208	1,2,4-trichlorobenzene-d_3	57	15 - 212	ns - 592	61 - 163	10 - 282
530	2,3,6-trichlorophenol (4c) (3)	30	58 - 137		56 - 180	51 - 153
731	2,4,5-trichlorophenol (4c)	30	58 - 137		56 - 180	51 - 153
631	2,4,5-trichlorophenol-d_2 (3)	47	43 - 183	21 - 363	69 - 144	34 - 226
321	2,4,6-trichlorophenol	57	59 - 205		81 - 123	48 - 244
221	2,4,6-trichlorophenol-d_2	47	43 - 183	21 - 363	69 - 144	34 - 226

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

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

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

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

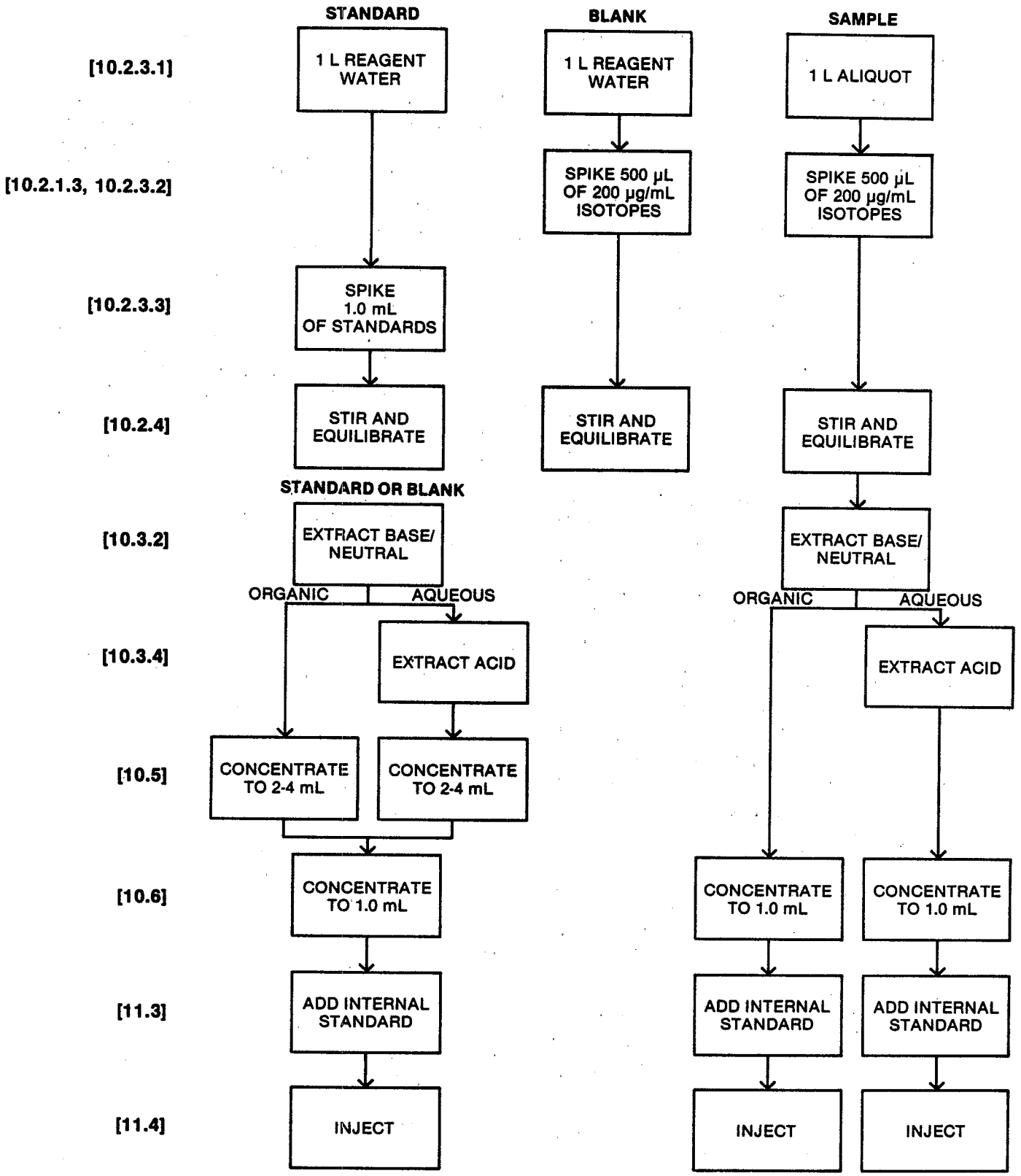

FIGURE 4 Flow Chart for Extraction/Concentration of Low Solids Precision and Recovery Standard, Blank, and Sample by Method 1625. Numbers in Brackets [ ] Refer to Section Numbers in the Method.

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 ± 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 ± 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 ± 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 ± 0.03 grams into a clean 400 - 500 mL beaker.

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

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

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

10.2.5.7 Spike 1.0 mL of the precision and recovery standard (Section 6.14) into the two remaining high solids reference matrix aliquots. Extract, concentrate, and clean up the high solids samples 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 ± 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 <u>not</u> 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%.

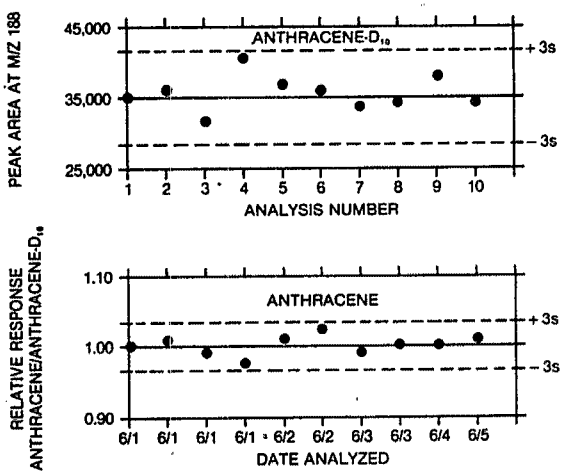

FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d_{10} (lower graph) Plotted as a Function of Time or Analysis Number.

13 QUALITATIVE DETERMINATION

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

13.1 Labeled compounds and pollutants having no labeled analog (Tables 1 - 4):

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

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

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

13.1.4 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 ± 30 seconds, or ± 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 ± 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 spectrometrist (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:

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

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 ± 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.

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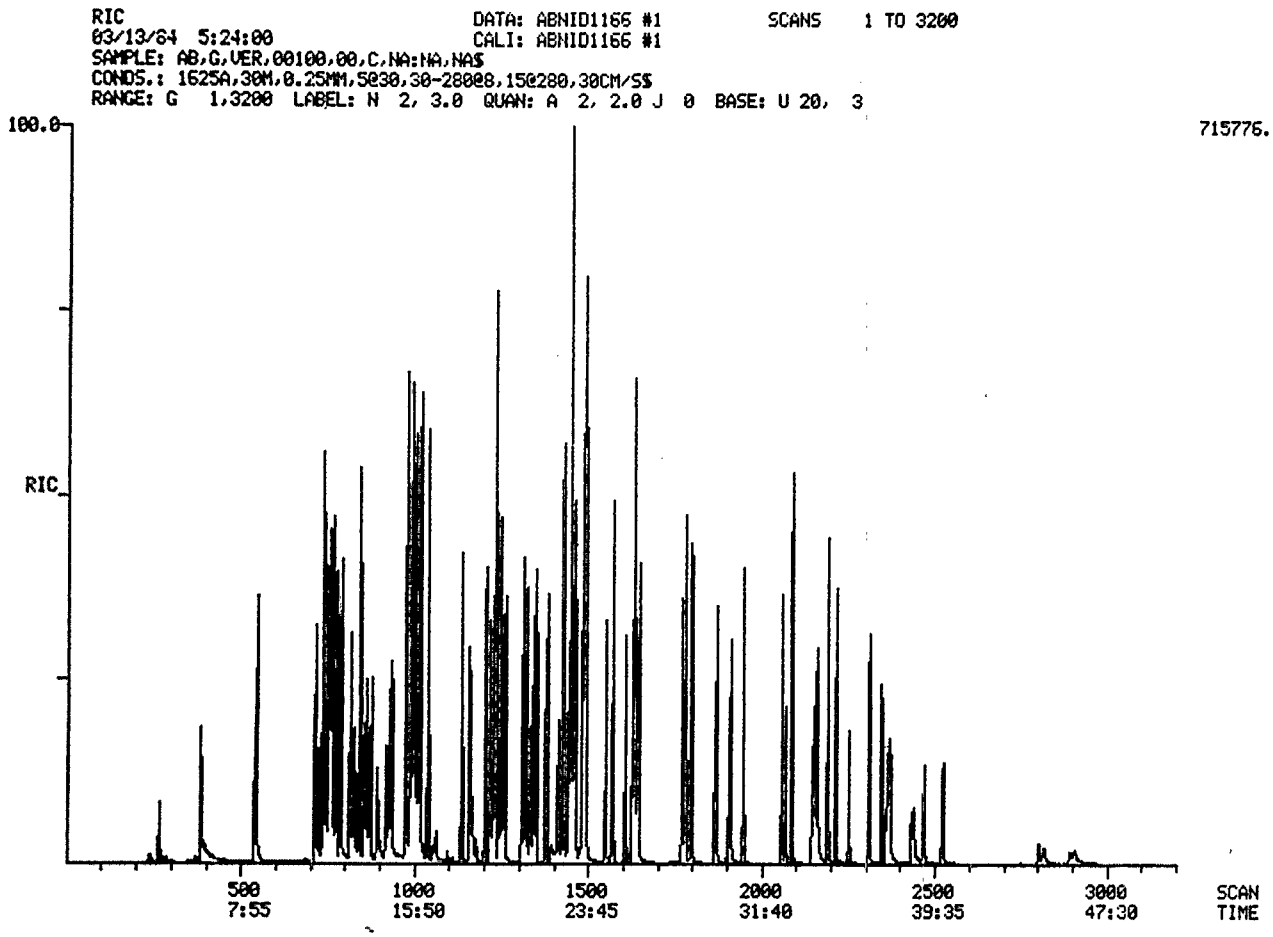

FIGURE 6 Chromatogram of Combined Acid/Base/Neutral Standard.

555 acetophenone

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

556 4-aminobiphenyl

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

557 aniline

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

558 o-anisidine

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

559 aramite

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

560 benzanthrone

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

561 1,3-benzenediol

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

562 benzenethiol

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

563 2,3-benzofluorene

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

943 benzoic acid

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

564 benzyl alcohol

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

565 2-bromochlorobenzene

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

566 3-bromochlorobenzene

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

567 4-chloro-2-nitroaniline

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

568 5-chloro-o-toluidine

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

569 4-chloroaniline

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

570 3-chloronitrobenzene

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

571 o-cresol

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

944 p-cresol

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

572 crotoxyphos

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

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

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

574 2,4-diaminotoluene

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

575 1,2-dibromo-3-chloropropane

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

945 3,5-dibromo-4-hydroxybenzonitrile

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

576 2,6-dichloro-4-nitroaniline

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

577 1,3-dichloro-2-propanol

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

578 2,3-dichloroaniline

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

579 2,3-dichloronitrobenzene

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

946 2,6-dichlorophenol

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

580 1,2:3,4-diepoxybutane

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

581 3,3'-dimethoxybenzidine

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

582 dimethyl sulfone

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

583 p-dimethylaminoazobenzene

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

584 7,12-dimethylbenzo(a)anthracene

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

585 N,N-dimethylformamide

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

586 3,6-dimethylphenanthrene

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

587 1,4-dinitrobenzene

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

588 diphenyldisulfide

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

589 ethyl methanesulfonate

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

590 ethylenethiourea

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

591 ethynylestradiol 3-methyl ether

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

592 hexachloropropene

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

947 hexanoic acid

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

593 2-isopropylnaphthalene

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

594 isosafrole

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